



Potenza, 19-21 September 2023

# ABSTRACT BOOK

a cura della Società Geologica Italiana



The Geoscience paradigm:  
resources, risks and future perspectives



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Pillow-lavas and pillow-breccias covered by red-green radiolarian cherts and reddish marly limestones (Middle-Upper Jurassic) in the Timpa delle Murge ophiolitic sequence (Pollino Massif, Basilicata) (Photo courtesy of G. Prosser).

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# Natura incontaminata e *paesaggi selvaggi*

## Il Parco nazionale del Pollino UNESCO Global Geopark

ricopre un'ampia area al confine tra Calabria e Basilicata in Italia meridionale, in cui rilevanti caratteristiche geologiche e geomorfologiche stanno insieme a molte risorse naturali e culturali.

Nel settembre 2015 il Parco Nazionale del Pollino è entrato a far parte della rete Europea e Globale dei Geoparchi, riconosciuta quale programma ufficiale dell'Unesco: "Programma Internazionale delle Geoscienze", pertanto ad oggi tutto il territorio del Parco può fregiarsi del riconoscimento di Pollino Geoparco Mondiale UNESCO.

Il Pollino Geoparco Mondiale UNESCO è caratterizzato da una grande varietà di forme geologiche (geositi) 69 in totale, censiti e suddivisi in aree

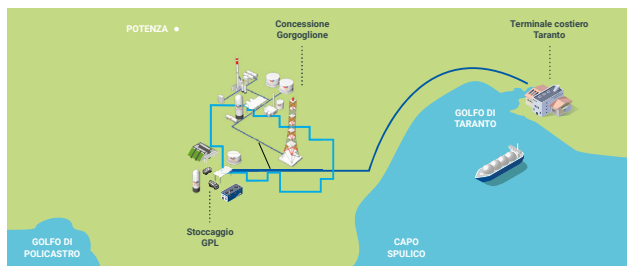
omogenee, dove ogni area rappresenta una porzione di territorio che contiene più geositi e diverse peculiarità non geologiche (ambientali e storico culturali).

Gli UNESCO Global Geoparks sono aree geografiche singole, delimitate da un unico confine continuo, dove i siti e i paesaggi di valore geologico internazionale sono gestiti secondo un approccio integrato per quanto concerne la tutela, l'educazione e lo sviluppo sostenibile.

Un UGG (Unesco Global Geopark) valorizza il patrimonio geologico locale, in stretta connessione con il patrimonio naturale e culturale presente nella medesima area, al fine di accrescere la consapevolezza e la comprensione di alcuni dei fattori chiave che la società sta affrontando oggi a livello globale quali l'uso sostenibile delle risorse del nostro Pianeta, la mitigazione degli effetti dei cambiamenti climatici e la riduzione dell'impatto dei disastri naturali.



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## Il centro olio più alto d'Europa a Corleto Perticara

Gli idrocarburi estratti dai pozzi sono trattati e separati in diversi prodotti: **greggio, gas metano, GPL e zolfo**. Il trattamento delle acque, di giacimento o piovane, rispetta le più stringenti norme nazionali e di settore. Tempa Rossa garantisce un incremento del 40% della produzione nazionale di petrolio.

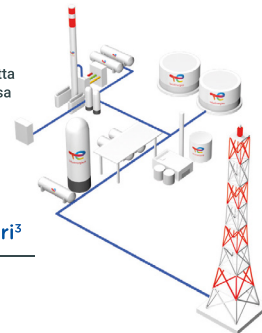
### Capacità giornaliera impianti:

Petrolio  
**50** mila barili

Gas naturale  
**230** mila metri<sup>3</sup>

GPL  
**240** tonnellate

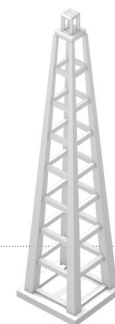
Zolfo  
**75** tonnellate



## Gorgoglione 2, il pozzo più profondo d'Italia

6 pozzi di profondità verticale da 5.000 a 7.148 mt

Tecnologia di punta come i dreni orizzontali e le pompe sommerse di tipo Dual ESP



## Il centro di stoccaggio GPL a Guardia Perticara



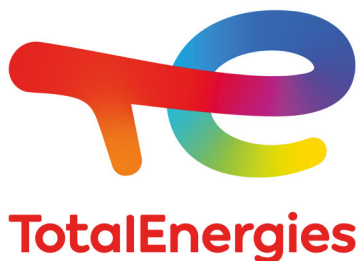
Il GPL separato al Centro Olio, viene inviato tramite tubazione al Centro GPL dove è stoccato in idonei serbatoi interrati nel rispetto della normativa nazionale e di settore.

Dal Centro GPL, il prodotto viene caricato su autobotti tramite apposite baie di carico e destinato alle stazioni di rifornimento veicoli.

3 baie di carico

2 serbatoi interrati

3 mila m<sup>3</sup> capacità totale



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**by accumulation chamber method.**

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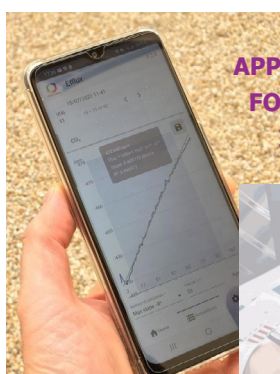
**FLUX CHAMBER PATENTED  
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SNPA 15/2018 guideline COMPLIANT**

**Managing all data in a  
Common Data Environment**

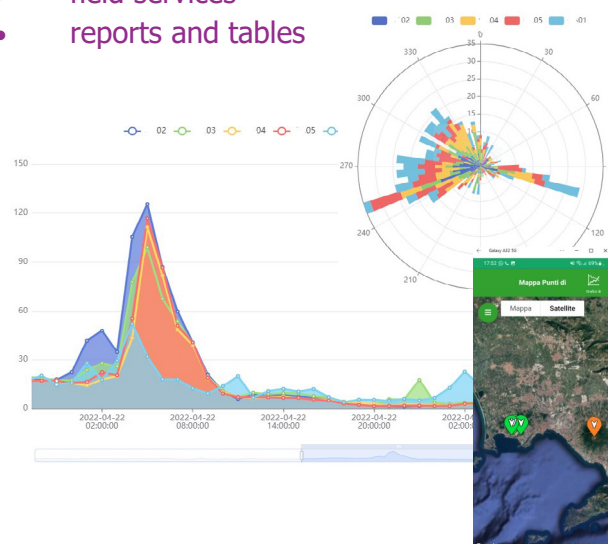
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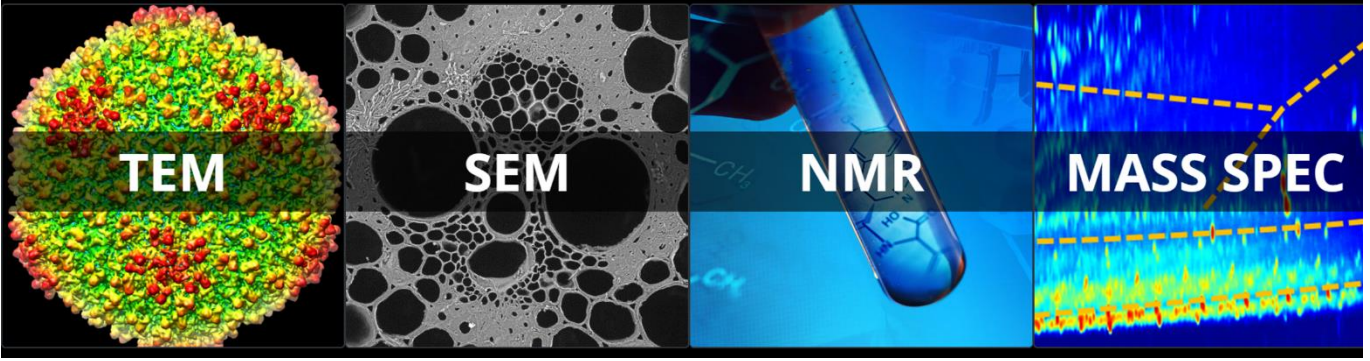
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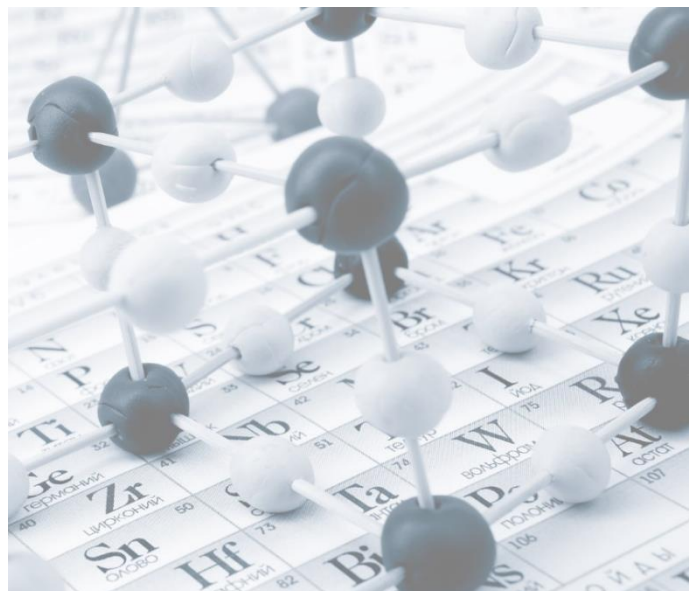


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a trovarci!



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## **PLENARY SESSIONS**

## Volcanic fingerprinting on modern and ancient sedimentary environments

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*Keywords:* volcanoclastic sedimentation, volcanic components, volcanic time scale.

Volcanism is a sediment-generating process that provides large volumes of sediment to the sedimentary environments via both primary eruption processes and as a source of erodible material susceptible to erosion and re-sedimentation at short (e.g., syn-eruptive by weather-related processes, alluvial activity or lahars) and long-term time scales (e.g., normal erosional processes). The quantification of the sediment budget and provenance of the sediments can shed new light on mass-wasting, erosion and sediment transport processes in volcanic environments, with the ultimate goal of better understanding how volcanic processes exert an influence on river, lake and marine sedimentary systems and in turn, how the sedimentary record of these processes can be interpreted as a record of volcanic systems (Di Capua et al., 2023). The dispersion of volcanic materials and their syn-eruptive and erosional reworking can drive morphological and sedimentary changes within lacustrine basins, fluvial systems, and volcanoclastic turbidites in marine environments provide a unique opportunity to investigate the number and scale of past sector collapses in the coastal volcanic areas. The influx of volcanoclastic sediments can go well beyond the volcanic source region, forming sharp sedimentological marker horizons in sedimentary sequences. These marker horizons are critical to reconstructing spatial-temporal landscape evolution and developing regional chrono-stratigraphic models considering sedimentary sequences/systems evolution across syn- to inter-eruptive periods.

This contribution should explore the intimate relationship between primary volcanoclastic sediments and their impact on landscape evolution, fluvial-lacustrine sedimentary systems, sediment budget and provenance and their use in developing chrono-stratigraphic frameworks for modern and ancient systems. These are extremely important to understand the stratigraphic and sedimentary evolution of the continental realm, which connects the volcanic and marine realms (source-to-sink).

The strong geodynamic control of the factors generating volcanism is reflected in the petrological fingerprint of volcanoclastic input into modern and ancient basins. Componentry analysis and the nature of the volcanic-derived fragments may reveal their provenance signature, origin and geological timescales.

Di Capua A., De Rosa R., Kereszturi G., Le Pera E., Rosi M. & Watt S.F.L. (2023) - Volcanic processes in the Sedimentary Record: When Volcanoes Meet the Environment. Geol. Soc. Spec. Publ., 520. <https://doi.org/10.1144/SP520>.



## **Geochemical and tectonic footprint of ophiolite factories of the Mesozoic Tethys in the Alpine-Mediterranean-Tibetan orogenic belts**

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*Keywords:* Ophiolite, Tethys, Tibetan orogenic belts.

Mesozoic ophiolites in the Alpine, Mediterranean, and Tibetan Orogenic Belts (AMTOB) display a complete record of the rift–drift, seafloor spreading, and subduction tectonic stages of the geodynamic evolution of Neotethys, an E-W-trending, latitudinal ocean basin with multiple seaways. The Neotethyan oceanic realm began its initial development during the Permo-Triassic, as evidenced by the widespread occurrence of calc-alkaline basalts, basaltic andesites and dacites, alkaline basalts, trachyandesites and trachytes, and subalkaline basalts with P-MORB, E-MORB and N-MORB compositions. Remnants of these earliest Neotethyan oceanic rocks occur mainly in sub-ophiolitic mélanges and along the rifted margins of Gondwana-derived continental fragments. The next phase of Neotethyan seafloor spreading occurred in the Middle to Late Jurassic and formed Hess-type oceanic lithosphere with G-MORB to N-MORB affinities, derived from DMM beneath different sub-basins within the entire Neotethys. While the northerly motion of Apulia caused significant shortening and ceased intraoceanic magmatism in Western Neotethys, continued seafloor spreading in Eastern Neotethys produced N-MORB to P-MORB oceanic lithosphere with seamount chains–oceanic plateaus, the remnants of which exist in the Mediterranean-Tibetan orogenic belts (MTOB). Evolution of the Cretaceous Neotethys involved the development of intraoceanic subduction zone systems, which led to the formation of suprasubduction zone (SSZ) ophiolites and subsequently to a series of collisional events. Collisions of Gondwana-derived ribbon continents, seamount chains, and intraoceanic arc–trench systems with incoming passive margins resulted in the emplacement of SSZ ophiolites. The SSZ ophiolites in the MTOB include mainly backarc (BA) and forearc (FA) ophiolites that formed during the Late Cretaceous. FA ophiolites exhibit a unique chemostratigraphy with progression from FAB at the bottom to IAT and Boninitic compositions on top that developed within < 10 million years, and commonly represent subduction initiation magmatism (SIM). This geochemical progression was largely a manifestation of variable subduction influence in the melt evolution of ophiolitic magmas due to: (1) lateral variations in slab-dip angles along-strike of convergent margins; and (2) variable amounts of subducted sediments, hydrous melts, and subduction-important elements (Th) incorporated into melt columns above subduction zones. This progression is also marked by the existence of extremely refractory harzburgites with minor dunites and chromitite deposits in the ophiolites. Inclusions of ultrahigh pressure minerals (i.e., diamonds) in chromites in the harzburgites of some ophiolites suggest P-T conditions of mantle transition zone (MTZ) depths for their incorporation into the peridotites. Thus, the mantle peridotites of the Neotethyan ophiolites within the MTOB show significant mineralogical, textural, and geochemical evidence for 2-way recycling of Earth material through time. Nowhere within the AMTOB do the ophiolitic suture zones mark the times and locations of the terminal closures of Neotethyan seaways.

## **A process-based approach to understanding and managing triggered seismicity in the Val d'Agri region, Basilicata, Italy**

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*Keywords:* induced seismicity, model verification and validation, geomechanics.

Seismicity can be triggered when small increases in shear stress or small decreases in fault strength bring tectonically loaded faults to failure. Seismic events can be triggered naturally or by human activities, including impoundment of water, production of water and hydrocarbons, injection of water, methane and CO<sub>2</sub> into the subsurface, and geothermal operations. Field experiments in the 1970's at the Rangely, Colorado (USA) oil field suggested that seismicity might be turned on or off by cycling subsurface fluid pressure above or below a threshold, although detailed subsurface information was not available. Unusually comprehensive and detailed information about the subsurface of the Val d'Agri hydrocarbon field allowed us to develop, test, and implement a process-based methodology for understanding and managing triggered seismicity. We integrated geological, geodetic and reservoir information, including stratigraphy and fault structure from field studies, seismic surveys, well logs, cores, fluid samples, and other information. We incorporated these into a structural and stratigraphic model that formed the foundation for coupled 3D fluid flow and geomechanical models. In contrast to studies that rely on proxies such as wellhead pressures, our models enable physics-based calculations of reservoir volume changes and the resulting stress and pressure changes on faults that are constrained by field-specific matches. We used these results to calibrate models of earthquake source processes, validating the models by comparing their predictions to subsequent observations made after calibration. We conclude: 1) Hydrocarbon production results in a decrease in pore fluid pressure in most of the reservoir, stabilizing most faults within and surrounding the reservoir, consistent with the observed decrease in regional seismicity rate; 2) Injection of produced water close to a small, hydrologically connected fault led to localized fluid pressure increases that triggered a sequence of events with  $ML < 2.2$ . Our model predictions of variations in seismic activity in response to fluid pressure variations on the fault match the observed variations remarkably well; 3) Most seismic events occur when fault fluid pressure exceeds its previous maximum. Our results differ from the interpretation of the Rangely experiment that seismicity is triggered at a constant threshold pressure; and 4) Injection at rates  $\sim 2,000$  m<sup>3</sup>/d is not expected to result in significant seismic activity, while substantially higher rates lead to an expectation of triggering seismicity. Applying our approach to other subsurface reservoirs where fluids are injected or produced could help to manage and mitigate triggered seismicity there. Our methodology also has the potential to help to understand seismicity triggered by hydrologic variations, an increasing concern given the growing variations in rainfall associated with climate change.

Val d'Agri Triggered Seismicity Team: James Dieterich, Cliff Frohlich, Ruben Juanes, Stefano Mantica, John H. Shaw, Francesca Bottazzi, Federica Caresani, David Castineira, Alberto Cominelli, Marco Meda, Lorenzo Osculati, Stefania Petroselli & Andreas Plesch.

## Biogeochemistry of rare earth elements in the critical zone

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*Keywords:* rare earth elements, biogeochemical cycling, geochemical modeling.

The value of the lanthanide series (also known as the rare earth elements, REE) as tracers of geochemical processes largely stems from their uniform trivalent charge ( $Ce^{4+}$  and  $Eu^{2+}$  can also occur), and the gradual decrease in their ionic radii with increasing atomic number (i.e., the lanthanide contraction) that accompanies the progressive filling of the 4*f*-electron shell across the lanthanide series. As a consequence, the REEs exhibit strong fractionation as a group due to size and charge, as well as substantial “within-group” fractionation resulting from the lanthanide contraction. These unique properties can thus facilitate investigations of both complex and subtle geochemical processes that other, single element or single compound (i.e., molecules) tracers cannot discern. Chemical weathering, solution and surface complexation, and oxidation-reduction reactions all play important direct and/or indirect roles in fractionating the REEs in low-temperature environments, and some biological processes may also fractionate REEs. Indeed, certain methanotrophic bacteria use the light REEs as important metal co-factors in an alternative methanol dehydrogenase enzyme to oxidize methanol during the conversion of methane to formaldehyde. The REEs are increasingly important economic resources as they are critical in many developing “green technologies” and in the production of several of today’s “high-tech” electronic devices. Here, the biogeochemistry of the REEs in low-temperature environments including soils, sediments, and natural waters is discussed with emphasis on the processes that fractionate the REEs in these systems. Some discussion of the behavior of REEs in subterranean estuaries along coastal regions of North America will be highlighted as well as recent reactive transport models to investigate the evolution of REE fractionation along groundwater flow paths.

## **S1.**

# **Biogeochemical processes in the Anthropocene: nutrients and pollutants cycling across the environmental matrices**

*CONVENERS & CHAIRPERSONS*

*Stefania Venturi (Università degli Studi di Firenze)*

*Nicolas Greggio (Università degli Studi di Bologna)*

*Marco Taussi (Università degli Studi di Urbino Carlo Bo)*

**From rural to urban areas: a transect along the Greve River Basin  
(Chianti territory, Central Italy) investigating greenhouse gases distribution and metal  
deposition with a combination of traditional and low-cost technical approaches**

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*Keywords:* air quality, greenhouse gases, metal deposition.

The adverse impact of human activities on the air quality is largely related to the use of fossil fuels and intensive agricultural exploitation, which cause the emissions in the air of a wide variety of climate-changing species and harmful gaseous, liquid and solid pollutants. Moreover, atmospheric particulate matter may affect soils, biota, and waters through wet and dry deposition. Therefore, the management of air quality is an impelling issue to limit damages and protect human and environmental health.

This study presents the results of a geochemical survey carried out in a study area of relevant hydrological, economic, and socio-cultural interest: the Greve River Basin (Chianti territory, Italy). The Greve River is a tributary of the Arno River and extends about 50 km south of Florence. The upstream side (845 m a.s.l.) is dominated by vineyards and olive trees, whilst downstream (45 m a.s.l.) several urban and industrial areas occur. The survey was led from May to September 2022 by adopting two measuring strategies: (i) along transects, deploying a mobile station equipped with a Picarro G2201-*i* analyzer to measure CO<sub>2</sub> and CH<sub>4</sub> concentrations and δ<sup>13</sup>C-CO<sub>2</sub> and δ<sup>13</sup>C-CH<sub>4</sub> values (‰ vs. V-PDB) by Cavity Ring-Down Spectroscopy; and (ii) at five fixed stations, measuring CO<sub>2</sub>, CH<sub>4</sub>, PM<sub>2.5</sub> concentrations, as well as air temperature and relative humidity, using low-cost multiparametric instrumental prototypes, coupled with atmospheric deposition and rain samplers to collect particulate samples for chemical lab analysis. The CO<sub>2</sub> and CH<sub>4</sub> sensors have been calibrated in-field based on parallel measurements with the Picarro G2201-*i* and elaborating the calibration data with a machine learning-based algorithm.

The measurements along the transects, combined with the monitoring at the fixed stations, showed that the downstream areas were affected by the highest concentrations of CO<sub>2</sub> and CH<sub>4</sub>, with isotopic signatures revealing an origin of these gases mainly due to vehicular traffic. The distribution of these air contaminants reflected the evolution of the Planetary Boundary Layer, with higher concentrations during the early morning, when gas accumulation occurred due to stable atmospheric conditions, and lower concentrations during daytime for the establishment of convective turbulences favoring the dispersion of contaminants. The distribution of particulate was consistent with that of the gaseous species, and the main sources were clearly distinguished based on the chemical composition of the depositions at the fixed stations. The downstream sites displayed anomalies in the *Traffic Related Elements* (e.g., Pb, Ni, Cd, Zn, As, etc.), whilst the upstream site was enriched in Cu and Se, possibly due to the use of fertilizers and pesticides. The promising results from the present study could result in an affordable approach to effectively improve air quality monitoring strategies and support data-driven policy actions to reduce pollutant emissions.



## Hydrogeochemical characterization of Asunción Mita (Jutiapa, Guatemala) pilot site: assessment of groundwater resources potentiality and pollution in the framework of the Agua Futura Project

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**Keywords:** hydrogeochemical characterization, groundwater resources, water pollution.

Latin America is characterized by renewable water resources representing an opportunity for sustainable environmental and socio-economic development. Promoting the knowledge regarding groundwater resources and capability is thus pivotal, also considering that water availability and sustainable use is often prevented by social inequality and lack of education and planning. The Agua Futura Project, supported by Italian Agency for Development Cooperation (AICS) and performed through a joint venture of research institutions (CNR, UNIFI, UNIROMA-Sapienza, INGV, USAC-Guatemala, UES-El Salvador) and ONGs (ISCOS, ACRA), concerned this topic by addressing water resources scarcity and quality of pilot sites in Guatemala and El Salvador.

The present work is specifically aimed at depicting the hydrogeochemical features of Asunción Mita pilot site, an urban/agricultural context located in an area of volcanic origin in the Rio Ostúa basin (Jutiapa, SE Guatemala) also characterized by the presence of mines and hydrothermal emissions. The effective groundwater potential and the possible causes of contamination, by identifying the main solutes and pollutant sources and the principal geochemical processes acting in both groundwater and surface waters, were verified and assessed. 3 surveys (March 2019, October 2019, February 2020) were carried out to highlight possible hydrogeochemical variability associated with the different seasonal conditions, during which physicochemical measurements and water samplings were performed. The analytical determinations concerned: i) main anions ( $\text{HCO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{F}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ ) and N-species ( $\text{NO}_2^-$  and  $\text{NH}_4^+$ ); ii) main cations (Na, K, Mg, Ca); iii) trace elements; iv) water isotopes ( $\delta^{18}\text{O}$ ,  $\delta\text{D}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$ ).

The  $\delta\text{D}-\text{H}_2\text{O}$  and  $\delta^{18}\text{O}-\text{H}_2\text{O}$  values indicate that most waters have a meteoric origin and a  $\text{Ca}-\text{HCO}_3$  composition, typically characterizing worldwide superficial waters and shallow aquifers. The  $(\text{Mg}, \text{Ca})-\text{HCO}_3$  composition of some samples could instead indicate interaction processes with mafic rocks (e.g., basalts). This distinction is also highlighted by Sr isotopes, as  $^{87}\text{Sr}/^{86}\text{Sr}$  greater than 0.7050 may indicate an interaction with carbonate rocks, whilst volcanic rocks in the region are generally near 0.7040. On the contrary, two samples are characterized by a  $\delta^{18}\text{O}$ -shift, which is typical of water-rock interaction processes under geothermal conditions, in accordance with their  $\text{Na}-(\text{Cl}, \text{HCO}_3)$  composition, relatively high TDS values and As, B and Li contents, and  $\text{Cl}/\text{SO}_4$  ratio  $>1$ . N-species indicate that inputs from anthropogenic sources are also present, e.g., sewage discharges, or farming activities to which the inhabitants are largely devoted.

Within this heterogeneous framework, some springs north of Asunción Mita, being fed by relatively high altitudes (like those of Suchitan volcano, 1700-1750 m a.s.l.), seem to represent a homogeneous groundwater body characterized by a good water quality, which is thus one of the main local water resources.

## Immobilization of leachable metals and metalloids in soil with dolomite-enriched biochar and comparison with commercial activated carbon

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*Keywords:* biochar, metals, remediation.

Soil contamination from toxic metals and metalloids (MM) is a major environmental issue that has serious impacts on human health and ecosystems. MM soil levels in Europe have increased over the last years and are among the main categories of contaminants affecting the quality of European soil. HM such as lead and arsenic are toxic to plants and animals, and can accumulate in the soil over time, leading to long-term environmental and health damage (EEA, 2011).

Biochar application to contaminated soils has gained interest due to its low cost and the possibility to produce it from even rather basic technologies (Gao et al., 2022). Biochar is defined as “a porous, carbonaceous material that is produced by pyrolysis of biomass” (EBC, 2022) and its interactions with HM that involve several mechanisms, including complexation with organic functional groups, ion exchange, complexation with mineral oxides, (co)precipitation, and redox reactions. The effectiveness of biochar in immobilizing MM in soil depends on several factors, including inherent properties of biochar, the type of MM and extent of contamination, and the soil characteristics.

In this study we assessed the ability of a dolomite-enriched biochar to immobilize the leachable fraction of MM compared to that of a commercial activated carbon. Biochar (BCD) was produced by mixing biomass and pulverised dolomite, and pyrolyzing them. Four anonymized contaminated soil samples from existing remediation sites containing varying amounts of As, Sb, Cd, Zn, and Pb were used for batch and column experimentation to determine suitability and amendment rate of biochar for soil remediation. Batch tests were carried out according to EN 12457-4:2002. The soils were mixed with different ratios of BCD and Norit: 0.5%, 1.0%, and 2.0%. A total of 30 g of these mixes were then added to 300 ml deionised water (1:10 solid to liquid ratio). The leachable amount of MM was measured in ‘control’ test samples with unamended soil only (30 g). Blank measurements with only the sorbents were included to ensure that the two sorbents did not release significant amounts of contaminants compared to the initial concentrations in the soils. Soil 1 showed the highest amount of leachable MM (924 µg/l of  $\Sigma$  Total MM), and Soil 4 the least (169 µg/l of  $\Sigma$  Total MM). Overall, BCD immobilised a higher amount of  $\Sigma$  Total MM than Norit. Only in Soil 2 the removal was comparable. In all cases, a 0.5% ratio of BCD was sufficient to immobilize the same percentage of MM or even more, than that at the highest amendment rate of Norit. Overall, both BCD and Norit showed great immobilisation potential for most of the MM analysed; the biggest differences were seen with As. Indeed, Norit had no effect on the immobilisation of As, whereas BCD removed between 75% and 100% leachable As in each soil. Ultimately, dolomite-enriched biochar can be a valid substitute for activated carbon to limit the leaching of MM, including As, in contaminated soils.

EBC (2012-2022) - European Biochar Certificate - Guidelines for a Sustainable Production of Biochar. Version 10.1 from 10th Jan 2022 (s.d.). European Biochar Foundation (EBC), Arbaz, Switzerland. <http://european-biochar.org>.

EEA - European Environment Agency (2011) - Progress in management of contaminated sites. <https://www.eea.europa.eu/data-and-maps/indicators/progress-in-management-of-contaminated-sites/progress-in-management-of-contaminated>.

Gao Y., Wu P., Jeyakumar P., Bolan N., Wang H., Gao B., Wang S. & Wang B. (2022) - Biochar as a potential strategy for remediation of contaminated mining soils: Mechanisms, applications, and future perspectives. *J. Environ. Manage.*, 313, 114973. <https://doi.org/10.1016/j.jenvman.2022.114973>.

## Development and testing of a new flexible, rapid and easily applicable Chemical Water Quality Index (CWQI)

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*Keywords:* water quality, chemical index, water management.

Water Quality Indices (WQIs) are numeric parameters that summarize the overall quality status of freshwaters compared to quality standards by aggregating multiple physicochemical data into a single value. The first WQI was elaborated by Horton (1965) and since then several new and updated WQIs were computed and developed. The formulation of a WQI is divided in four steps: (i) selection of the variables, (ii) transformation of the variables to a common scale, (iii) weightage of the variables and (iv) computation of the index.

Among the available WQIs in the literature several criticalities were recognized, including: (a) mathematical complexity of the computation, (b) lack of inclusivity, as several WQIs are formulated for specific sets of variables, thus preventing the inclusion of other parameters such as emerging chemical pollutants, (c) weight assignment, often based on arbitrary criteria, and (d) site-specificity of most of the indexes.

The proposed Chemical Water Quality Index (CWQI) aims to overcome these flaws and provides a computation based on simple mathematic equations that are easily manageable on Excel software.

The computation is divided into two steps: (i) parametrization of the variables and (ii) index determination. The parametrization consists in assigning a score (s) from 1 to 10 to each chemical variable based on (i) measured concentrations and (ii) quality targets (e.g., the limits provided by the Italian legislation for drinking waters). In the second step, a weight (w), directly proportional to the score (s), is assigned to each parameter, allowing to overcome any bias related to subjective assignments from the user. The resulting CWQI ranges from 1 (excellent quality) to 10 (extremely poor quality). The reliability of the CWQI was assessed by (i) applying the computation to more than 500 waters with a known “chemical quality status” and (ii) comparing our results with already published and available WQIs.

Due to the simplicity of its computation, the absence of arbitrariness in the weightage of selected variables, and the independency of the proposed approach regarding the choice of the chemical parameters, CWQI can be easily and universally applied.

Horton R.K. (1965) - An index number system for rating water quality. *J. Water Pollut. Con. F.*, 37, 300-306.

## **Disentangling natural vs. anthropogenic sources of heavy metals in river ecosystems: a geochemical perspective to support biodiversity in multiple sourced environments**

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*Keywords:* heavy metals, isotopes, biodiversity.

River ecosystems are suffering a profound biodiversity crisis being threatened by multiple stressors, e.g., pollution, land use modifications, climate change. These ecosystems can be regarded as open thermodynamic systems, whose stability derives from a delicate balance between their biotic and abiotic components. The introduction of persistent and non-biodegradable heavy metals (HMs) that can be accumulated in living organisms, including humans, as they are exposed to contaminated food and water, can modify this equilibrium. As HMs can derive from both natural (rock weathering) and anthropic (e.g., urban and industrial activities, agricultural practices) sources, geochemical and isotopic tools able to discriminate the origin of these elements are of pivotal importance in the perspective of ecosystem management and biodiversity conservation.

As part of the CN5-Spoke 3 *Assessing and monitoring terrestrial and freshwater biodiversity and its evolution: from taxonomy to genomics and citizen science* project, supported by the National Biodiversity Future Centre (NBFC) and funded by the Ministry of University within the National Recovery and Resilience Plan (PNRR), Mission 4-Component 2-Investment 1.4, the present study aims to identify the source(s) of HMs in the Ombrone Grossetano river basin (OGRB, Italy) by combining geochemical (major, minor and trace elements) and isotopic (Sr, Nd, Pb) analysis of water, sediments, and suspended solids. OGRB represents one of the major river ecosystems in Tuscany. It drains an area of 3,500 km<sup>2</sup> and is an ideal site to identify and test innovative geochemical tracers able to discern the origin of HMs having potential impact on biodiversity considering i) its low population density (50 people/km<sup>2</sup>), and ii) the co-presence of protected areas, abandoned mining sites and thermal discharges contributing to the Ombrone river and its tributaries.

Water and suspended solid samples will be collected during 6 sampling surveys in 2023-2025 during both high and low river discharges and diverse seasonal and weather conditions, whilst bottom sediments will be retrieved during one single campaign. Sediments and suspended solids will be analysed for total HMs content and by sequential extraction procedure to assess the potential bioavailability of metals. Major focus will be on the isotopic composition of Pb, Nd and Sr from different environmental matrices.

A further step of the project is to combine the geochemical and isotopic data with river biodiversity assessments based on innovative monitoring techniques (eDNA and eRNA analysis) to explore the relationships between abiotic and biotic components of fluvial ecosystems and identify specific perturbations induced by HMs on the riverine biota.

## **Enrichment of Potential Toxic Elements (PTEs) in sediments of drainage canals in a low-lying coastal area**

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*Keywords:* Potential Toxic Elements (PTEs), sediments of drainage canals, Fe- and Mn- hydroxides.

Drainage systems made of artificial canals and pumping stations are worldwide used to control water table and water excess in low-lying coastal areas, allowing human activities. However, in coastal areas where the local aquifer is phreatic, drainage activities promote vertical seepage, a rapid decrease in freshwater availability and a contextual groundwater salinization (Cozzolino et al., 2017). Here, the drainage network of canals is the interface among surface water from terrestrial agro-ecosystems and local groundwater, and their sediments register and reflect peculiar enrichments in PTEs coming from both environments. Moreover, the excavation of the canal itself, typically 2 meters deep, exposes different depositional environments with their own characteristics, depending on the sediment typology and provenance (Greggio et al., 2018; Buscaroli et al., 2021).

This study aims to investigate the enrichments of Potential Toxic Elements (PTEs) in sediments from a land reclamation drainage network of canals, in order to describe and discuss the involved geochemical processes. The investigated area is located in the south-eastern part of the Po River plain in Italy (surrounding of the Ravenna city). This area is at or below mean sea level, highly oriented to tourism, industry and agriculture activities, as well as frequently exposed to inundation, and groundwater and soil salinization. The underneath coastal aquifer is a complex sandy body, 30 m thick, that is phreatic close to the coastline in correspondence of the actual or historical dune belts.

A geochemical database of 203 sediment samples collected at the canal's bottom, along with drainage water inside the canal and local groundwater samples, were analysed for major and trace elements.

The distribution of PTEs was assessed in relation to the local depositional environments in order distinguish between background concentrations and enrichment phenomena resulting from drainage and groundwater interaction or other human activities.

Sediment samples revealed concentrations of As, Co, Pb, and Zn that exceeded national regulations. The As and Co enrichments were predominantly found in the low-lying canals that collect upward seepage of anoxic saline groundwater from the salinized coastal aquifer. A strong correlation was observed between the abundance of Fe and Mn and Co, As, and Mo in sediment samples. The drainage of anoxic, Fe-enriched groundwater into oxygenated canals resulted in the precipitation of Fe- and Mn- hydroxides, controlling the distribution and enrichment of As and Co in canal sediments. The results of Principal Component Analysis (PCA) confirmed the dependency of the As and Co enrichments on the distance from the sea and elevation, which are both directly related to groundwater interaction, while anthropogenic activities are responsible for the enrichments of Cu, Pb, Zn, and U.

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## Microplastics agglutinated in Sabellariid bioconstructions (Polychaeta, Annelida) of northern adriatic sea – Part 2: first attempt to quantify their amount

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Keywords: microplastic, mediterranean bioconstructions, arenaceous tubes.

Microplastics (MPs) are a widespread pollutant found in lands, rivers, seas and oceans across the globe (Villarrubia-Gómez et al., 2018). The Mediterranean Sea, a semi-enclosed basin whose coasts are densely populated, has been referred as the sixth highest region for accumulation of plastic litter, due to its presence in both benthic and pelagic domains (Cózar et al., 2015). MPs, beyond entering the sedimentary record, directly affect marine life, with a broad spectrum of consequences from individual to community level. A new perspective concern is the inclusion of MPs within arenaceous cases of some marine benthic organisms, as observed in sedentary polychaetes. Sabellariid reefs grow in the littoral environment and are made by a multitude of gregarious arenaceous tubes built up of agglutinated sand particles. The bioconstruction is a highly dynamic system that constitutes a nutrient and sediment sink (Lisco et al., 2017), increasing local biodiversity and enhancing coastal protection. This work aims at evaluating MPs content accumulated within *Sabellaria spinulosa* (Leuckart, 1849) bioconstructions through a comparative approach: sea-floor sediment and bioconstruction samples (twenty replicates in total) were collected along artificial boulder barriers at Misano Adriatico (RN) to assess MPs abundance in both substrates. A multidisciplinary approach, which combines analytical techniques from Micropaleontology, Applied Petrography, Marine Ecology and utilizes different instruments for microplastic identification (stereomicroscope, SEM-EDS,  $\mu$ Raman – see Lo Bue et al. abstract, part I), was applied to achieve a quantitative estimate of MPs in studied samples. Results document that MPs, mainly fibers and more rarely fragments, occurred in all analyzed samples, recording higher absolute abundances in bioconstruction with respect to sediment samples. The higher concentration of MP fibers within bioconstruction samples was unexpected, if considered along with their morphological characteristics: it is in fact documented that *Sabellaria* spp. selects medium to fine sand grains, with flattened or biconvex morphologies (Lo Bue et al., 2022) to build the arenaceous tubes. We hypothesize that the superior buoyancy performance of fibers with respect to fragments could increase their availability, resulting in higher rates of uptake and incorporation within the polychaetae bioconstruction. This work represents the first successful attempt to quantify MPs in *Sabellaria* spp. bioconstructions from Mediterranean Sea, pointing out the importance of a quantitative approach as a basis for understanding potential effects of this anthropogenic pollutant in environmental matrices.

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## **Microplastics agglutinated in Sabellariid bioconstructions (Polychaeta, Annelida) of northern adriatic sea – Part 1: an integrated approach for a correct identification in environmental matrices**

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*Keywords:* microplastic, analytical methods, spectroscopy.

Microplastics (MPs) are ubiquitous pollutant on Earth. Highly anthropized coastal areas are at risk as they represent land to sea plastic input, fragmentation place and dispersion source. Mediterranean Sea has been addressed as a “plastic soup” for MP presence in both pelagic and benthic domains (Suaria et al., 2016). A new perspective concerns is the inclusion of MPs in the bioconstructions of some marine benthic organisms, as recently observed in *Sabellaria alveolata* (Linnaeus, 1767) (Mancin et al., 2022), a sedentary polychaetae, which builds arenaceous reefs in the littoral environment. In the literature there is no uniquely accepted protocol for recognizing and quantifying MPs in environmental matrices from the coastal marine environment and particularly in the arenaceous bioconstructions built by polychaete sabellariids. To this purpose, five samples from *Sabellaria spinulosa* (Leuckart, 1849) bioconstruction and fifteen samples from nearby coastal sediment were collected at Misano Adriatico (Emilia Romagna-Italy; Northern Adriatic Sea). The aim is to provide a replicable analytical protocol for MP identification in environmental samples. All collected replicates were digested in H<sub>2</sub>O<sub>2</sub> (130 vol), dried at low temperature in an oven and weighted. MPs were extracted from sandy residues through a high-density brine solution (NaCl); density separation process was repeated three times for each replicate (Quinn et al., 2017). Suspended particles were filtered on a 23 µm filter, dried and then observed at the stereomicroscope. Every suspected MP was isolated and classified based on morphology: fragments, pellets, fibers, films, and agglomerates. The subsequent analysis of the suspected MPs at the scanning electron microscope equipped with X-ray Energy Dispersive Spectroscopy (SEM-EDS), allowed to distinguish sedimentary grains and biogenic remains from true MP fragments. The last step consisted of MP characterization through micro-Raman spectroscopy (µ-RaS) in order to identify mainly the fibers and distinguishing between those made of natural textile material (cotton, line, silk) from fibers of synthetic materials. This technique also allowed to recognize those ambiguous fragments from bioconstruction samples which were particularly altered on the surface and partly encrusted by clay. The proposed integrated approach is an innovative, practical method to correctly identify and quantify MPs accumulated in environmental matrices.

Linnaeus C. (1767) - Systema naturae per regna tria naturae: secundum classes, ordines, genera, species, cum characteribus, differentiis, synonymis, locis. Ed. 12.1, Regnum Animale 1 & 2, Holmiae, Stockholm, Laurentii Salvii, 533-1327. <http://www.biodiversitylibrary.org/item/83650#5>.

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Quinn B., Murphy F. & Ewins C. (2017) - Validation of density separation for the rapid recovery of microplastics from sediment. Anal. Methods-UK, 9, 1491-1498. <https://doi.org/10.1039/C6AY02542K>.

Suaria G., Avio C.G., Mineo A., Lattin G.L., Magaldi M.G., Belmonte G., Moore C.J., Regoli F. & Aliani S. (2016) - The Mediterranean Plastic Soup: synthetic polymers in Mediterranean surface waters. Sci. Rep.-UK, 6, 37551. <https://doi.org/10.1038/srep37551>.

## Critical trace elements and REE in abiotic and biotic environments: geochemical inferences from the Apulian karst (Southern Italy)

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*Keywords:* REEs, terra rossa, hormesis.

Rare earth elements (REEs) are key constituents of modern technologies and play important roles in several industrial and chemical applications. They are also utilized in medical, agricultural and zootechnical applications, such as tracers, fertilizers and feed additives, thus contributing to REE increases in ecosystems with effects on the environment and biotic communities not yet completely understood. More information about REE's presence and biological effects is required for environmental risk monitoring and management.

The present work aims to investigate concentrations, mobility, and effects of REEs passing from the abiotic environment to model organisms considering rock substrates and soils as REEs sources. With this objective, “terra rossa” and bauxite deposits from the Apulian karst, significantly enriched in critical trace elements and REE relative to the carbonate substrate, have been considered natural study cases. Starting from the calcareous bedrock to karst products (red calcite incrustations and nodules up to fine-grained “terra rossa”) a regular increase in REE contents (as also in SiO<sub>2</sub>, TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, Ni, V, Cr, Th and U) is regularly observed. This strong silicate character requires a considerable supply of allochthonous material providing a silica component on the calcareous bedrock. Speculatively, the Quaternary terraced marine deposits (mixed carbonate/siliciclastic sediments) may represent the source of this siliciclastic input. Different environmental conditions can also be envisaged based on changing Ce anomaly from negative in calcareous bedrock and associated alteration products to no anomaly in fine-grained “terra rossa”.

These preliminary data indicate that the karst alteration process on limestone was promoted and accelerated by allochthonous siliciclastic material supply and silicate solution circulation between the carbonate bedrock and the overhead pelite materials (Micheletti et al., 2023). These processes seem to favor the mobility and increase of REE contents from the carbonate substrate to the residual deposits.

The final step is to evaluate the available evidence for adverse and/or positive effects of REE exposures in plant, soil-borne plant-pathogenic fungi and animal models and their physiological/molecular evidence (Gjata et al., 2022). The overall information points to shifts from toxic to favorable effects in model systems according to their concentrations suggesting the occurrence of hormetic behavior (Tommasi et al., 2022). This analytical approach will be easily extended to anthropic sources such as active or inactive mining/industrial sites.

Gjata I., Tommasi F., De Leonardis S., Dipierro N. & Paciolla C. (2022) - Cytological alterations and oxidative stress induced by Cerium and Neodymium in lentil seedlings and onion bulbs. *Front. Environ. Sci.*, 10. <https://doi.org/10.3389/fenvs.2022.969162>.

Micheletti F., Fornelli A., Spalluto L., Parise M., Gallicchio S., Tursi F. & Festa V. (2023) - Petrographic and Geochemical Inferences for Genesis of Terra Rossa: A Case Study from the Apulian Karst (Southern Italy). *Minerals*, 13(4), 499. <https://doi.org/10.3390/min13040499>.

Tommasi F., Thomas P.J., Lyons D.M., Pagano G., Oral R., Siciliano A., Toscanesi M., Guida M. & Trifuoggi M. (2022) - Evaluation of rare earth element-associated hormetic effects in candidate fertilizers and livestock feed additives. *Biol. Trace Elem. Res.*, 1-9. <https://doi.org/10.1007/s12011-022-03331-2>.

## Road dust, a vector for potentially toxic elements (PTEs) and microplastic contamination in the urban areas of Ravenna and Marina di Massa (Italy)

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Keywords: road dust, metal contamination, microplastic.

In urban areas road dust (RD) resuspension represent a pathway for environmental contamination. RD is a heterogeneous mixture of particles created by the physical abrasion of organic and inorganic materials derived from anthropogenic activities (vehicular traffic, construction works). Potentially toxic elements (PTEs) and microplastic (MP) particles are among the main pollutants in RD, representing a potential risk for urban ecosystems, accumulating in waterways, soils, sediments and finally the sea via storm water run-off or air transport. In this study, RD was analysed to assess the potential risk to the ecosystem associated to i) the presence and mobility of PTEs (total fraction) and their ability to accumulate in organisms (bioavailable fraction) and ii) to the presence of MP. Samples were collected in two residential and touristic coastal cities, Ravenna and Marina di Massa (Italy), characterized by industrial and ports activities, from roads with varying levels of vehicular traffic densities, in residential and industrial areas during summer 2021 and 2022.

Preliminary results show higher concentrations of As, Ba, Cd, Co, Cu, Ni, Pb, Zn, Sn and Hg in samples from Marina di Massa in 2021. Zn, Cu and Ni are above the Italian law limits defined for soils (DL 152/2006) (up to 763, 352 and 147 mg/kg respectively) with an enrichment up to 11, 14, and 3 times UCC crustal values. The bioavailable fraction of metals shows values up to 335 mg/kg of Zn, 6.5 mg/kg of Cu and 1.4 mg/kg of Ni in Marina di Massa. Analyses of 2022 samples are undergoing. MP was manually separated from three grain size fractions (2000-1000, 1000-500, 500-250 µm), observed and quantified (range 7.6-38 MP/g). The 500-250 µm fraction contained the highest number of MPs (58 MP/g), representing in few samples up to 73% of the MPs in the three fractions. The highest number of MP was found close to the industrial area in Marina di Massa. Tyres wear-out black particles; yellow and blue fragments, probably formed by the disaggregation of road traffic signs, with associated transparent glass spheres (microbeads); white, brown, and black fibres; and metal spheres form the majority of MPs. Chemical characterization of MPs is planned by FTIR and TD/Pt-GCMS.

In the two areas exposure to RD may cause adverse effects to the human and ecosystem, because of PTEs concentrations and of MPs, which represent a risk for ingestion by terrestrial (birds) or aquatic organisms (zooplankton, fishes), potentially limiting their functioning. The study confirms a key role of RD as a “potential contamination vector” for PTEs and MPs trough wind and rainfall across different environmental matrices (soil, sediments, water) affecting the biological cycle at different levels. Future work should use RD as a proxy to assess the environmental state of urban areas, identifying polluted sites and contributing to select remediation strategies to limit its dispersion in the environment (e.g. increasing green areas).

DL 152/2006 (2006) - Decreto Legislativo 3 aprile 2006, n. 152 - Norme in materia ambientale. GU S. Gen., 88, Suppl. Ord. 96.

## **Linking earth sciences, terrestrial ecosystems and social sciences in critical zone study: the project ABRESO (Belmont Forum)**

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*Keywords:* geo-bio-chemistry, earth observations, transdisciplinarity.

The term *Critical Zone* (CZ) has become in the last decades a main focus of interdisciplinary studies in the field of natural sciences. Defined as the system of chemical, biological, physical and geological processes operating together to support life at the earth surfaces (Brantley et al., 2007), the CZ supplies nutrients and energy that sustain terrestrial ecosystems.

The impact of humans on the CZ has significantly increased over time, radically changing the chemistry of atmosphere, hydrosphere and pedosphere, and reshaping earth's surface. The challenge of crossing disciplines, space and timing is becoming a peculiar feature in the study of CZ's processes.

Earth scientists are involved in CZ studies investigating weathering, soil formation, erosion, surficial water cycle, element mobility, fluxes and provenance, abiotic and biotic redox reactions, rate and reaction mechanisms at the mineral-organism-water interface. Isotopic systematics significantly contribute to these CZ topics and currently include traditional and non-traditional stable isotopes, radiogenic isotopes, and fission products. The multi-isotopes toolbox is successfully applied also to investigate nutrient cycling at the soil-water-plant boundary.

The ABRESO project (Abandonment and rebound: Societal views on landscape and land use change and their impact on water and soils) is part of the pull of international projects funded by the Belmont Forum to orientate CZ researches on soil and water sustainability in landscapes undergoing transitions. The transdisciplinary approach is the main feature of the ABRESO project, where natural and social researchers share the goal of studying land abandonment in different contexts and countries (United States, Italy, Taiwan, France and Japan). In Italy, three case studies have been selected in the eastern and western part of the Alps. Here, land use changes from grazing and terrace cultivation to abandonment and forest recolonization are observed. In the project, processes occurring at the ground level (involving soil and vegetation) are investigated using chemical and isotopic tools that include carbon and nitrogen concentration and isotope composition in soil and plants, CO<sub>2</sub> fluxes, soil physical properties (e.g., texture, aggregates stability, pH, electrical conductivity). These parameters are applied to characterize the transition between old forest-young forest-pasture. We upscale these observations in space and timing (20 years) using remote sensing. We work on time series of land cover maps extracted from satellite and aerial images and trends in snow cover duration over the past 20 years.

In ABRESO, the natural science complements with the social scientists, given that bio-geo chemical processes associated to land use and land use change respond also to social and economic drivers. An effort is done to compare the main ecosystem services deduced by the bio-geochemical investigation with the perception of local stakeholders in charge of land management practices and policies. Ongoing findings of our project underlines that the interaction between natural science scientists, providing conceptual modelling on the soil-water-vegetation system, and social science scientists, addressing stakeholders' perception on the socio-economic impact of land-use change on the local population, is nowadays becoming a priority to promote a sustainable management of the evolving ecosystem.

Brantley S.L., White T.S. & Ragnarsdottir K.V. (eds.) (2007) - The Critical Zone: Where Rock Meets Life. Elements, 3(5).



## Magnetic carbon-based biomaterials for the recovery of inorganic pollutants from contaminated water

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Keywords: functionalization, adsorption, CRMs.

Magnetic carbon-based adsorbent or biochars (MBs) have been widely studied for the removal of pollutants from wastewater (Hassan et al., 2020), due to easy separation and high reusability of the adsorbent, and the improved physico-chemical properties of the carbon (Hassan et al., 2020; Wurzer & Mašek, 2021). Generally, MB is produced by functionalizing the initial feedstock with synthetic iron (Fe-) containing precursors, specifically chloride or sulfate salts of Fe<sup>2+</sup> and Fe<sup>3+</sup> ions (Sewu et al., 2020). However, these salts may have toxic properties, so their use raises environmental concerns.

Iron-rich waste represents a more sustainable alternative to iron salts to introduce magnetic characteristics to biochar (Sewu et al., 2020; Wurzer & Mašek, 2021). In this research, Fe-rich sludge produced during the potabilization process of drinkable water is used for the production of MB. Therefore, magnetic biochar was produced from the pyrolysis of Fe-rich sludge and vine pruning, a local, highly available, organic waste. The resulting magnetic biochar has been tested for the adsorption of boron and arsenic from solution.

Boron is an essential micronutrient that has raised much interest, given the narrow balance between its necessity and toxicity. Boron's presence in the Critical Raw Material list highlights its importance in developing sectors such as renewables and e-mobility.

Arsenic is an ever-present worldwide environmental contamination issue. The process of As sorption with magnetic biochar for treatment of contaminated water has been demonstrated by many studies (Hao et al., 2018).

Preliminary results of adsorption tests showed that magnetic biochar is more effective in the removal of B and As from solution, compared to pristine biochar. The effect of contact time and adsorbent dosage were also investigated in batch experiments.

This study shows that functionalization of organic biomass with Fe-rich sludge, an abundant and environmentally sustainable Fe rich source, is a viable way to produce a magnetic biochar applicable for pollutants removal from wastewater.

Hao L., Liu M., Wang N. & Li G. (2018) - A critical review on arsenic removal from water using iron-based adsorbents.

RSC Adv., 8(69), 39545-39560. <https://doi.org/10.1039/c8ra08512a>.

Hassan M., Naidu R., Du J., Liu Y. & Qi F. (2020) - Critical review of magnetic biosorbents: Their preparation, application, and regeneration for wastewater treatment. Sci. Total Environ., 702, 134893. <https://doi.org/10.1016/j.scitotenv.2019.134893>.

Sewu D.D., Tran H.N., Ohemeng-Boahen G. & Woo S.H. (2020) - Facile magnetic biochar production route with new goethite nanoparticle precursor. Sci. Total Environ., 717, 137091. <https://doi.org/10.1016/j.scitotenv.2020.137091>.

Wurzer C. & Mašek O. (2021) - Feedstock doping using iron rich waste increases the pyrolysis gas yield and adsorption performance of magnetic biochar for emerging contaminants. Bioresource Technol., 321, 124473. <https://doi.org/10.1016/j.biortech.2020.124473>.

## Release of volatile organic compounds (VOCs) from hydrothermally altered soil: biological, physical, and chemical constraints

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**Keywords:** vocs, hydrothermal soil, laboratory experiment.

Two sources of volatile organic compounds (VOCs) in hydrothermally altered soils can be recognised: (1) microbial activity and (2) geogenic degassing. So far, the contribution of hydrothermally altered soils to the overall VOC load discharged by geogenic degassing to the atmosphere is unclear. In this study, we measured the release of VOCs from soils collected from the hydrothermal area of Solfatara di Nepi (Viterbo, Italy) under laboratory conditions. A total of 12 soil samples were collected at 0-10 (surface) and 35-45 cm (deep) depths from six sampling sites, equally distributed across two zones characterised by high (>800 g m<sup>-2</sup> d<sup>-1</sup>; HH) and low (<155 g m<sup>-2</sup> d<sup>-1</sup>; LH) CO<sub>2</sub> emissions measured by the accumulation chamber method, respectively. Chloroform fumigation extraction showed that most LH soils had higher contents of microbial biomass C and N than HH soils. Total dissolved organic C and N contents showed the opposite trend. Triplicate 30-min jar incubations were carried out in a dynamic flow-through system on 10-50 g of soil. Real-time VOC analyses were performed using a proton transfer reaction–time of flight–mass spectrometer (PTR-TOF-MS). Surface and deep soil samples were flushed with oxidic (air) or anoxic (N<sub>2</sub>) gas streams, respectively, according to their field redox conditions. The soils were incubated separately at 7°C and 30°C: first to mimic field conditions and then with soil heating to reflect volcanic conditions. To investigate whether microbial activity influenced soil VOC exchange, a further incubation was performed at 7°C after sterilising soils by gamma-radiation (25,000 Gy). Up to 362 different VOCs (mass-to-charge ratios ranged from 34-259) were detected by PTR-TOF-MS. Overall, total VOC emissions ( $\sum$ VOCs) were higher for the HH (summed total of all detected masses ranging from 0.22±0.02 to 97±8 nmol gdw<sup>-1</sup>h<sup>-1</sup>) than LH (ranging from 0.15±0.04 to 75±8 nmol gdw<sup>-1</sup>h<sup>-1</sup>) soils, which may have been related to higher rates of organic matter decomposition in the HH soils (evidenced by higher total dissolved organic C and N contents). However, a significant geogenic VOC contribution to the overall soil VOC emissions was expected for HH soils given their lower microbial biomass C and N contents. As expected, higher amounts of VOCs were released from soils incubated at 30°C than 7°C. Deeper soil samples always exhibited higher  $\sum$ VOCs than the shallower ones, suggesting a positive response of VOC release to low-oxidising soils. Notably, the  $\sum$ VOCs of sterilised soil samples were, on average, 75 times higher than their non-sterilised homologues. This evidence underlines the pivotal role of soil microbes to act as a sink for VOCs.

## **Anthropogenic and natural factors affecting the water quality of the Metauro River valley groundwater resource (Central Italy)**

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*Keywords:* water pollution, hydrogeochemistry, Metauro river.

In this work, the ground- and surface waters from the Lower Metauro River Valley (LMRV; Central Italy) were sampled and analyzed in two distinct surveys (spring and autumn 2022) to assess the natural and anthropic factors possibly influencing the chemical features and quality of the water resources used for drinking purposes. LMRV develops orthogonal to the Adriatic Sea and is bordered by outcropping formations constituted by carbonates, marlstones, evaporites, and clays, which form the bedrock above which the alluvial deposits are deposited. The latter, mostly consisting of calcareous gravels, sands, and silty clays, with intercalated lenses of fine materials, host a mainly single-layer phreatic aquifer, in connection with the main river course. The geochemical investigation shows that the waters are meteoric in origin, as supported by the  $\delta^{18}\text{O}\text{-H}_2\text{O}$  and  $\delta^2\text{H}\text{-H}_2\text{O}$  isotopic values that approach the Mediterranean and Local Meteoric Water lines. Waters have a chemical composition which reflects the interaction with carbonatic lithologies since the groundwater samples are characterized by hardness values 30 to 74°F (mean 47°F, i.e. “really hard” waters) and oversaturated with respect to  $\text{CaCO}_3$ .

The electrical conductivity (EC) stretches from 530 to 2,440 (mean 1,155)  $\mu\text{S}/\text{cm}$ . The lower values are generally associated with the fluvial waters and those wells located near the Metauro riverbed, testifying important surface and groundwater exchanges. Increasing EC values (up to 1,000  $\mu\text{S}/\text{cm}$ ) are commonly related to increasing contents of  $\text{NO}_3$  (up to 400 mg/L), which frequently exceed the threshold value for drinking waters indicated by the WHO and Italian Law of 50 mg/L (mean and median: 52 and 50 mg/L, respectively).

The highest EC values (>1,000  $\mu\text{S}/\text{cm}$ ) are however mostly controlled by high concentrations of Na and Cl (up to 280 and 640 mg/L, respectively) and due to water-rock interaction processes of waters with the evaporitic deposits related to the Messinian salinity crisis that sporadically outcrops at the border of LMRV as suggested by several samples showing Na/Cl molar ratios near 1. Nonetheless, some Na or Cl excesses are also recorded. High Cl contents, coupled with low  $\text{NO}_3/\text{Cl}$  molar ratios (<1), seem to derive from sewage waste and manure used for agricultural purposes. On the contrary, Na-excess seems to be originated by dissolution processes suffered by silicate minerals characterizing the bedrock. Increasing EC and Na contents affect the quality of the waters, determining a SAR (Sodium Adsorption Ratio) index up to 4, which coupled with the EC values >1,500  $\mu\text{S}/\text{cm}$  indicates a medium salinity hazard and caution in the use of water for irrigation purposes. The investigation suggests that action should be taken to minimize the anthropic impact on the water resource and limit the private use even in those areas naturally enriched in dissolved compounds as they are potentially able to affect the agricultural practices.

## Historical trends of metal pollution in the metropolitan area of Milano: a combined dendro-chemical, dendro-magnetic and dendro-X-ray diffractometric study

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*Keywords:* metal pollution, urban areas, dendrochemistry.

Temporal records of air pollution for metals in metropolitan areas are usually limited to a few decades. However, a long-range view is essential to better constrain potential sources of pollution for the assessment of containment strategies and protocols. The metropolitan area of Milano suffered a rapid development after WWII with a fast growth of population, vehicular traffic, and industrial activities, with the side effect of introducing toxic metals into the environment. Here, we explored an innovative approach for the reconstruction of the historical trends and potential sources of metal pollution in the Milano metropolitan area by combining dendro-chemistry, dendro-magnetometry and dendro-XRD.

Tree cores from *Ulmus* species were sampled in Milano municipal parks. Single tree rings were analyzed with laser ablation ICP-MS for the heavy metal concentrations, with a VSM for the magnetic properties of the ferromagnetic microparticulate, and with XRD for the mineralogical nature of the various solid particles. Results show that heavy metal concentrations in tree cores from the Milano city center are historically lower than those in the more peripheral areas. An *Ulmus* tree core has returned the longest historical record (more than 70 years) and its location close to an ARPA air monitoring station allowed a crosscheck of the results since 2005. Here, for example, Pb concentrations show an abrupt enrichment after WWII, a steady decrease after mid 50s and then a new increase during mid 70s with a maximum in the mid 90s. After this period, a steady decrease begins, likely related to the unleaded gasoline introduction, and only in 2020 Pb levels are comparable with those of the mid 70s. The dendro-magnetic study reveals the presence in the tree rings of ferromagnetic particles in variable amounts, which are periodically correlated with the heavy metal distribution. Ongoing hysteresis analyses allowed to interpret these ferromagnetic particles as very fine (titanio)magnetite grains likely at the nanometer scale-range, or in the micrometric range when arranged in aggregates, as observed also at the scanning electron microscope (SEM). Results from the X-ray diffraction reveal the occurrence of (Fe,Ti)<sub>3</sub>O<sub>4</sub> (magnetite structure, in agreement with the VSM analyses), micro/nano crystalline *silica* and clay minerals (with the structure of chlorite and smectite).

This study, still in progress, represents a first attempt for an innovative approach to the investigation and monitoring of the environmental contamination of metals in metropolitan areas. We are confident that, although the physiology of the single tree may, in part, control the uptake of metals and thus alter or temporally shift the registry of the contamination peaks, the combined dendro-chemical, dendro-magnetic and dendro-XRD approach is the key for better identifying the source of contaminants.

## **Rain or shine, flowing from the spring to the outflow: geochemical evolution of stream waters across a rural-to-urban transect (Greve River, Tuscany, Italy)**

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*Keywords:* river water geochemistry, climate change, anthropocene.

Stream ecosystems are experiencing dramatic upheavals during the Anthropocene as a consequence of multiple stressors including pollution, urbanization, and climate change. Being topographical low points, they collect sediments and runoff from the surroundings, resulting in disproportionately high impacts on biodiversity and water quality. Moreover, changes in precipitation regimes, resulting in prolonged droughts interspersed with concentrated and intense rain events, induce augmented perturbations and pose challenges to the resilience of stream ecosystems undermining their self-purification capability (i.e. a combination of physical, chemical and biological processes able to remove pollutants from water, either immobilized in particulate forms or released as gaseous compounds).

In this study, the results of multiple sampling campaigns, conducted under diverse climatic conditions and aimed at collecting and analyzing stream waters and suspended solids along the Greve River (GR; Tuscany, Italy) are presented. GR rises in the Chianti hills and flows across rural landscapes covered by vineyards and olive groves, encountering minor urban settlements. The final part of the stream course crosses an intensely industrialized and urbanized area in the eastern outskirts of Florence until the confluence with the Arno River.

Six sampling campaigns were performed between May and October 2022 for a total of 71 water samples and 39 suspended sediments. Water samples were analyzed for (i) major and minor dissolved ionic species, (ii) nutrients (total phosphorus and total nitrogen), (iii) chemical oxygen demand (COD), (iv) trace elements, (v) dissolved gases, and (vi) stable water isotopes. Suspended sediments were gravimetrically quantified and subjected to leaching tests in CO<sub>2</sub>-saturated water to investigate the potential release of trace elements under intense interaction with meteoric waters.

Stream waters experienced a geochemical evolution along the stream course, mainly affecting the total dissolved solids, nutrients and COD. The comparison among the different sampling campaigns highlighted the augmented stressed conditions suffered by the watercourse during drought periods, producing oxygen depletion. Nutrients and trace elements were affected as well as the concentrations of dissolved CH<sub>4</sub> with potentially augmented fluxes of this greenhouse gas to the atmosphere. Trace elements recovered from leaching tests on suspended materials mimed the variations of their dissolved counterparts, testifying that their origin was mainly related to water-rock interaction and sediment transport through surface runoff. Both spatial and temporal variability was observed in dissolved metals in response to land use and precipitation regime. Rural sites were enriched in Cr, Cu and Se, whereas urbanized sites were enriched in V, As, Sb. Seasonality and weather conditions particularly affected the levels of Sb, Cr and Pb.



## **S2.**

### **Geodiversity vs Geobiodiversity: a multidisciplinary approach to describe the Earth surface**

*CONVENERS AND CHAIRPERSONS*

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## **A geological path to enhance geodiversity in the Gravina of Laterza ("Terra delle Gravine" Regional Park, Puglia, Southern Italy)**

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*Keywords:* geotourism, geodiversity, Gravina of Laterza.

Geodiversity represents the variability of features and geological heritage that characterises an area, and is also defined as the silent partner of "biodiversity" in natural systems. The variability of geological features enables different landscapes and environments, fostering biodiversity even in limited portions of territory. The important relationship between geodiversity and biodiversity is particularly evident considering the deep incisions, locally named "gravine", that characterize the southwestern Murge area (Puglia, Southern Italy). One of these "gravine", Gravina of Laterza, geosite that recalls the North American canyons, represents the most extensive and deepest of them (about 12 km long and up to 200 m depth). Along this geosite, in order to make "visible" how geodiversity affects biodiversity, has been proposed a geological path with several different stops. Among the many geological elements that can be observed and described along the path, the site of "Grotta Croce" ("grotta" is the Italian term for cave) is frequently visited but little known geologically. Before to describe the peculiarity of the cave, it is necessary to shortly introduce the visitors to the regional geology of the area. The geological background of the area is that of the transition between the Murge and the Bradanic Trough. The Murge corresponds to a structural high made up of Cretaceous limestones; the Bradanic Trough is the area where the same rocks are tectonically displaced toward southwest and covered by a Quaternary sedimentary succession. At the border of the morpho-structural high, a stream originally flowing on the flat top of the quaternary succession, has deepened its course and reached the Cretaceous bedrock creating the spectacular fluvial incision of the Gravina of Laterza. Along this canyon, the evolutionary history of the area, spanning millions of years, can be revealed. The "Grotta Croce" site, located in the upper part of the gravina and easily accessible, allows to observe unique features in the limestones, such as the various nests of the autochthonous rapacious of the area embedded in the folded and faulted layers. Three distinct areas can be identified: (i) the area above the cave, where the residual deposit of "Terra rossa" lies above the limestones, partially covered by calcarenite and characterized by Mediterranean scrub vegetation; (ii) the less vegetated calcareous portion of the cave and (iii) the area below the cave where the Gravina stream flows, i.e., a humid rich-vegetation area. Through the examination of this restricted area, it is evident how the geological and evolutionary history of the region supports the harmonious coexistence of different sub-environments within small plots of land. Hence, describing sedimentary, structural and landscape features can lead to a more complete geoturistic offer and conservation of the natural system.

## Geodiversity versus biodiversity in Oceanic Islands

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*Keywords:* geodiversity, biodiversity, Oceanic Islands.

Geology and Biology interact closely in most environments at the upper levels of our Planet. Oceanic islands are no exception. We consider two types of islands with contrasting structure, composition and origin. One, St. Peter-Paul Islets, are a group of small rocks emerging barely from the equatorial Atlantic (Bonatti, 1990). Darwin visited them in 1832 (Darwin, 2018) and realized they are different from common oceanic volcanic islands. Today we know these islets are composed of ultramafic mylonites of mantle derivation, probably uplifted by compressive tectonics. An example of the other type is Easter Island, a mostly basaltic volcanic system emplaced > 1 million years ago in the South Pacific off the East Pacific Rise. Humans settled on Easter Island causing controversial events including its deforestation (Flenley & King, 1984). The contrasting biodiversity of these two island systems will be reviewed and discussed.

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## On the contribution and possible role of mollusks to coralligenous build-ups: results from CRESCIBLUREEF project

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*Keywords:* malacofauna, microhabitat, bioconstruction.

Coralligenous is one of the most monumental bioconstruction of the Mediterranean Sea. It forms biogenic framework mainly made by crustose coralline algae, with a minor contribution of skeletonized invertebrates such as bryozoans, serpulids, sponges, and of autochthonous micrite. Coralligenous forms discrete build-ups or tabular banks, which represent a complex and very heterogeneous substrate providing microhabitats and niches at different scale. Mollusks are the most common vagile and sessile organisms among the rich macro and micro fauna supported by coralligenous. Despite that, the malacofauna of the coralligenous has been poorly studied and its possible role in the structure not quantified or defined.

The FISR project CRESCIBLUREEF - "Grown in the blue: new technologies for knowledge and conservation of Mediterranean reefs" is aimed at exploring the components, growth rate and accretion style of the Mediterranean coralligenous bioconstructions. In the framework of this project, we collected several samples, both whole structure (two build-ups) and scraped materials (four build-ups), from a discrete build-up field offshore Marzamemi (Ionian Sea, Sicily) at a depth between 34 m and 37 m respectively, from which we recover all the alive and dead mollusks. Moreover, we also prepared thin sections for inner structure description and quantification from the two whole build-ups.

Living mollusks and thanatocoenoses comprises 155 species (59 bivalves, 96 gastropods), among which 67 alive. Shannon Indexes range between 3.42 and 3.66, whereas Pielou's Evenness is 0.88. At least 15 new species of mollusk have been identified respect to the CorMol database. Statistics indicate that heterogeneity occurs among samples. These results lead to consider that the biogenic hard substrate provided by Coralligenous do not host a specific mollusks assemblage, but the complexity of this kind of substrate supports in turn a much more complex and not straight-forwarded assemblage, with a mixing contribute of species indicating different settings. Some of them derive from surrounding bottoms. The study of the inner structure, through petrologic analysis, does not allowed us to identify mollusks at species level. It provides indication on the limited contribution of this phylum to the bioconstructional process. In fact, point-counting analyses of thin sections indicates a mean contribute of mollusk corresponding to less than 1%, with only rare thin sections with values reaching 10%.

## On the biogeomorphology of crustose coralline algae in the Mediterranean Sea

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Keywords: biocostruction, Mediterranean seascape, biogeomorphology.

The shelfal benthic zone of the Mediterranean Sea host a wide variety of habitats, some of which already well known because of their biological importance and their fundamental role in protecting the coast (e.g., *Posidonia oceanica* meadow). In the mesophotic (< 30 m of water depth), algal reefs and rhodolith beds recently gain more and more interest, because they represent hotspots of biodiversity, and they are listed in European and National directives for the protection and monitoring of the marine environment. These habitats are of extreme importance not only, or not exclusively, because of their biodiversity, but also because they express the geodiversity, as they are the “combination” of both biological and geological processes trough time. Marine bioengineers are organisms able to increase complexity at the seafloor. Among them, bioconstructors are the ones able to produce biogenic carbonate as permanent (or long-term) structures at the seafloor. The most known are hermatypic corals forming the coral reefs, where their growing not only develop a very special marine habitat, but also drives the geomorphological development of coasts and atolls. Unfortunately (or not), no hermatypic corals yet in the Mediterranean Sea, but, luckily, crustose coralline algae (CCA). CCA are sciaphilous algae with skeletal thalli that form newly hard and mobile substrates or encrusted available ones. They grow in dim-light conditions, and therefore able to colonize both shallow water with low level of irradiance, and relatively deep bathymetric interval. In shelfal waters, the Mediterranean Sea hosts abundant coralline algae forming algal reefs, referred to as coralligenous, or mobile bottoms, known as rhodolith beds. One of the most underexplored and under-considered concepts is that they contribute to the carbonate precipitation, to the sedimentary regime and to the seascape sculpturing and geomorphological development of the seafloor. Consequently, they provide one of the most interesting examples of biogeomorphological constructive phenomenon, in which the development and faith of the structures depends on both the maintenance of appropriate environmental conditions for biodiversity, but also a geological approach that takes into account the geological processes involved trough appropriate timescale. We will give insights on the biogeodiversity of CCA structures across the Mediterranean Sea, both algal reefs and rhodolith beds, pointing out some of the main scientific challenges, problematic aspects (nomenclatural for example), and exploring how geodiversity is fundamental for the appropriate measure of knowledge and conservation of biodiversity.



## Culturable mycobiome in serpentinite soils

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Keywords: serpentinite, PTE, mycodiversity.

Serpentinite soils are characterized by severe edaphic conditions due to low content of essential nutrients (e.g., Ca, K, P, N), adverse Ca/Mg ratio, low water holding capacity, and high contents of geogenic potentially toxic elements (PTEs), in particular Cr, Ni, and Co (Marescotti et al., 2019 and references therein). The site chosen for this study (Sassello, Liguria, Italy) is located in the serpentinites of the High Pressure–Low Temperature (HP–LT) metaophiolites of the Voltri Massif. The soils of this site are shallow to moderately deep (40–100 cm) and developed on massive to strongly foliated serpentinite bedrocks. Eight soil profiles were selected based on the bedrock heterogeneity and sampled by manual core drilling. In each sampling point, the bedrock and one soil sample were collected following the criteria of GEMAS project (Albanese et al., 2015). The studied soil profiles are characterized by a weakly developed A horizon, which is directly in contact with the C horizon, and a very thin O horizon (5–10 cm) and were classified as Magnesian Leptic Skeletic Cambisols. Soil samples are composed by high quantities of unweathered to partially weathered primary minerals (antigorite, clinocllore and spinels) with variable amount of authigenic clays and Fe-oxyhydroxides. They are characterized by high content of PTEs, exceeding, up to one order of magnitude, the threshold values according to Italian law. PTEs are hosted both in primary and authigenic minerals, demonstrating the geogenic origin of these metals, which derive from the natural weathering of parent rocks and redistribution during pedogenetic processes.

Biological diversity contributes significantly to the biogeochemical cycling and balancing within the ecosystem (Aravind et al., 2021). Despite the stressing conditions related to the toxic elements, this kind of habitats can provide ecological niches to a wide range of organisms, including fungi (Shu & Huang, 2022). The main goals of this work were i) the evaluation of the mycodiversity in a naturally polluted serpentinite soil and ii) the isolation of culturable fungal strains, which could be later used in mycoremediation protocols. Soil sampling was conducted at the previously mentioned eight sites. The samples were plated on three replicates of two different media, for a total of 48 plates. To promote fungal growth, the plates were incubated at 24°C for 7 days and monitored for further 7 days. Regarding the mycobiome characterization, cultural and molecular methods were used. A total of 877 fungal colonies were counted on the growing media, and grouped into 62 morphotypes, which differently partitioned throughout the sites. The predominant identified genus was *Penicillium*, with 312 colonies, accounting for 35.6% of the total. Our research group investigations reveal a significant soil mycodiversity and have allowed us to isolate several strains employable in mycoremediation protocols.

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## Geodiversity national scale map of Italy: challenges and opportunities

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Keywords: geodiversity, spatial analysis, conservation.

Natural diversity includes bio- and geo-diversity (Brilha, 2016). The first one describes the genetic, species and ecological variability of living organisms on Earth. The second consists of the variety of abiotic elements of natural systems, such as rocks, landforms, soils and hydrological features (Gray, 2004). Geodiversity is a key component for natural diversity evaluation and preservation, and it is in fact increasingly being included in traditional bio-based conservation plans (Anderson et al., 2015).

A national-scale geodiversity map of the Italian territory has been proposed. A “grid analysis” approach in a GIS environment was adopted for a quantitative assessment of geodiversity. The method consists of superimposing a grid on each thematic map, whose cell with a side of 25 km represents the spatial unit to summarize and process the data. The Geodiversity Index (GI) was assessed integrating geological (lithology), morphological, pedological and hydrological (surface and underground waters) data. Geodiversity results very high for the eastern Alps and for central and southern Apennines, while it shows the lowest values in the plains and many coastal areas.

Furthermore, a map showing the distribution of geodiversity classes for all Italian regions, which represent the most significant administrative entity in Italy, has been also assessed by calculating the Regional Index (RI). The highest RI typify the Umbria, Trentino-Alto Adige, Liguria, Abruzzo, Basilicata and Campania regions, while the lowest ones characterize Puglia and Emilia-Romagna regions.

Future developments may lead to a comparison between geodiversity and habitat richness of the territory. Geodiversity and biodiversity are related terms and concepts because greater geodiversity reflects greater heterogeneity of natural environments and ecological niches, resulting in increased species richness (Tukiainen et al., 2023).

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## The dual role of sponges in Coralligenous build-ups: competitors of carbonatogenic bacteria and promoters of unusual biomineralizations

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*Keywords:* sponge, bacteria, biomineralization.

The morphological growth of Coralligenous build-ups of Marzamemi (SE, Sicily, Italy) is strongly influenced by the activity of sponges since: (i) they drive the direction of encrustations of the skeletonized builders; (ii) weaken the framework through bioerosion processes; and (iii) induce the precipitation of autochthonous micrite. Here we focus on the role played by these sponges in an observed unusual biomineralization process. The characterization and dating of these products may reveal the ecological evolution and functional role of the sponge associations during the growth of the build-ups, indeed the relict spicules, preserved in the autochthonous micrite, represent the fossil record of the past Coralligenous demosponges (Bertolino et al., 2019).

In the coralligenous build-ups, sponges pervasive colonization is clearly testified by the high amount of spicules occurring both on external surfaces and internal framework (cavities and microcavities). As observed by Guido et al. (2013) for cryptic bioconstructions in submerged marine caves, these microcavities are useful for the development of carbonatogenic sulphate-reducing bacteria; however, in the studied coralligenous build-ups cryptic micro-cavities are occupied by sponge that play a limiting role in the development of heterotrophic bacteria. The competition for space between sponges and carbonatogenic bacteria has been also observed in biogenic crusts common in Aegean Mediterranean caves (Guido et al., 2019), and suggests that: (i) this ecological relationships is not habitat-specific and, (ii) it may develop in a range of environmental settings (from open to confined systems). Moreover, the geobiological features and the role of skeletonised and non-skeletonised communities (e.g., bacteria) forming the Coralligenous, have still not been explored in detail. Several techniques of investigation have shown that the massive presence of spicules engulfed in the autochthonous micrite suggests a carbonate precipitation in association with non-living organic substrates of sponges like those observed in some biogenic crusts of submerged caves (Guido et al., 2019). This organomineralization is supposed to form via Ca<sup>2+</sup>-binding ability of acidic amino acids, particularly humic and fulvic acids, that may be derived from degraded metazoan organic matter during early diagenesis (Neuweiler et al., 2007). Despite subordinate in comparison to the skeletonized organisms, the occurrence of autochthonous micrite suggests a possible contribution of this non-skeletal carbonate component in the strengthening of the primary framework due to the in-situ cementation of this micrite type. The increase the knowledges on the build-ups developed in the open settings and comparison with those forming in confined environments, could be used to clarify the role of unusual sponge biomineralizations in the palaeoecological reconstruction of the fossil record.

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## Unusual biomineralization processes in marine invertebrates: the example of Cirratulid polychaetes from Peru

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*Keywords:* cirratulidae, bioconstructions, biomineralization.

Carbonate biomineralization in marine organisms normally occurs as three distinct types, known as: “controlled”, “induced” and “influenced”. Among invertebrates, reef-building polychaetes of the family Cirratulidae appear to provide the first example of “dual-phased” biomineralization as they simultaneously combine “controlled” and “induced” types in the formation processes of their aggregated tubes. Recently, Kočí et al. (2020) described the general morphology and internal framework of some bioconstructions of a Miocene cirratulid species and stressed the need of further comparative studies to better understand the nature of the calcareous matrix, tube ultrastructure and biomineralization processes. The main purpose of this work is to study the mineral structure of some Miocene (Diplochaetetes) and Recent (Dodecaceria) cirratulid bioconstructions from southern Peru through optical microscopy, epifluorescence, SEM-EDS analyses and morphometry. Results have also been statistically processed in order to highlight the possible relationships between size and chemical composition of the skeletal component with the morphology of the bioconstructions themselves, which in turn hints to environmental parameters. Three linear correlations, considering as variables morphological parameters (i.e., tube diameters) and the weight concentration of the main elements (Ca and Sr), were tested. Both fossils and recent specimens show similar correlations among composition and morphometric parameters, suggesting that the growth/evolution of these bioconstructions is presumably unaffected by environmental chemo-physical conditions. The primary ultrastructure of the tube walls points to controlled biomineralization, while the “intertube” areas of the bioconstruction, filled by a calcareous matrix frequently agglutinating extraneous sand grains, would be the product of an induced biomineralization. Agglutinated sand grains have various compositions and many of them are igneous, their origin being attributable to nearby coastal batholiths. Until now the means by which the “dual-phased” biomineralization processes take place in cirratulids have not been described in detail, probably due to several systematic misinterpretations occurred in the past prior to the description of Fischer et al. (1989), where fossil cirratulid specimens were frequently reported as sponges or corals instead. We also highlighted that the unique dual-phased biomineralization system of cirratulids seems not to have evolved since the Eocene, when they appeared.

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## Comparison between different mesophotic bioconstruction substrates in the current systems of Apulian coasts

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**Keywords:** marine bioconstructions, mesophotic reef, Apulia shelf.

Mesophotic bioconstructions are biogenic structures widespread in the Mediterranean Sea that characterize habitat in deep water. The main mesophotic bioconstructors are marine invertebrates, which live in deeper water than coralligenous formation. In the Southern Adriatic Sea and Northern Ionian Sea, mesophotic bioconstruction develop at 35-70 m depth along the Apulian continental shelf, in environment characterized by dim light conditions. The principal bioconstructors are the corals *Phyllangia americana mouchezii* and *Polycyathus muelleri* and the oyster *Neopycnodonte cochlear*. These bioconstructions develop on submerged horst and ridges or along steepness slope, where microhabitats are enriched by different biodiversity.

In this work, we investigate the different kinds of substrate on which mesophotic bioconstructions develop along the Apulian coasts.

The methodological approach allows to analyze the structure at different spatial scales to quantify the interaction between physical and biological processes, which define the bioconstruction evolution. Some samples were collected in the areas of Monopoli, Capitolo, San Foca and Santa Maria di Leuca, located at depth between 40 and 60 m. The samples were fixed into epoxy resin and cut along the growth direction in order to obtain sections of the bioconstructors. High-resolution images were analyzed through a digital labeling in order to classify the microfacies of growth, defining in detail the bioconstruction structure and in some cases thin sections were performed.

The investigations carried out allow us to observe the evolution over the time of the bioconstructions and to quantify the impact of the presence of these structures on the marine environment.

The study of current bioconstructions and their relations with the substrate on which they developed allow to understand how these bioconstructions have been evolved; furthermore, the study of these bioconstructions could enhance a new knowledge about deep ecosystem and their relations with environmental parameters.



## **Geochemical composition and fractionation of trace elements in biocement of Sabellaria (Polychaeta) as proxy for short- and long-term environmental studies**

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Keywords: *Sabellaria alveolata*, trace elements, environmental pollution.

*Sabellaria alveolata* is a polychaete sabellariid that lives in tubes of agglutinated sediment using a particular proteinaceous glue secreted by specialized glands (Gruet et al. 1987; Waite et al. 1992; Zhao et al. 2005). The species forms bioconstructions of aggregated tubes in shallow bottoms dominated by high hydrodynamic energy, catching suspended sand grains to build its tubes (Gruet, 1972). Like all Sabellariidae, *S. alveolata* builds bioconstructions up to 1 m high and hundreds of square meters wide, thus modifying the morphology of substrates, stabilizing beach sediments, and protecting the coast from wave action. A two-year study on bioconstructions from three Sicilian sites (Simeto, Portopalo, and Falconara) investigated the balance between reef status and environmental parameters through a geochemical comparison of biocement tube portions and the surrounding waters. Water pollution by heavy metals, which is monitored in marine waters, is a result of river, domestic, and industrial discharges. The major constituents from the biocements of the three sites showed concentrations comparable to those in the seawater, while trace elements (Cr, Ni, Cu, Zn, and As) showed concentrations significantly higher than the mean seawater composition. These similar trends confirm a close dependence between the presence of trace elements (metals) in the seawater and the subsequent bioaccumulation in the biocement produced by the worm.

Among the three sites, Falconara showed the lowest normalized average trace element values, while Simeto and Portopalo had the highest average values of Zn overall. This trend was also observed in the biocements, where the highest percentage of zinc was found in the samples from Simeto and Portopalo. These data indicate a correlation between the chemistry of the trace elements in biocement and that of the seawater. Such high values of Zn at all three sites suggest elevated environmental pollution caused by waste incineration as well as industrial and other wastewater. Water pollution due to heavy metals has been observed in coastal marine waters as a result of river, domestic, and industrial discharges.

The results also showed that the comparison of the Ca/(Ca+Mg) ratio calculated using the average values of both the seawater and biocement from the three sites showed opposite trends between the ratios of the Ca and Mg concentrations of biocement and seawater from the same sites. The data showed that Ca and Mg are fractionated by biocement independent of the concentrations present in the formation environment, in contrast to the trace elements (Cr, Ni, Cu, Zn, and As), which showed good correlations.

Further studies addressing the biomineralization processes and the relative fractionation of trace elements in *Sabellaria* biocement will allow it to be validated as a valuable proxy for short- and long-term environmental studies.

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## Continental vs. marine stalactites: differences and similitudes between two peculiar geobiological system

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Keywords: speleothems, biostalactites, caves, geobiology.

Biom mineralization is a naturally occurring process where biological activity influences the formation of minerals and the productions of geological structures. Biom mineralisation can be directly controlled by organisms secreting their skeletons, indirectly mediated by metabolic activities of microorganisms or influenced by organic matter decay. The role of organisms in building geological structures in open marine settings is well known and spans in time and space with a huge variability of types of skeletons and depositional geometries, both driven by organisms' evolution during Earth history and environmental parameters. Recently, the formation of biologically driven structures in confined both continental and marine settings, have attracted attention. Peculiar macroscopical similarity can be observed between speleothems, like stalactites, which form in continental karst caves, and biostalactites from submarine caves. Knowledge on geobiological processes involved in the formation of these carbonate concretions is still fragmentary and to date no studies have been carried out on their comparison.

Whether the formation of continental cave speleothems is biogenic, abiogenic or a combination of both is a matter of debate. A few laboratory experiments demonstrated that bacteria isolated from continental cave environments are able to form crystals from organic calcium salts. The precipitation of carbonate biominerals by bacterial communities associated to cave concretions supports the hypothesis that similar processes may occur in nature (Banks et al., 2010; Dhami et al., 2018). Moreover, the noticeable variations in carbonate polymorphs nucleated during the in vitro experiments highlight the effect of microbial metabolism on carbonate mineralogy. Despite processes leading to mineralization are still not fully understood, the absence of skeletal organisms suggests that speleothems' morphologies are controlled by physical processes, notably the gravity and the fluid flux.

By contrast, the biogenicity of biostalactites has been recently demonstrated through a detailed geobiological characterization, coupling optical and electron microscopy whit biogeochemical analyses (Guido et al., 2013; 2022). Two types of building engineers were detected: sessile skeletonized organisms and microbialites. These contribute to the formation of two boundstone frameworks: 1) a pure skeletal-supported boundstone of large *Protula* tubes, whit the contribution of other Polychaeta and Bryozoa; 2) microbialite/skeletal boundstone, in which the skeletal framework is reinforced by the precipitation of autochthonous micrite induced by the metabolic activity of microbial communities. Even if the so-called biostalactite show distinctive growth from the ceiling and walls of the submarine caves, differently from the stalactite of the continental caves, they are influenced by the vital effect of the organisms and the final growth morphology is not controlled by physical processes.

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## On the outstanding geo and biodiversity of the submarine volcanic edifice of Linosa island (Sicily Channel, Mediterranean Sea)

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*Keywords:* multibeam data, rhodolith beds, benthic foraminifera.

The Sicilian Channel is an energetic site with a dynamic and highly variable current system that exchanges water between the western and eastern Mediterranean basin. Specifically, a mass of Modified Atlantic Mediterranean waters (MAW; about 200 m thick) moves east and, after entering the Sicilian Channel, divides into two main branches, the Atlantic Ionian Current (AIS) and the Atlantic Tunisian Current (ATC). This complex circulation pattern, together with bottom structures such as seamounts, banks, volcanoes, pockmarks and steep-walled basins, are the main factors responsible for the biodiversity richness of the Sicilian Channel, where healthy deep coral communities find favourable habitat and several pelagic species such as anchovies, bluefin tuna and fin whales have spawning and feeding areas. The Sicilian Channel includes the Pelagie Islands (crossed by the ATC current), which are known for their peculiar characteristics of very high biodiversity. Linosa, the focus of this study, is one of the three islands of the Pelagian archipelago with the characteristic of being of volcanic origin, and recent studies have shown that its submarine volcanic complex and its biodiversity are much more extensive than previously known (Innangi et al., 2019; Tonielli et al., 2019; Ferraro et al., 2020; Romagnoli et al., 2021). This study aims to present the high underwater biodiversity by realising the seabed map around Linosa, which was mapped using bathymetry and backscatter multibeam systems, together with ground truth data in the form of grab and box corer samples and ROV video observations. By extending and improving the coastal map previously produced with RSOBIA (in 2019), a thematic seafloor map classification was produced from the coastal area down to approximately 400 m water depth. The final map contributes to the knowledge of Linosa's peculiar marine ecosystem, including sediment types, coralligenous habitat and benthic foraminiferal distribution.

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## A new approach for the remote 3D study of Mediterranean marine bioconstructions

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*Keywords:* marine bioconstructions, technological innovation, hyperspectral imaging.

Marine bioconstructions are biodiversity-rich systems topographically distinct with respect to the surrounding marine landscape and characterized by good resistance to the action of destructive agents. In the Mediterranean Sea, the most common bioconstructions are represented by coralligenous build-ups, vermetid reefs, deep-sea coral build-ups, sabellarid build-ups, and polychaeta/bryozoans bioconstructions; they form in a wide range of marine settings, from shallow to deep sea and from open to confined sectors. To date, most of the current knowledge concerns tropical coral reef, whereas Mediterranean marine bioconstructions have not received the same attention and their knowledge in term of distribution and biological, ecological and geobiological processes are still fragmentary. Recently some researches have been addressed to the geobiological characterization of Coralligenous build-ups (Bracchi et al., 2022), that form in open marine settings, and biostalactites (Sanfilippo et al., 2015), that form in confined marine settings, but no studies have been addressed to high-resolution mapping coupled with 3D reconstruction of these build-ups.

Traditionally, underwater habitat mapping has been carried out coupling acoustic remote sensing techniques with RGB images, videos, and bottom sampling. During the last decade, the implementation of hyperspectral devices has become a viable alternative to regular photography. In contrast to ordinary cameras that acquire three color bands (RGB), hyperspectral cameras record the full spectrum of reflected light, in each pixel of the acquired image and allow to explore the properties of the seafloor (Foglini et al., 2019). Recently, different instrument carriers for the underwater hyperspectral imager have been used in underwater field applications, such as Remotely Operated underwater Vehicle (ROV). Underwater manipulation conducted by means ROVs in both shallow and deep water is an essential operation for performing underwater works in several application fields like marine science and underwater archeology (Bruno et al., 2018 and references therein).

The main purpose of the project is to suggest a new protocol for the study of the Mediterranean marine bioconstructions based on: 1) geobiological characterization of bioconstruction and, 2) implementation of high-resolution mapping and 3D reconstruction models of marine build-ups, starting from the data remotely acquired through ROVs equipped with specific optical-stereo and hyperspectral cameras. This protocol could represent a highly innovative tool, in the scientific and environmental fields, useful for monitoring and enhancing of these relevant but fragile and threatened habitats, which are protected by European Union.

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## **The mylonitic rocks of the Ulivarella Staks (Palmi - RC): a natural laboratory unravelling the Mediterranean microplates geodynamics**

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*Keywords:* mylonitic rocks, rock rheology, geotourism.

The Ulivarella Stacks of the Taureana beach close to the northern side of the Palmi town (Calabria, Italy), are one of the most attractive natural landmarks on the entire Costa Viola (CV). CV is one of the most striking stretches of coastline between Scilla, Bagnara, and Palmi (RC), where natural beauty and scenery are intertwined with a centuries-old culture that has been rooted since Greek times, passing through mysterious peoples such as the Taureans, an ancient Italic population from the Reggio area attested - from historical sources (Agostino, 2005) - to the south of the Metauros (now the Petrace River) from the mid-fourth century BC.

The Ulivarella Stacks are aligned along one of the most important meso-Alpine tectonic strike-slip shear zones (Cirrincione et al., 2015; Ortolano et al., 2020), marked, 400 m wide and 1500 m inland, by amazing mylonitic rocks, perfectly preserved.

These rocks, originally belonging, at the end of the Paleozoic, to the lower crustal portion of a sector of the southern European Variscan chain, were successively involved, during Paleocene, by the deep-seated strike-slip kinematic activity of the western Mediterranean realm, due to the relative movement of the Africa-Europe colliding plates. This geodynamics brings to the roto-traslation of the Sardinia-Corsica block and the following drifting of the kabilo-calabride microplate system (Cirrincione et al., 2015). Remnants of these strike-slip high strain-rate zones are characterized by rheological behaviors controlled by the selective activation of its specific interconnecting weakening phase as well as by the rheology and abundance of porphyroclasts.

Recently, a collaboration between researchers from Catania University, a Geologist of the UNESCO Aspromonte Geopark, and the Palmi municipality, have started the procedure for the accreditation of the Ulivarella stacks as a geosite of international interest, according to the ISPRA (Istituto Superiore per la Protezione and Environmental Research) rules. This is in order to include this area among those already identified in the first activation of the Aspromonte Geopark. At the moment, the growing Aspromonte Geopark counts 89 geosites, eight of which are of international importance and five inserted within territorial and cultural landscape units.

The initiative aims to implement the development of geotourism (viewed as the tool for the knowledge and enhancement of the territory in harmony with the principles of environmental sustainability), in the Costa Viola area, through territorial animation methods that involve all the local actors present therein in a synergic key.

The challenge that has already been launched is, therefore, to adopt a whole series of dissemination initiatives aimed at generating knowledge about the variety and richness of geodiversity, and to raising awareness of the value of this asset not only for individual local realities but also for society at large, under the concept of safeguarding geodiversity.

Agostino R. (2005) - Gli Italici del Métauros. Laruffa Editore, 226 pp.

Cirrincione R., Fazio E., Fiannacca P., Ortolano G., Pezzino A. & Punturo R. (2015) - The Calabria-Peloritani Orogen, a composite terrane in Central Mediterranean; its overall architecture and geodynamic significance for a pre-Alpine scenario around the Tethyan basin. *Period. Mineral.*, 84, 3B (Special Issue), 701-749.

Ortolano G., Fazio E., Visalli R., Alsop G.I., Pagano M. & Cirrincione R. (2020) - Quantitative microstructural analysis of western Mediterranean strike-slip kinematics: the Palmi Shear Zone, southern Calabria, Italy. *J. Struct. Geol.*, 131, 103956.



## Geodiversity of Oceanic Back-Arc Spreading Centers

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*Keywords:* geodiversity, ocean floor morphology, seafloor spreading.

Most of the studies on geodiversity focus on the diversity of non-living elements “on-land” and/or in shallow waters. Geological diversity of the ocean floor, which makes up more than 70% of the Earth’s geodiversity, remains largely unexplored (Seijmonsbergen et al., 2022). Here we focus on two oceanic spreading centers where seafloor spreading origins along a back-arc basin (BAB): the Mariana Spreading Center (MSC) in the Pacific Ocean, along the basin formed by the subduction of the Pacific plate under the Philippine Sea plate, and the East Scotia Ridge (ESR) in the Atlantic Ocean, along the basin formed by the subduction of the South America plate under the Scotia plate. We performed a regional bathymetry of the MSC using grid data with a 30 arc-seconds resolution downloaded from the GEBCO website; for the ESR, the GEBCO bathymetry has been merged with the bathymetric and topographic compilation of South Sandwich Island Volcanic Arc available from the British Antarctic Survey site. Based on a morphological analysis, we divided the MSC and the ESR in 9 segments offset by short perpendicular transfer zones; we identified the median valley of the spreading center (interval of 10 km along the MSC and 5 km along the ESR) providing a range of its depth variation along the basin. Furthermore, we carried out 100 km long bathymetric profiles across the MSC and the ESR to show and compare their geomorphological diversity (i.e., depth and slope). We improved existing spreading rate literature data calculating the magnetic anomalies along 3 track lines available from the Marine Trackline Geophysical Data. We estimated a full spreading rate of 23,6 mm/a along the MSC, and of 52,3 mm/a and 62,0 mm/a relatively along the ESR. We improved the diagram of the classification of the mid ocean ridges (MORs) (Dick et al., 2003) adding our bathymetric and magnetic data. Result shows that MSC and ESR resembles only partially the morphology of slow and intermediate MORs. Furthermore, we computed the subduction rates along the Mariana and Sandwich subduction zones in order to evaluate the effective velocity with which the subducting slabs enter the mantle (Ficini et al., 2020). Results show that the full spreading rate along the studied back-arc basins is not always related to the velocity of subduction: they are directly proportional along the ESC, whereas they are indirectly proportional along the MSC. The MSC and the ESR provide a good example of oceanic geodiversity in a similar geodynamic context.

Dick H.J.B., Lin L. & Schouten H. (2003) - An ultraslow-spreading class of ocean ridge. *Nature*, 426, 405-412.

Ficini E., Cuffaro M. & Doglioni C. (2020) - Asymmetric dynamics at subduction zones derived from plate kinematic constraints. *Gondwana Res.*, 78, 110-125.

Seijmonsbergen A.C., Valentijn S., Westerhof L. & Rijdsdijk K.F. (2022) - Exploring ocean floor geodiversity in relation to mineral resources in the Southwest Pacific Ocean. *Resour.*, 11, 60.

## Geo- and bio-diversity interaction and human impacts in an area subject to climate change: the case of Thi Nai Lagoon, central Vietnam

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Keywords: geosphere, biosphere, human impacts.

Coastal lagoons in tropical monsoon areas subjected to fast economic development are systems prone to highly variability, to dynamic conditions and increased vulnerability due to the complex interaction between geosphere, biosphere and anthroposphere. Adding to these, they are increasingly at risk of experiencing the effects of climate change along the low coastal areas.

The Thi Nai Lagoon, (Quy Nhon province - central Vietnam) is a saltwater enclosed area connected to the sea by a narrow water gate. The lagoon is strongly influenced by Kon and Ha Thanh Rivers during the monsoon seasons and, in the last decades, faced large human impacts. Here we define the sediment processes which drive and modify the dynamic of sediments as function of the basin morphology, essential information for its correct management.

Lagoon surveys were performed during an extreme dry period in May 2010. The data monitored can be considered as a representative of a mid-endpoint between the intermediate saline ingression and minimum effect of the rivers loads in the lagoon.

High sand contents are registered on the two edges of the lagoon: in the north-west side they evidence the input of sand from rivers branches, while in the east a sandy tongue jets out from the dune system on the edge. Over the rest of the study area, the granulometric composition is associated with bathymetry and evidences the influence of the river discharge connecting river inlets to the gradual formation of a single shallow channel along the central axis of the basin.

These findings agree with the work of Dung & Tu (2021) which located the seagrass on the sandy tidal flat and dunes area, with a reduction in correspondence of higher turbidity areas. At the same time, biodiversity studies on phytoplankton and zooplankton communities in the lagoon (Duyen et al., 2021; Nguyen & Hai, 2020) found a significant seasonal pattern trend between 2004 to 2020 reflecting seasonal variations of freshwater input, nutrients, salinity, and hydrodynamic changes. In particular, diversity indices and species distribution highlighted a zonation linked to the salinity, and hydrodynamics during the dry seasons. On the contrary biodiversity reduces in the entire lagoon during the rainy season, and it is observed an increase of Cyanobacteria presence in the last decades.

In Thi Nai Lagoon geodiversity and biodiversity features define: 1) its zonation, with more conservative areas versus more dynamic ones; 2) the resilience potentiality, and 3) human impacts in term of evolution of territory vulnerability due the increase of meteorological anomalies caused by the climate changes.

Dung T.T.T. & Tu T.T. (2021) - Application of the planetScope-based depth invariant index method in seagrass mapping: the study in Thi Nai Lagoon, Binh Dinh province. *Sci. Technol. Dev. J.*, 24(3), 2110-2122. <https://doi.org/10.32508/stdj.v24i3.2737>.

Duyen H.T.N., Minh Hue T.T., Le Van T.T., Luom P.T., Ngoc Lam N. & Hai D.N. (2021) - Phytoplankton community structure changes in Thi Nai lagoon (South - Central Vietnam) from 2004 to 2020. *Academia Journal of Biology*, 43(4), 75-94. <https://doi.org/10.15625/2615-9023/16531>.

Nguyen V.T. & Hai D.N. (2021) - Zooplankton community in Thi Nai lagoon in the period of 2001-2020. *Vietnam J. Mar. Sci. Technol.*, 20(4A), 35-44. <https://doi.org/10.15625/1859-3097/15645>.

## **MIS 5a carbonate deposits (MIS 5a) of Capo Colonna (Crotone, Southern Italy): microfacies and biosedimentary processes**

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*Keywords:* coralligenous, microfacies, late pleistocene.

Interglacial MIS 5a mixed carbonate and siliciclastic deposits, cropping out along the marine terrace of Capo Colonna (Kr), were studied. Two main bio-sedimentary facies can be recognized: 1) Red algae-dominated decimeter- to meter-scale domal to stratiform bioconstructions (Coralligenous), rich of encrusting red algae, with less bryozoans, serpulids, and encrusting foraminifera; laterally, these are associated to medium to coarse mixed bioclastic grainstone/packstones that also fill most of the cavities of the skeletal framework; 2) Maerl facies, mainly composed of free branches and fragments of red algae immersed in mixed bioclastic medium to coarse grainstone/packstone. In mixed bioclastic sediments of both biofacies, micrite is ubiquitous and generally well preserved. Several typical microbialite fabrics characterize most of the micrite: aphanitic, peloidal/dendritic, pseudo-thrombolitic and stromatolitic. Primary marine cements are commonly micritic isopachous rims, whereas vadose and botryoidal are rare. Late diageneses affect all the deposits with dissolution, aragonite conversion into calcite, neomorphic recrystallization of calcite (e.g., micrite to microspar), and precipitation of meteoric dogtooth cements.

The primary skeletal framework of the buildups is composed of encrusting red algae, foraminifera, bryozoans, and serpulids, while both primary micritic cement and early indurated microbialites contribute to bind skeletal and detrital components in both biofacies. Physical and biological destructive processes are commonly detected, producing erosional surfaces and dissolution cavities mainly due to endolithic sponges.

## **Cold-Water corals on the southern Apulian margin (Mediterranean Sea): unveiling the role of geodiversity for ecosystem-based management of offshore resources**

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*Keywords:* submarine biogenic landforms, biogeomorphology, submarine geomorphology.

Cold-Water Coral (CWC) mounds represent intriguing biogenic submarine landforms that hold great ecological significance. The role of submarine geodiversity in promoting their distribution at the seafloor has recently been increasingly highlighted, especially in those areas where extensive multiscale geospatial dataset and non-invasive seafloor observations (performed by work-class remotely operated vehicles - ROV), have begun to uncover how their complex ecological dynamics evolved along long-time scales, involving critical interactions with geological processes.

In the Mediterranean Sea, the north-eastern Ionian margin hosts one of the largest Mediterranean province of living stony CWC, which greatly contributed in forming a spectacular landscape dotted by more than 1000 sub-conical and elongated coral-topped mounds (here indicated as coral mounds), located in water depths of 500-900 meters. Thriving colonies of *Lophelia pertusa* and *Madrepora oculata* formed patchy distributed reefs on the exposed summits and flanks of mound-like structures (up to 300 m wide and 25 m high), these latter originated as a result of Pleistocene mass wasting events. A bathymetry data set with sub-metric resolution was acquired on a single coral mound, using the Remotely Operated Vehicle (ROV) VICTOR6000, equipped with a high-frequency multibeam sonar (Reson Seabat 7125) and deployed from the R/V Pourquoi Pas? during the 2007 MEDECO Expedition (October 2007). Fine-scale bathymetric profiles and geomorphometric analysis on the obtained Digital Terrain Model (DTM), coupled with published data on periods of coral accretion and demise in the study area, well imaged how coral growth enhanced the mound elevation with respect to the surrounding seafloor, from the onset of cold-water coral growth at ~13.4 cal kyr BP (as indicated by the oldest dated coral reported in literature) to the present time. However, also the quaternary evolution of the entire Apulian margin played a pivotal role in determining the overall distribution of coral mounds all over the area affected by late Pleistocene gravity-driven resedimentation processes.

Our research underscores the need for a comprehensive understanding of geodiversity and its role in shaping marine ecosystems over different time-scales. By recognizing the significance of specific geological features and their influence on biodiversity hotspots, policymakers, and conservation practitioners can develop targeted strategies to protect and sustainably manage vulnerable habitats.

## Radiolarians biostratigraphy at the Carnian/Norian boundary from Pizzo Mondello section (western Sicily, Italy)

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Keywords: radiolarian, Carnian Norian boundary, Pizzo Mondello section.

The Pizzo Mondello (PM) section in Western Sicily (Italy) is one of the best localities for the study of the Carnian/Norian boundary. At this site, a 450-m continuous succession of upper Carnian to upper Norian marine limestones is well-exposed and very easily accessible. The succession shows high sedimentation rates, almost uniform facies, and a rich palaeontologic record combined with paleomagnetic and stable isotope records. For these features, the PM section has recently been selected as the GSSP of the Norian stage (Hounslow et al., 2021).

Radiolarians are very useful for biostratigraphy calibrations, however, they are currently not well studied at the Carnian/Norian boundary of the Pizzo Mondello section. The rich radiolarian associations obtained from the limestones and chert layers of the PM section yield common species with those collected from British Columbia and Japan. In particular, the radiolarian *Capnuchosphaera crassa* and *Sepsagon asymmetricus* characterizing the Ass. 4 at Haida Gwaii (British Columbia) (Carter & Orchard, 2013) were documented in PM between the upper part of the conodont *Carnepigondolella orchardi* Zone up to the mid *Epigondolella vialovi* Zone, while *Xiphothecaella munda* corresponding Ass. 5 occurred at the very base of the *Met. communisti* Zone (Rigo et al., 2018). In addition, the radiolarian assemblages in this study have good correspondence with the radiolarian zonation of the Upper Triassic time interval from Japan. For instance, *Kahlerosphaera norica*, *C. lea*, *C. theoides*, *C. tricornis*, and *Poulpus piabyx* characterized the TR5B Zone by Sugiyama (1997) was documented from the upper part of conodont *Ep. vialovi* Zone to the very base of *Met. communisti* Zone, while *Capnodoce anapetes*, which defines the TR6A radiolarian zone occurred in PM in the uppermost part of *Met. parvus* to the lower *Ca. gulloae* Zones. It is noteworthy that *Xiphosphaera fistulate*, which defines the Ass. 7 of Carter & Orchard (2013) and the TR6B by Sugiyama (1997), range down to the very base of the *Met. communisti* Zone in PM section.

As a result, we collected a large number of radiolarians from the Carnian/Norian interval at the PM section, which can provide new material for biostratigraphy correction. The radiolarian investigation at the PM section is still in progress. Further studies will provide fine comparisons with the Upper Triassic radiolarians from other regions to better understand the correlations between conodonts, bivalves, and ammonoids and thus better characterize the base of the Norian stage.

Carter E.S. & Orchard M.J. (2013) - Intercalibration of conodont and radiolarian faunas from the Carnian-Norian boundary interval in Haida Gwaii, British Columbia, Canada. In: Tanner L.H., Spielmann J.A. & Lucas S.G. (eds.), The Triassic System. New Mexico Museum of Natural History and Science, 61, 67-92.

Hounslow M.W. & Carnian-Norian boundary working group (2021) - Albertiana Working Group Report: the case for the Global Stratotype Section and Point (GSSP) for the base of the Norian stage. *Albertiana*, 46, 25-57.

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Sugiyama K. (1997) - Triassic and Lower Jurassic radiolarian biostratigraphy in the siliceous claystone and bedded chert units of the southeastern Mino Terrane, Central Japan. *Bulletin of the Mizunami Fossil Museum*, 24, 79-193.



### **S3.**

## **The coastal environment paradigm: landforms, deposits and sediment dynamics**

*CONVENERS AND CHAIRPERSONS*

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*Gaia Mattei (Università degli Studi di Napoli Parthenope)*

*Marta Pappalardo (Università di Pisa)*

*Pietro Aucelli (Università degli Studi di Napoli Parthenope)*

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## Unravelling a mystery box: valorization and dissemination of Poggiorosso's "Hyena's den", from the Pleistocene of upper Valdarno, through virtual paleontology

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Keywords: virtual paleontology, photogrammetry, 3D fossil.

The museum of Geology and Paleontology of the University of Florence has one of the most prestigious and consistent collections of the Plio-Pleistocene vertebrate fauna, with its roots dating back to the XVII century. Amongst the wide arrange of specimens, the bone accumulation from Poggiorosso (Upper Valdarno), known as the "Hyena's Den", stands out as an exceptional finding, a true screenshot of how life looked like in the Valdarno basin 1.8 Ma. The block housed in the museum is part of a wider bone accumulation made by hyenas (*Pachycrocuta brevirostris*) in a river bank. The specimen bears bones of at least 10 different taxa, including the scimitar-toothed cat *Homotherium crenatidens*, the giant deer *Eucladoceros dicranios* and the extinct wolf *Canis arnensis*. The bone accumulation was made over about a year, at a time when hyenas had cubs and the Valdarno basin was going through a period of severe drought (Mazza et al., 2004). The specimen is on permanent exhibit at the Museum, but the common visitor is provided with only few information about it. As a result, the intricate tridimensional puzzle of bones that the specimen is gets unnoticed or ignored by the most.

With the recent development of Virtual Paleontology, museum curators can now rely on a new set of techniques for valorization and dissemination purposes, often easier, cheaper and faster than the standard installation methods. Hence we created a 3D model of the fossil assemblage that allowed different approaches for dissemination purposes. Both sides of the block were 3D digitized using close-range photogrammetry (Agisoft Metashape), and manipulated with various 3D editing software (e.g. MeshMixer). First, we highlighted the different taxa by using different colors. Then, we virtually extracted the bones from the block to: 1) provide the material for a virtual interactive map of the block; the 3D color coded fossil will be displayed on a touch-screen alongside the actual specimen for visitors' use, with notes on the different taxa's lifestyles and life-like representation of the extinct fauna; 2) to provide the base for a physical 3D- printed jigsaw. This will be placed in the exhibition to enhance the visiting and learning experience of children and, at the same time, improve the museum's visiting experience for visually-impaired people.

Mazza P.P.A., Bertini A. & Magi M. (2004) - The late Pliocene site of Poggio Rosso (Central Italy): taphonomy and paleoenvironment. *Palaios*, 19, 227-248.

## **Coastal human-induced changes in the context of Climate Change: the case study of South-East Sicily**

Borzi L.\*, Barbagallo V., D'Andrea N.M., Distefano S., Marino M., Urso S., Tavilla G., Sciandrello S., Grasso R., Spina M.T., Cavallaro L., Di Stefano A., Foti E. & Musumeci R.

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*Keywords:* coastal evolution, restoration, climate change.

Coastal areas are highly dynamic environments, and their behaviour is the complex result of multiple processes occurring and interacting on a variety of time and spatial scales. However, human interventions have become driving coastal change forces as natural physical processes over the last decades and the increasing coastal urbanization is significantly modifying coastal dynamics. As such, coastal management should provide prompt and efficient predictive tools for coastal development to protect them from erosional and flooding risks. Past shoreline evolution studies are thus the base tools to assess coastal variability and forecast future trends. Here, the study on the shoreline evolution of the south-eastern coastal area of Sicily (Italy) is presented. The south-eastern coastal area is characterized by a coastal lagoon system that can provide a wide buffer zone for the beach and together with dune ridges represent a significant sediment reservoir. The shoreline change analysis was performed over the time between 1955 and 2021, considering oceanographic variables and coastal human-induced changes. The south-eastern Sicilian coast is well-known to be a densely populated area highly sensitive to natural risks (e.g. tsunami, flooding, sea-level changes). The Digital Shoreline Analysis System (DSAS), a free application of the ESRI ArcGIS© software, was used to compute the shoreline migration rates (SCE, NSM, EPR, LRR, WLR) over the considered time range coupled with the assessment of the coastal land use analysis performed by the Corine Land Cover program maps. The shoreline evolution analysis showed that more than 75% of the coasts experienced landward migration with an average WLR value of -0.5 m/year and that the highest erosional values were recorded where both such natural processes (subduction, sediment supply changes) and human-induced disturbance (loss of dune ridge, coastal armouring, increasing urbanization and cultivation) took place.

## Shoreline change dynamics along the Augusta Coast, Eastern Sicily, South Italy

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*Keywords:* shoreline evolution, coastal armouring, DSAS.

The coastal region of Augusta, Eastern Sicily, Italy, is a densely populated region with approximately 200,000 inhabitants. Human activity factors, such as the development of settlements and ports, and natural phenomena, as extreme events, contribute to shape coastal geomorphology. To protect community economic and social activities, monitoring these variations is needed in coastal management. Therefore, this research aim was to firstly investigate the medium-term shoreline changes along Augusta Bay between 1972 and 2021, and then assess the main local coastal changes determining by the increasing coastal armouring. Shorelines dataset was extracted by satellite imageries as Landsat and Sentinel-2 images through the NDWI and mNDWI method and then statistical parameters were computed by applying Digital Shoreline Analysis System (DSAS). As shown by the rate-of-change statistics, landward shoreline migration occurred along most of the coast with rates up to -1.4 m/year and higher rates were detected in correspondence of the long low-lying sandy beach of the Magnisi Peninsula, and since the 1970s, artificial coastal length significantly and a coastal armouring index of Maximal level was today reached. As such, the high level of artificial coast altered sediment transport and impacts coastal dynamics locally.

## Reconstructing Holocene RSL changes in the Bay of Cádiz: the influence of local and regional dynamics

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*Keywords:* relative sea-level change, sea-level markers, holocene.

The Bay of Cádiz, located in South-western Spain (Andalusia Region), constitutes an example of a typical estuarine saltmarsh environment with a long human occupation affected by notable historical changes that have conditioned the sedimentary evolution of emerged and submerged zones. The Bay is constituted by two semi-circular embayments and the sediment supply of the area is mainly related to the presence of the Guadalete River estuary in the northern one.

The aim of this study is to reconstruct the Holocene morpho-evolution and the relative sea-level (RSL) change history of the study area by assembling a geodatabase standardized to the most recent international guidelines for RSL studies of geological sea-level markers (SLMs) derived from new boreholes and bibliographic data (Dabrio et al., 2000; Arteaga et al., 2008; Salomon et al., 2020; Caporizzo et al., 2021).

The SLMs, mainly derived from salt marsh, intertidal, and fluvial deposits were interpreted as high-precision sea-level index points (SLIPs) or limiting points based on the characteristics of the related depositional environments. The identified SLIPs were compared to a number of new site-specific glacio-hydro-isostatic adjustments (GIA) models in order to discriminate between the different components which influenced the sea-level evolution and finally obtain the vertical displacement (VD) trends that affect this coastal area by using a Bayesian statistical approach implying Montecarlo simulations.

Comparing the resulting VD values, it is possible to assume that the whole area was affected by general subsidence related to the local sediment compaction which influenced the morpho-evolution of the different zones with a variable entity and completely outclassed the GIA-driven component.

In particular, the oldest data from the northern sector showed that the area was characterized by subsidence rates of about - 0.65 mm/yr between 6.7 and 3.0 ka BP. On the other hand, during the last 3.0 ka, the general trend appears to be homogeneous for both the main sectors of the Bay with an average subsidence rate of - 1.6 mm/yr.

Moreover, the interplay between new data from the boreholes and bibliographic sources allowed the realization of three sketches representing the morpho-evolution of the Bay of Cádiz during the last 6.0 ka BP, respectively related to 6.0-5.0 ka BP, 3.0-2.0 ka BP, and the present-day coastal configuration.

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## **Photogrammetry as a tool to preserve and enhance rare fossil mollusks studied by Arcangelo Scacchi**

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*Keywords:* Arcangelo Scacchi, pleistocene, 3D models.

Arcangelo Scacchi (Gravina in Puglia, 1810 - Napoli, 1893), a geoscientist well known for his contribution to the fields of mineralogy and volcanology, in his youth was a paleontologist. He published “Notizie intorno alle conchiglie e agli zoofiti fossili delle vicinanze di Gravina in Puglia” (1835), in which he reported many fossils, mostly molluscs, collected in “Contrada Albanello” locality (in the vicinity of Gravina in Puglia Town, Southern Italy). Among the 170 molluscs species reported by Scacchi, 16 were described as new (Cretella et al., 2004). The original Scacchi collection from Gravina in Puglia, that contained some rare type material, is housed in the Museum of Paleontology of the University of Naples “Federico II”, but some of the original material was lost (Cretella et al., 2004). A modern still on-going study on the fossil molluscs from Gravina in Puglia, allowed to found numerous taxa and some rare type material. A new collection, that also includes precious type material gone lost, is now available and ready to be exposed. The following project involves the 3D digitization, with photogrammetry techniques, of the fossils collected during last years research; this can help to protect fragile specimens from handling, to prevent future loss of rare material, and to study the most minute morphological details (i.e. sculptures, hinges). In recent years, due to their level of interaction and spectacularity, 3D models have proven to be a valuable tool for museum education and outreach; the idea is to use this powerful tool to introduce the work of Scacchi and the fossils he studied, to younger generations, taking advantage of the possibility of visualization on tablets, PCs and smartphones, as well as the option of 3D printing.

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## Interaction between ground deformations and human sphere along the unstable coastal area of Campi Flegrei volcano (Southern Italy)

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*Keywords:* vertical ground movements, coastal changes, volcanic areas.

Many scientists since the 19<sup>th</sup> century have tried to reconstruct the ground motions that occurred in the Campi Flegrei caldera, which is one of the most dangerous volcanos of the Mediterranean area, since the first Roman occupation. However, these reconstructions are affected by a low accuracy due to different reasons: the low number of control points; the archaeological dating made during the first studies was modified by following discoveries and analysis; the misinterpretation of the archaeological structures in terms of sea-level markers (bad correction for indicative meaning, *sensu* Shennan, 2015). This study aimed to assess the joint effects of ground deformation trends and anthropic forcing along the coasts of this volcanic area. A huge dataset of hundreds of archeo-stratigraphic boreholes was coupled with direct and indirect surveys of the main underwater archaeological sites scattered along the whole coastal sector (Mattei et al., 2023) and the reinterpretation of bibliographic sources.

Clear evidence of a differential volcano-tectonic behaviour led us to divide the study area into three coastal stretches with homogeneous ground deformation trends. In each sector, a new relative sea level (RSL) curve was reconstructed, by interpreting our stratigraphic and archaeological data in terms of SL markers covering a wider timespan compared to the previous studies, from the first Roman urbanization to the present day. The comparison between RSL curves and GIA models allowed for calculating vertical ground movements that occurred along the coast with decimetric precision. For each recognized phase of uplift or subsidence, we also studied the effects they had in terms of coastal geomorphological change, and advantages or negative impacts on ancient human activities. We measured an overall subsiding trend that brought the RSL from -12 m (4<sup>th</sup> century BC) to 7 m during three different episodes between 5<sup>th</sup> and 15<sup>th</sup> centuries, which was interrupted by short-lived falls of RSL. During the phases of RSL fall and/or volcano-tectonic stability, a basinward shift of the coastline created newly emerged land even at the base of the local sea cliffs, where wide shore platforms emerged, favouring intense phases of urbanization on them. This trend also favoured the closure of the Lucrino lagoon with an extended spit bar during the 2<sup>nd</sup> century BC, allowing the establishment of a large oyster farming system by Sergio Orata. On the contrary, the subsiding phases resulted in the flooding of coastal areas and anthropic structures such as villas, nymphaea and ports inducing the construction of coastal protection works. In the extreme case of Portus Julius, subsidence led to the abandonment of the military port and its move to nearby Miseno.

Shennan I. (2015) - Handbook of sea-level research: framing research questions. Handbook of Sea-Level Research. Wiley Online Library, 3-25.

Mattei G., Amato L., Caporizzo C., Cinque A., Pappone G., Sorrentino A., Stocchi P., Troisi S. & Aucelli P.P.C. (2023) - Reconstructing anthropic coastal landscape of Campi Flegrei volcanic area (Southern Italy) during the Roman period from multi-technique surveys. *J. Maps*, 1-14.

## Can the Mediterranean coastal plains be resilient to the ongoing climate change?

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*Keywords:* climate change, coastal flooding, future sea-level rise.

Global sea level rise represents one of the most evident impacts of climate change. This phenomenon is expected to entail widespread environmental changes, such as coastal retreat, marine flooding, and loss of land (Zhongming et al., 2022). The low-lying coastal areas, in particular, are thought to be the most vulnerable in the context of climate change. But is it possible to define a common response for this type of coastal environment to climate change? Furthermore, what are the natural/anthropic drivers that mostly control their evolution?

This study aims to present a statistical approach to evaluate the response of coastal depositional systems to past and future climate changes. It focuses on several Western Mediterranean plains (Sele, Volturno, Tiber, Arno, Rhone, Valentia) for which the potential resilience to be flooded due to future relative sea level rise (RSLR) was measured, by examining the geomorphological behaviour that occurred in response to the Holocene RSLR.

Specifically, the proposed methodological approach involves the definition of the time intervals of the different Holocene evolution phases lived by the studied plains, with the definition of three geomorphodynamic evolutionary phases (progradation, equilibrium, retreat). Furthermore, for each plain, the RSL changes curve was calculated using the model “Errors in Variables Integrated Gaussian Process (EIV IGP)” (Cahill et al., 2015) that performs Bayesian inference on historical rates of sea-level change.

The objective of these analyses is to compare the rate of sea level change related to each different Holocene evolutionary phase in each plain with the local RSLR rates expected for the next decades (up to the year 2100) calculated taking into account different IPCC predictive scenarios (i.e., SSP2-4.5, SSP3-7, SSP5-8.5) corrected with present local coastal subsidence (<https://egms.land.copernicus.eu/>). The comparison between past behaviours and future RSLR allowed hypothesising the potential geomorphodynamic response of each plain to future sea level variations. The results demonstrated that only in the case of the SSP2-4.5 scenario, which foresees a global RSLR of 0.56 m, the most westward coastal plains can be resilient with a probability not higher than 18%.

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## Late-Quaternary paleo-environment evolution and structural constraints in the Gulf of Genoa (Ligurian Sea, Italy): new evidence from CARG survey

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*Keywords:* palaeo-environmental reconstruction, structural inheritance, ligurian basin.

We present a 3D reconstruction of the late-Quaternary littoral submarine paleo-environments that have occurred in the Gulf of Genova (Ligurian Sea, NW Italy) since the Last Glacial Maximum (LGM).

The integration of new high-resolution bathymetric data (multibeam) and reflection seismic data (chirp and sparker) acquired in the framework of the CARG Project (213-230 “Genova Sheet”) provided new pinpoints for the late-Quaternary modelling of sedimentary bodies, the paleo-morphological features and the morpho-structural setting of the Genoa Gulf. Along the coastal area of Genoa, the post LGM sea-level rise led to the flooding of a 8 km wide alluvial plain extended along the continental shelf, subdivided in two physiographic areas (the Polcevera and the Bisagno sectors) by the prominent NNE-SSW trending Lanterna structural high. Until the end of the Pleistocene, the architecture of this coastal plain was chiefly controlled by the sedimentary input of the Polcevera and the Bisagno rivers, whose paleo-deltas were located close to the homonymous canyon heads. Since the LGM, the marine transgression controlled the retrogressive migration of the sedimentary littoral systems and related morphologies (Locatelli et al., 2022).

In the western sector of the Genoa Gulf, transgressive beach ridges of considerable size and high lateral continuity are dominant and locally associated with the development of lagoon environment deposits. In the eastern sector, transgressive deposits are smaller in volume with reduced lateral continuity and retrogressive terraced geometry. These represent the remnants of coarse paleo-coastal deposits. The transgressive beach ridges and terraces landforms are frequently associated with seismic facies (e.g., bright spot reflections and acoustic blankets within sediments) produced by fluid vents. These are generally associated with NW-SE and NNE-SSW trending fault systems which control the geometries of local grabens and structural highs along the continental shelf. Based on our studies, the evolution of the paleo-coastal landforms during the post-LGM transgression was likely controlled by the action both of the eustatic sea-level rise and the inherited morpho-structural setting (Morelli et al., 2022). The coastal promontory of the Lanterna high allowed the formation of two inlets where the sedimentary input of the Polcevera and Bisagno rivers fed the transgressive littoral deposits. Fluids escape along faults likely promoted precipitation of authigenic carbonates, allowing the rapid lithification of the surficial transgressive deposits, which increased their resistance to the erosion and reworking operated by transgressive processes.

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## **Investigating the cranial morphology of Quaternary rhinoceroses: benefits and limits in virtual environment**

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Keywords: 3D models, morphology, variability.

Quaternary rhinoceroses are relatively well-documented in Eurasia and Africa and they are included within the faunal lists of several fossiliferous localities. Although several studies have been devoted to highlight morphological and morphometric differences among the fossil Quaternary rhinoceroses, isolated specimens are sometimes difficult to identify because of our poor knowledge of the intra and inter specific variability of fossil and extant species. Several crania belonging to the extant rhinoceroses are therefore analyzed and compared in order to detect morphological differences among adult individuals and to highlight ontogenetic patterns within the same taxon. Cranial remains of the extant *Ceratotherium simum*, *Diceros bicornis* and *Rhinoceros* from different European Institutions are here digitalized and virtually compared. 3D models enable to better visualize the cranial material and also to perform morphometric analyses aimed to underline variations in shape and size. Taking into account the observations on the extant rhinoceroses, the validity of some cranial traits, often used for specific attribution in Quaternary fossil rhinoceroses, is discussed and revised. Sexual dimorphism and ontogenetic stage drive the development of some important features in rhinoceroses, such as the nuchal crest, and a detailed comparison lead to new considerations on taxonomy, and, therefore, on paleobiogeography and biochronology of the different species.



## Chemostratigraphy of a lower pleistocene section from the siderno paleostrait, Calabria, Southern Italy

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Keywords: chemostratigraphy, paleostrait, Mediterranean.

In this presentation we summarize the preliminary results of a sampling field campaign carried on an outcrop section exposed in the SE sector of the Siderno Basin, Calabria, southern Italy. The aim was to obtain an uninterrupted series of data to reconstruct  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  isotope ratio curves. It is well known that these two proxies can provide paleoclimate information, such as water temperature, salinity and primary productivity.

The studied stratigraphic section is exposed along an artificial road trench, for a total length of 105 m and a stratigraphic thickness of ca. 50 m, located near the village of Bombile, in the Siderno Basin. It exhibits large-scale cross-stratified biocalcarenic deposits, representing the sedimentary record of the Siderno paleo-strait, a tide-dominated passageway connecting the Tyrrhenian Sea to the Ionian Sea during the Early Pleistocene. The investigated lithofacies represent the deposition of quartz-rich sand reworked into subaqueous dunes under the effect of strong tidal currents, mixed with abundant bioclasts deriving from in-situ foraminifera and foraminifera, including planktonic specimens.

In order to obtain the isotopic composition, a systematic sampling has been performed, perpendicularly to cross-strata master surfaces, with sampling space of 25 cm. Samples have been then treated with  $\text{H}_2\text{O}_2$  at the University of Basilicata, to remove any organic matter, then wet sieved at 75  $\mu\text{m}$  to eliminate the finer fraction. From the remaining coarser fraction, specimens of *Orbulina universa*, a low-Mg calcite planktonic foraminifera, have been hand-picked and powdered for carbon and oxygen isotope analyses, since they are known to be well resistant to diagenetic overprint. Stable isotope analyses have been performed with a Delta V Thermo mass spectrometer coupled with a GasBench Device at the Sapienza University of Rome.

The isotope curves established for the Siderno Basin have been correlated with coeval reference curves for the Mediterranean area to assess the potential of a strait succession to record the major climatic events in its stable isotope record, as well as to evaluate the role of regional controlling factors, such as the oceanographic connection with the Atlantic Ocean, in controlling the response of the Mediterranean basin to climate changes during the Early Pleistocene.

## **Detecting submerged palaeo-shoreline landforms created by sea level variation during Late-Quaternary in the Ligurian-Provençal continental shelf, facing an outstanding Palaeolithic archaeological site, through multibeam and high-resolution seismic data**

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*Keywords:* pleistocene sea-level change, Ligurian-Provençal continental shelf, high-resolution seismic data.

A wide part of the lowlands exploited and settled by humans during Prehistory is currently submerged. On the continental shelf traces of landforms developed in a subaerial environment are preserved in the form of topographic as well as of sediment architecture features. Detecting them is extremely informative in order to reconstruct the palaeogeography of the territory where palaeolithic cultures thrived. The SPHeritage Project proposes a new interdisciplinary approach to investigate evidence of Palaeolithic human occupation and cultural heritage in the NW Mediterranean area in conjunction with Pleistocene sea-level change studies. Part of the Project activities have been devoted to interpreting the continental shelf palaeolandscape in front of the Balzi Rossi archaeological area (NW Mediterranean), through the high-resolution seismic reflection techniques, multibeam and sediment corings data. In the study area, a unique assemblage of archaeological sites dating to the Palaeolithic were found in a rocky coast geomorphological setting where sea-level indicators of the last 3 or 4 interglacials are present.

The outstanding heritage represented by this site includes evidence of multiple settlement of different human species. The sediments within which human bones and artifacts belonging to Acheulean, Musterian, Proto-Aurignatian, Gravettian and Epigravettian cultures were found, yield witness of the environment where these populations lived. The deposits were preserved along a steep cliff and in caves and rock shelters opened in it.

A dense grid of seismic reflection data associated to a high-resolution digital topo-bathymetric model of the study area revealed landforms associated to palaeoshorelines associated to sea-level variation. Particularly, a submerged cliff that replicates the features of the present day coastal cliff. Sediment corings were performed in selected locations along the continental shelf in order to retrieve sediments associated to palaeoshorelines, where future activities should be directed to verify the presence of submerged archaeological sites.

## Late Pleistocene (MIS 5e) SST estimate: a multiproxy study on a macrofossil assemblage

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Keywords: SST, MIS 5e, fossil fauna.

This contribute presents a multi-proxy palaeoclimatic study performed on a macrofauna coming from a MIS 5e calcarenite, exposed along the coastline of the Mar Piccolo of Taranto (MP). Three bulk samples returned 120 molluscs species, including four of the tropical “Senegalese Fauna”.

Mollusc species with a southern or warm affinity are present in a double percentage in respect to today, whereas the northern or cold affinity species are equally represented, indicating warmer, but not tropical, SST during MIS 5e. This is supported by the most recurring preferred SST ranges of the assemblage, that indicate 20°C in average.

For further SST estimations, trace elements (Mg/Ca and Sr/Ca), and oxygen stable isotope ( $\delta^{18}\text{O}$ ) analyses, were performed on well preserved specimens of *Thetystrombus latus*, *Spondylus gaederopus*, *Venus verrucosa*, *Pinna nobilis*, and corallites of *Cladocora caespitosa*. Only some SST estimations, derived from equations available in literature, are realistic and converge on similar mean annual SST, on average of  $20.8 \pm 0.9^\circ\text{C}$ .

As the modern annual mean SST of the study area ranges from 18°C to 18.8°C in the semi-closed MP basin and in the facing open sea Gulf of Taranto (GT) respectively, the final estimate of the MIS 5e SST falls in the range 1.2 - 2.0°C for the GT, and 2.0 - 2.8°C for the MP. Albeit warmer than today, this is not a firmly warmer tropical-like SST setting as it would be derived from the mean annual SST requirement of the Senegalese *T. latus*, that would suggest at least +2.7°C in respect to modern GT, and +3.5°C in respect to modern MP.

Concluding, the approximations and assumptions made for obtaining SST values with any single proxy-based method return a wide uncertainty, strongly suggesting the need of a multi-proxy approach to infer the most reliable SST estimation.

## **From sea-level proxies to coastal changes: a new geostatistical approach to reconstruct the Late-Quaternary coastal evolution of Cilento promontory (Southern Italy)**

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*Keywords:* palaeo-environmental coastal reconstruction, sea level proxy, geostatistics.

This research aims to propose a new geostatistical approach for the computer-aided reconstruction of environmental changes related to millennial sea-level oscillations, applied to the Cilento coastal sector between the Alento plain and the mouth of the Bussento River.

Located along the Tyrrhenian coast of Southern Italy, this area preserves a massive amount of geological and geomorphological features witnessing sea-level fluctuations in response to climate changes, which have been intensely studied since 1940 both in the emerged than in the submerged part (Blanc, 1940; Antonioli et al., 1994; Ferraro et al., 1997; Esposito et al., 2003). The whole coastal sector shows an alternation of high rocky coasts, such as those of Agropoli and San Marco, where massive cliffs are often associated with wave-cut platforms, and low-lying coasts, such as those of Santa Maria di Castellabate, Ogiastro Marina, and Alento plain characterized by wide beaches.

Considering that the area can be considered tectonically stable since Late Pleistocene – as testified by a series of evidence well discussed in literature – and the subsequent absence of other components that have modified the landscape in the last 125 ka other than climatic and sea-level oscillations, it is a highly suitable area to test palaeoenvironmental reconstruction methodologies.

The procedure is based on the creation of a geodatabase for managing sea level data and related palaeo-environmental indicators derived from the reinterpretation of previous bibliographical geological, geomorphological, and seismo-stratigraphic data, as well as palaeontological/ecological information collected in the Campanian cave registry, coupled with direct and indirect survey data carried out using robotic technologies and remote sensing.

These data were elaborated in a GIS software in order to obtain geomorphological and geoarchaeological reconstruction during the late Quaternary through a multivariate spatial analysis of the massive dataset. We used all the sea-level proxies (SLPs) to evaluate the palaeo-shoreline position, starting from SLIPs which were considered anchor points. In the absence of SLPs, palaeo-ecological data were interpreted as additional variables to assess the possible location of the shoreline and related uncertainty. The spatial distribution gave us the opportunity to reconstruct the palaeoenvironment and the position of the shoreline, while the altimetric position gave us clues on the sea level.

The resulting scenarios at various time scales obtained thanks to this all-encompassing methodology allowed us to reconstruct an evolutionary model – at various levels of precision – during the period from MIS 5 to the present, both in high- and low-stand periods.

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## The response of a tectonically stable area to Holocene sea-level rise by means of remote sensing and direct Surveys: The case study of Punta Licosa Promontory (Southern Italy)

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*Keywords:* Holocene, retreat rates, rocky coasts.

Punta Licosa promontory is considered one of the most attractive coastal landscapes located in the northern part of the Cilento coast, in the southern Tyrrhenian basin. This promontory is bordered by sandstone sea cliffs connected to a wide shore platform sloping slightly towards the sea. It represents a great example of a coast whose evolution was not particularly influenced by anthropic pressure, and therefore it is a suitable area for those analyses aimed at evaluating the interplay between glacio-hydro-isostatic sea-level rise and coastal retreat rates. The area has been considered tectonically stable at least since Late Pleistocene, as testified by a series of evidence well known in the literature (Bini et al., 2020) allowing to neglect the influence of the tectonic component on the RSL variation. The aim of this research is to reconstruct the main coastal changes that have occurred in this area since the middle Holocene by means of literature data, aerial photo interpretation, satellite images, GPS measurements, direct underwater surveys, GIS elaborations of high-resolution DTMs, bathymetric data and high-resolution orthophotos taken by UAV. Particular attention was paid to the wide platform positioned between  $-7.2 \pm 1.2$  m MSL and the present MSL, this being the coastal landform interpreted as the main consequence of sea cliff retreat. The elevation of this landform was compared with a suite of GIA models specifically calculated for the southern Tyrrhenian area (Mattei et al., 2022), allowing establishing that it was shaped during the last  $7.6 \pm 1.1$  ky BP. Moreover, the interpretation of this geomorphological markers led to the reconstruction of the shoreline evolution of this coastal sector since 7.6 ky BP. In a final step, this research evaluates the cliff retreat rates under the effect of Holocene RSL variation in the different sectors of the promontory according to their exposure to wave action. Results show that calculated retreat rates (RR) slightly differ and, considering the overall lithological uniformity of the coast, this behaviour may be ascribed to local wave climate variation. In fact, the central sector, which is characterised by the maximum extension of the platform and by the highest RR (RRmax 0.104 m/y), is also the sector most frequently exposed to waves with a height higher than 2 m. Conversely, the southernmost sector shows the lowest extension of the platform and the lowest value of RRmax (0.020 m/y) as a response to the lowest exposure to wave events. The applied method can be considered more effective and less complex and expensive if compared to other effective approaches, highlighting the importance of detailed and extensive assessments of the rocky coast response to sea-level changes.

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## Drivers of Holocene sea-level changes along the Italian coasts

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Keywords: sea-level, Holocene, Italian coasts.

Placed in the middle of the Mediterranean basin, the Italian peninsula and the two major Italian islands (Sardinia and Sicily) represent an ideal connection between the northern and the southern side of the Mediterranean Sea. This geographical setting resulted in an impressive variability of coastal landforms driven by both climatic and tectonic processes. Italian coasts have also preserved a wide range of morphological and sedimentological proxies of late Quaternary sea-level fluctuations which were widely investigated since the end of the 19<sup>th</sup> century. In the Holocene period (e.g., last 12 millennia) sea-level reconstructions carried out along the Italian coasts were often coupled the geology with archaeology. These investigations were mainly triggered by presence of several remains of submerged or semi-submerged coastal archaeological structures which has attracted the attention of generations of sea-level scientists. Here we present an updated and quality-controlled database (Mattei & Vacchi, 2023) of the Holocene RSL data available for the Italian coast assembled according to the international protocol developed in the recent INQUA project Holsea (Khan et al., 2019). We have produced sea-level data from cores performed in transitional and marine deposits, from beachrocks, from fossil remains of intertidal bioconstructions and from archaeological indicators. The final database includes 391 SLIPs and 179 limiting points. The temporal range covers the last ~14 ka BP with a general increase in the number of data-points through time. The present overview of the Italian sea-level evolution indicates that the entire RSL in the last ~13 ka BP was within 50 m. We observe a rapid rise in the RSL between 13.0 to 7.0 ka followed by a sudden RSL stabilization in the last 7 millennia driven by the end of the major deglaciation period of the northern hemisphere ice-sheets. Since that period, land-level changes controlled by GIA, tectonics and sediment compaction have become the main drivers of the RSL change evolution along the Italian coast. In particular, we observed major subsidence trends (driven by tectonics and sediment compaction) in the coastal plains of the north-eastern Adriatic and in northern Tuscany. Major uplift trends (often co-seismic) were found in NE Sicily and in the southernmost tip of Calabria. A peculiar case constitutes the Phlegrean fields volcanic district where the short-lived alternation of subsidence and uplift has induced abrupt coastal landscape transformations in the last millennia.

The comparison of the assembled dataset with the GIA models routinely (Lambeck et al., 2011; Roy & Peltier, 2015) used for the prediction of the RSL position through time yielded contrasting results. In particular, none of the models is able to reconcile the RSL evolution in the Early Holocene period. For this reason, any paleogeographic reconstruction for periods older than 8.0 ka BP and only based on geophysical predictions should be used with caution.

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## Late-Holocene sea-level reconstruction in the archeological site of Nora (southern Sardinia)

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*Keywords:* sea-level, late Holocene, Nora Sardinia.

We present an innovative sea-level study carried near the archeological town of Nora, a major Punic-Roman town placed in southern Sardinia (western Mediterranean Sea). We have carried out a multiproxy analysis involved biostratigraphic and palynological analysis performed on two new cores collected in the coastal lagoons surrounding the archeological site. Furthermore, we carried out a geomorphologic and petrographic study of a number of beachrocks (paleo-shorelines) found few meters below the present sea-level.

The chronological frame, based on a new set of 17 radiocarbon dates, allowed to provide fresh insights into the coastal modification of the last 4.3 millennia BP. The sea-level evolution was statistically analyzed by applying a Error-In-Variables Integrated Gaussian Process (EIV-IGP) model on the new dataset. Our results show that, in this sector of Sardinia, the sea-level changes which did not exceed the 1.35 m in the last 3500 years. These data contrast with previous assessment only based on archeological sea-level indicators. These data further allowed to reconstruct the shoreline evolution of the area during the main period of occupation of the archeological site (e.g., from the Nuragic to the late Roman periods). This has been compared with the high-resolution mapping of the archeological structures in order to reconstruct their relationship with the paleo-shoreline at the time of their functioning period. Furthermore, palynological data elucidated the millennial variability in the vegetation dynamics as well as the anthropic influence in the changes of vegetational cover during the different archeological periods.

## Unraveling sub-millennial central Mediterranean climate variability across the Piacenzian/Gelasian boundary: insights from high-resolution $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ isotopes analysis

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*Keywords:* Piacenzian/Gelasian boundary, isotopes, high resolution.

The central Mediterranean region has long been recognized as a crucial reference area for studying global climate variability during the Pliocene and Pleistocene series (5.33 Ma 11.7 ka). Its significance stems from the remarkable preservation of its open marine successions, which serve as a treasure trove of paleoclimatic and paleoecological proxies. Along the coasts of southern Italy, specifically in the Calabria and Sicily regions, these successions offer an extraordinary pristine and diverse record, rich in invaluable insights into past climatic conditions and ecological dynamics (Cita et al., 2008).

In this context, the Monte San Nicola area in southern Sicily stands out with its exceptional stratigraphic succession, which served as the reference point for defining the Gelasian Global Stratotype Section and Point (GSSP) in 1998 (approximately 2.58 Ma). The succession covers one of the most compelling and critical time intervals for the recent global climate evolution, namely the Piacenzian-Gelasian boundary at 2.58 Ma, which witnessed profound changes in Earth's climate system, epitomized by the onset of "ice ages" at around 2.6 Ma and the definitive establishment of large ice caps in the Northern Hemisphere. Recently redefined as the basal Pleistocene Stage (Head et al., 2008), the Monte San Nicola section reveals a triplet of glacial episodes found immediately above the Gelasian GSSP (i.e., the MIS 100 - MIS 98 - MIS 96 glacials) correlating to the definitive onset of the Northern Hemisphere Glaciation (NHG). Despite recent studies on both the historical Monte San Nicola section, where the Gelasian GSSP is located, and adjacent profiles (such as the "Mandorlo section" by Capraro et al., 2022) provided information on the long-term climatic evolution across the Gelasian and the MIS 100 glacial in particular (Becker et al., 2005), a detailed documentation across the Piacenzian/Gelasian boundary is still sparse.

Our current research focuses on reconstructing a high-resolution and chronologically sound benthic isotopic ( $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ ) record across the Mandorlo section, with a specific focus on the interval straddling the Piacenzian/Gelasian boundary. Results gained so far proved critical for pinning the Gauss-Matuyama geomagnetic reversal and establishing the relative positions of the main key criteria for recognizing the boundary, as well as new insights on the oceanographic and climatic evolution of the central Mediterranean at the beginning of the Northern Hemisphere Glaciation.

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## **S4.**

### **Geomaterials and Cultural Heritage**

*CONVENERS AND CHAIRPERSONS*

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## Experimental investigation of historical processing of cobalt and arsenic phases to obtain blue as-free pigment by roasting erythrite and clinosafflorite

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**Keywords:** cobalt pigments, glaze, calcium arseniates.

Cobalt blue has been one of the longest and most widely used pigments in art history. What most characterizes this pigment is a strong compositional variability due to the use of different minerals and techniques to produce it. In particular, two similar cobalt blue pigments are found to occur in ceramic glazes and glasses produced between the 15<sup>th</sup> and 16<sup>th</sup> centuries and distinguished by the presence of arsenic exclusively in the group of artefacts produced after 1520. One hypothesis is that both pigments could have been produced using erythrite, smaltite and skutterudite coming from the Erzgebirge mining district (Gratuze et al., 1996; Soulier et al., 1996). Therefore, the differences between the two pigments would be ascribed to different production processes. The removal of arsenic could be due to the roasting of the ores, which was used to produce saffre, or the use of different fluxes employed to make the smalt, two cobalt by-products that began to be produced in the Erzgebirge region respectively from 1520 and 1540-60 (Meltzer, 1716).

If investigations on the thermal behavior of skutterudite (CoAs<sub>3</sub>) (Molera et al., 2021) showed the difficulty of removing arsenic from the mineral, it cannot be excluded that this element can be more easily removed from other minerals in which the Co/As ratio is greater than 1:3.

This study investigated the possibility of producing an As-free or low As content cobalt blue pigment starting from erythrite and clinosafflorite. The two minerals both occurring in the Erzgebirge region may have been used in the past to produce the pigment. Indeed, many historical recipes seem to describe the use of erythrite, referred to as a red mineral also called cobalt bloom, in the production of cobalt blue.

Starting from the study of three mineralogical associations (2 from Bou Azzer in Morocco and 1 from Huércal Overa, Almería) several roasting experiments were carried out (up to 1020°C) also using different fluxes whose use is described in historical treatises to produce enamel and to study the products obtained through different techniques (XRD, XRF, SEM-EDS). A mixture of CaO and borax with erythrite heated up to 900°C resulted in the formation of a Co-Fe-Ni oxide and a Ca-Co-Na-Ni arsenate phase. Roasting of clinosafflorite powders at 1020°C allows the formation of Co-rich phases and As-Co-Fe-Ca phases. The reaction and blue colouring of a quartz grain and the formation of different phases of Co-Na-Ca silicates, Co-Fe-Ni phases and different types of arsenates were obtained by heating clinosafflorite with borax at 1020°C. The experiments demonstrated that arsenic is not fully removed, but cobalt phases with a low arsenic content were often obtained and the presence of Ca, Na and Pb promote the formation of different arsenates inside the glaze.

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## **The characterization of construction materials of the Arno riverbanks (Florence): comparison between the techniques and raw materials of several sections of the Florentine Lungarno**

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*Keywords:* Florence riverbanks, historical masonry, construction materials.

The characterization of construction materials used in the structural masonry of riverbanks is crucial for evaluating their stability to geo-hydrological risks. The study of ancient riverside masonry is a topic that calls for examination of a number of factors, including the analysis of employed materials. For example, to better understand the mechanical characteristics of civil architectural heritage walls, it is crucial to characterize the mortars, which have an impact on the structural behaviour of masonry. The riverbanks of the Arno River, located in the city of Florence, known as Lungarno, represent a particularly interesting case due to their resistance and behaviour, as demonstrated even during destructive events (floods, landslides, and riverbank failures). Giuseppe Poggi expanded all the riverbanks, in some already existing sections dating back to 1250, in the 1800s as part of the town redevelopment program. According to the Poggi project, the retaining walls of the Lungarno consist of various squared stones quarried near Florence, bound by mortars. The aim of this research concerns a mineralogical-petrographic (XRD and OM), chemical (SEM-EDS), and physico-mechanical (ultrasonic investigations and porosity) characterization of the mortar and stone samples taken from the masonry of three Florence riverbanks (Lungarno degli Acciaiuoli, Lungarno delle Grazie and Lungarno Torrigiani) (Calandra et al., 2022; 2023) in order to identify the raw materials, manufacturing technologies, and state of conservation. Some differences were observed in the mortars of the three Lungarno although the raw materials used are always the same. The mortars of the three Lungarno have a binder obtained by burning of two variety of Pietra Alberese (Fratini et al., 2020) and silicatic aggregate with different grain size. Also, the choice of the masonry stones is sometimes different (sandstones, and/or marly limestone and bricks). About the physical data the three Lungarni have similar porosity and imbibition coefficient while about the capillarity absorption and the ultrasonic velocity Lungarno Torrigiani has lower values. This could be due to the higher hydraulic behaviour of Lungarno degli Acciaiuoli and Lungarno delle Grazie mortars, confirming the use of a different variety of Pietra Alberese with a higher content of clay minerals. In any case, the findings indicate that all riverbanks exhibit favourable properties. These data highlight the level of compactness and cohesion of the masonry, which is useful for planning emergency interventions and restoration activities. The results provide valid support for the design of riverbank safety projects, to mitigate the risk of their collapse and to decrease the flood risk in the historic center of Florence.

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## An outstanding example of volcanic geomaterials utilization: pozzolana and Phlegrean materials with pozzolanic activity

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Keywords: pozzolan, geomaterials, Campi Flegrei.

Whenever one thinks of cultural heritage, the mind immediately goes to history and literature and not to geological sciences. However, geology should be considered since technological advances in history were achieved through wise and intensive use of available georesources. In Roman times, ability to build roads, aqueducts, temples, and monuments was so technologically developed that these artifacts still withstand weathering after two thousand years.

Many authors have described the building art such as M. Vitruvius Pollio (1<sup>st</sup> Century B.C.) in «De Architectura», and Pliny the Elder (23-9 A.D.) within his «Naturalis Historia». Roman builders knew that combining lime with special volcanic materials, pozzolan, allows mortars to become hydraulic, granting them to harden under water and increasing their mechanical strength (Collepari, 2003).

The use of pozzolan marked a great advance in construction technology, due to its fastest reaction speed than carbonation of slaked lime. The original pozzolana is *Pulvis puteolana*, from Campi Flegrei (specifically from NYT formation). As reported by Vitruvius, this was considered a “prodigious powder,” outcropping in a wide region, from Baia and Cumae to Vesuvius and Sorrento Peninsula. The term “puteolana” was first used by Pliny, locating the origin of the material in the ancient city of Puteoli (today, Pozzuoli, Naples). Geologically, *Pulvis puteolana* is identified as the incoherent facies of NYT, related to the eruption that occurred ca. 15.4 Ky in CF (Morra et al., 2010), and consists of volcanic ash, poorly vesiculated magmatic slag and lithic fragments. Other products of the NYT eruption, namely zeolitized tuffs (containing phillipsite and chabazite) deriving from lithification processes of volcanic ash (de Gennaro et al., 2000) have also been used for preparation of concretes, both as aggregates and presumably, once pulverized, with similar functionality to pozzolan s.s.

The strength of Roman-era concretes, made with those geomaterials, is clear to scientists: the extraordinary adherence at the pozzolan and/or tuff/lime interface is due to the reactivity of lime towards both glassy component (pozzolan) and zeolitic minerals (tuff fragments). Recently, Jackson et al. (2017) emphasized the importance of the pozzolanic reaction of volcanic ash with lime in the cementing processes and durability of concrete from ancient (2000 y.o.) Roman ports. Formation of Al-tobermorite, a rare hydrothermal calcium-silicate-hydrate mineral, has been previously recognized in relict lime clasts of concretes as well as in the voids of glassy shards in other volcanic settings as well.

Here, examples of uses of these volcanic geomaterials in archaeological artifacts particularly, but not only, in the Phlegraean Fields district (one of the most important archaeological and volcanic contexts in the world), are reported, in one with the characterizations used to explain their role in durability of the artifacts themselves.

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## Implementation of a non-destructive method to assess weathering deterioration on sandstones in cultural heritage

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*Keywords:* sandstone weathering, equotip hardness tester, cultural heritage.

The problem of deterioration of building stones is particularly important in Cultural Heritage rich countries; Italy is one of these, with the highest number of UNESCO World Heritage Sites. To reach sustainable monument preservation, proper countermeasures are required to protect stone monuments from weathering or to provide more efficient restoration actions on damaged buildings from catastrophic events (i.e., earthquakes).

In this framework, together with granite and limestones, sandstones are the most used construction materials in Central Italy and all over the world. Due to their high compositional heterogeneity, the characterisation of weathered sandstone is difficult. For this reason, the development of an innovative non-invasive methodology is essential to better understand the behaviour of weathering on protected monuments.

The sandstone columns of Palazzo Ducale, one of the main historical buildings in Camerino town (Central Italy), are protected by the Superintendent for cultural heritage of Marche Region (peripheral body of the current MiBAC Ministero per i Beni e le Attività Culturali) and display a different range of weathering in terms of discolouration, significant scaling and loss of large volumes of stone.

In this study, an innovative methodology which couples non-destructive rebound measurements with Mercury Intrusion Porosimetry (MIP), Scanning Electron Microscopy (SEM), X-Ray diffraction and grain size analyses, has been proposed and tested on some columns of the palace. The methodology has been further validated on a few rock cores from the original extraction site.

It was found that weathering action on the columns’ surface has caused a 25% strength reduction with respect to the core samples. Based on the physicochemical analyses, it was identified that freeze-thaw cycles have caused a reduction in volume of micropores in favour of an increase in macropores, weakening the rock surface. In ochre zones pyrite oxidation has occurred, releasing iron and sulphur, promoting dissolution of calcium carbonate and its reprecipitation and reorganization in the outer and superficial macropores. This results in a significant decohesion of the material in crusts and scales as well as an important loss of material, which leads to a strong heterogeneity in the alteration of the artefacts. In fact, the lithic material’s surface alteration does not occur in a predictable and uniform manner; instead, it can have different speeds in adjacent points depending on the mineral-petrographic properties.

Eventually, our study aims to provide a valuable contribution to future restoration work in light of the damages suffered by the building after the 2016-2017 seismic sequence of Central Italy and it might be a representative example for understanding sandstone decay in historical artworks.

## Formulating restoration mortars for improved substrate compatibility: insights from Vitruvius' recipe

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*Keywords:* restoration mortars, compatibility, substrates.

Aim of this research is to improve the understanding of compatibility criteria for restoration mortars. The study stems from the description of M. Vitruvius Pollio in his "De Architectura" for the preparation of mortars, which recommends a mixture of lime and pozzolanic sand in a one-to-two ratio. To reproduce this mix-design, two pozzolanic sands from the Phlegraean Fields were selected. A sample was taken from the deposit of Fondi di Baia (Bellavista Lithosome), which is the exact location indicated by Vitruvius. As quarrying is no longer possible in this site, a commercial pozzolanic sand (Neapolitan Yellow Tuff) was selected. A traditionally produced lime putty (CL90-S) was chosen as a binder. The mineralogical and petrographic characterisation of raw materials reveals that both pozzolans have a trachytic composition consistent with Phlegraean products.

The reference admixtures (named mortars zero) were prepared using the two pozzolanic sands following Vitruvius' recipe: M0L (with the pozzolanic sand from Fondi di Baia) and M0C (with the commercial pozzolanic sand). The ratio of binder, aggregate, and water (1:2:0.5) was defined by volume. The two mortars, M0C and M0L, were characterized at 28 and 90 days of curing using mineralogical-petrographic techniques (PLM, SEM-EDS, XRPD, XRF, FTIR, TG-DSC with EGA-FTIR) and physical-mechanical test, such as mercury intrusion porosimetry (MIP), and UNI EN standards for the determination of flexural and compressive strength, apparent density, water absorption by capillarity and at atmospheric pressure, ultrasonic test. The results obtained on the two mortars are comparable and consistent with those in the literature. Therefore, the decision was made to continue the research by using only the commercially available pozzolanic sand to make the mortars repeatable for any conservator.

The admixture M0C was applied to three distinct substrates: brick, tuff, and limestone. These were chosen for their different composition and, above all, for their dissimilar porous system. The adhesive strength of the mortar on the substrates was evaluated using the UNI EN standard test for masonry, which showed low adherence strength values although consistent with the literature data of lime-based mortars. The test showed differences in the behaviour of the mortar depending on the substrate to which it was applied.

In the light of the obtained results, new restoration mortars will be formulated to enhance compatibility with substrates. These mortars will be made of the same materials, with only the binder-to-aggregate ratio and aggregate grain size being varied. The interaction with substrates will be deeply studied through the development of composite specimens that consist of a sandwich-like structure: substrate-mortar-substrate. The outcomes of this study will provide insights into formulating restoration mortars optimized to improve compatibility and interaction with various substrates.

## Vitruvian and “alternative” volcanic pozzolans in the ancient world. A brief review based on recent scientific advances

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*Keywords:* volcanic pozzolan, provenance analysis, ancient mortars and concretes.

The use of volcanic pozzolans to improve the hydraulic properties and cohesive capabilities of aerial lime-based mortars represents one of the most brilliant achievements of antiquity. Several Latin authors, such as Vitruvius and Pliny, celebrated the outstanding properties of the *Pulvis puteolana*, a particular pyroclastic ash, outcropping in the territory around the Gulf of Naples, indicated for enhancing the longevity of concretes in underwater conditions. As demonstrated by recent research, the spread of the Neapolitan pozzolans in the Roman territories of the Mediterranean from the Augustan Age (beginning of the 1<sup>st</sup> c. CE) onwards grew in a short timeframe, and this product obtained the monopoly in the markets as an excellent material for the manufacture of long-lasting hydraulic mortars and concretes (Brandon et al., 2014; Dilaria et al., 2023). The reasons for this massive commercialization probably lie in trade logistics: the outcrops are located close to the coast of the Bay of Naples, where the large Roman harbors of Puteoli, Baia and Miseno were located. These factors played a key role in the commerce of the material, which travelled the sea as ship ballasts, together with handbooks and craftsmen, during Rome’s rapid expansion throughout the Mediterranean Sea.

However, it was known by certain Roman engineers that the Vitruvian *Pulvis* was not the unique pyroclastic product effective in improving the performances of ancient mortars, thus the exploitation in the Provinces of the Empire of possible “alternative” volcanic pozzolans (i.e. Columbu et al., 2019; Uğurlu Sağın et al., 2021) is a question that is gaining an increasing interest in the field of geochemistry and materials science of ancient construction materials.

The present contribution aims at reporting a brief overview of the state of the art on this topic. We will discuss some new evidences from different Mediterranean sites (Nora and Sant’Antioco in Sardinia, Aquileia in Friuli Venezia Giulia, Padova and Montegrotto in Veneto, Lio Piccolo in the Lagoon of Venice), currently under investigation by a joint collaboration between the University of Padova and the University of Calabria, on the different ways of utilization of “Vitruvian” and “alternative” volcanic pozzolans in ancient constructions, providing intriguing insights about the in-dept technological confidence of ancient craft in the properties of local land resources and in their optimal utilization, which should be investigated further for the refinement of sustainable concretes in modern civil engineering as possible replacements for Portland cement.

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## Microanalytical approach for archaeometric characterization of glazed ceramic

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Keywords: glazed pottery, SEM-EDS, T-XRF.

The study of ancient glazed pottery is essential to transfer millennia-old know-how to the modern ceramic industry. Also useful for dating, unraveling their production technologies, their sources, and trade rules, their restoration and preservation. Alchemical recipes include many modifiers such as arsenic, phosphorus, tin, cobalt and antimony. In Italy, the composition of glazed pottery is little studied, but our preliminary study using Italian and non-Italian samples suggests good potential as an indicator of production age and provenance (Klesner et al., 2021). Archaeometry is the tool for material characterisation, but its application is limited to a nondestructive analytical approach. Therefore, Total Reflection X-Ray Fluorescence (TXRF) is a valid analytical technique requiring a very small amount of analyte. However, the TXRF technique does not allow the measurements of all elements’ concentrations in the sample. In the attempt of gathering the most complete analysis of historical glazed pottery, we combined SEM EDX and TXRF (EDXRF) analytical techniques. Based on the promising data from previous archaeometric studies on lead glazed pottery and the growing demand of the ceramic industry in the past, the study on the evolution of materials to make the glazes is realistic. The main types of glazed pottery used are lead glaze pottery, silica glaze pottery, and alkali glaze pottery. In general, as reflected in the literature, the main advantages of using high-lead transparent glazes over alkaline transparent glazes are the greater ease of preparation and application of the glaze suspension, less susceptibility to glaze “crazing” and “crawling,” and greater optical brilliance (Tite et al., 1998; Walton & Tite, 2010). Decorated ceramic forms would complement the knowledge of technological and functional as well as socio-cultural aspects, enabling the reconstruction of late medieval and early modern patterns. This study focuses on Italian glazed ceramics and beyond through trade in order to find the exact types of glazes, pigments, modifiers, and composition and firing techniques of the ceramic body, as well as the association of form, design, and technology. The exact correspondence between functional and technological aspects in order to a substantial database of samples that tell us the evolution of glazed ceramics. This novel analytical approach being practically nondestructive has a high potential for obtaining major and trace elements composition of Cultural Heritage materials with broad applications.

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## Characterization of ancient mortars: an archaeometric protocol of analysis

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Keywords: mortars, archaeometry, multi-analytic protocol.

The petrographic and geochemical study of mortars could provide many answers about supply areas, variation of raw materials over the time, network/transportation systems, development and production processes (Lezzerini et al., 2017). The petrographic study allows to recognize the type of binder and the nature of the aggregate (Pecchioni et al., 2018). In particular, it is possible to understand which kind of raw material has been used to produce the lime, the ratio between binder and aggregate, the origin of the aggregate (from sediment or through grinding of rocks) and its composition.

A new semi-automated image processing procedure based on multivariate statistical analysis of X-Ray spectrum images has been here applied to mortar samples coming from Ancient Roman Theatre of Aosta (NW, Italy) to compute the element distribution between and within specific mineralogical phases. Different methodologies have been applied: polarized light microscope, cathodoluminescence and SEM-EDS system. At first, starting from SEM backscattered, cluster imaging analysis has been carried out in order to furnish the ratio of aggregate, binder and porosity. In addition, by mean of simple algebraic operations, full quantification, point by point, of each EDS spectrum (expressed as oxides) were performed in order to calculate the distribution of Hydraulicity Index (HI), with its statistical error, inside the investigated domains. On the base of HI map distribution, preserved from altered mortars could be distinguished. In addition, the classification obtained allowed to point out that the relict lime clast show the richer Ca contents and are diversely interested by hydraulic reactions in its external portions. Maps also show that HI increases towards the Si-Al-K rich phases. The outcome of this kind of approach is the constitution of an analytic protocol that could be applied for every kind of mortar

At Roman Theatre of Aosta, applying this protocol, four different varieties of restoration mortars have been identified, in addition to the original Roman mortars.

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## **The BEGIN project: from the census to the geoconservation and valorisation of Italian “ghost towns”**

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*Keywords:* ghost town, census, geoconservation.

The abandonment of inhabited places is a phenomenon well-known in many countries over the world and it goes through the centuries since ancient times. During the last decades of the twentieth century the abandonment has taken on a relevance in Europe because of extensive social, economic, and cultural changes. These transformations have led rapid urban expansion to the prejudice of both smaller settlements and remote rural villages that have been deserted by inhabitants with the consequent birth of “ghost towns”.

The causes that can lead to the abandonment of places can be grouped in two main categories: a) natural causes (e.g., earthquakes, landslides, floods, volcanic eruptions, environmental conditions, diseases), and b) anthropogenic causes (e.g., wars, economic fluctuations, demographic aspects, transfer of the population to urbanized areas, marginalization and isolation of villages, catastrophic events, technological and industrial in nature) (Gizzi et al., 2016; East, 2017; Masini et al., 2018; Gizzi et al., 2019).

The “ghost town” phenomenon takes on a statistically significant especially in Italy, Greece, Spain, Portugal, and Albania. However, even if Italy is among the Mediterranean countries hosting the largest number of “ghost towns”, a census of them is not available. The activities of the BEGIN (“abBandonno vErsus riGenerazioNe”) project are also devoted to fill this gap. The project is financed by ERDF, ROP Basilicata 2014-2020.

BEGIN aims to develop the following outputs:

- the census and cataloguing of abandoned towns in Italy;
- the establishment of an Information, Documentation, and Interpretation Centre (GOTIDIC) on the abandonment phenomenon in the Mediterranean area. GOTIDIC will be placed in Craco vecchia (Basilicata region, Italy), the main test site of the Project;
- a prototype Web GIS platform for multilevel and multitemporal knowledge of Craco vecchia;
- a pilot project for the geoconservation of Craco vecchia;
- a manual of best practices for (geo)conservation, restoration, and valorisation of “ghost towns”;
- a prototype platform for virtual reality applications for the knowledge, valorisation, and fruition of “ghost towns”.

In this work, the methodology and the first results of the project will be discussed, with special attention to both the census of Italian “ghost towns” and the pilot activities for the geoconservation of Craco vecchia.

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## Prehispanic lime plaster production technology at Ichkaantijoo, Yucatán, México: an analytical study for archaeological conservation of Maya architecture

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Keywords: lime plaster, Maya area, archaeological conservation.

Understanding the pre-Hispanic lime plaster production technology in Mesoamerica is of great utility for the conservation of archaeological architecture. Identifying the materials used on culturally important objects is vital, as it provides information for decision making on a conservation level (Stuart, 2007). Archaeological materials are in constant deterioration due to exposure to environmental factors, time, and inappropriate conservation or restoration processes. This is the case of archaeological lime plaster material in Yucatán Peninsula, México (Lorenzo & Carrascosa, 2013). We aim to analyze and characterize archaeological lime plaster floors from eight archaeological Maya sites located in the Yucatán Peninsula, México, from different time periods (1000 BC - 1300 AD), at a molecular and elemental level, to gather information for a future conservation plan. We used different analytical techniques applied to heritage materials, such as Fourier transform infrared spectrometry (FTIR), fiber optics reflectance spectroscopy (FORS), X-ray diffraction (XRD), X-ray fluorescence (XRF), and petrography through optical microscopy (OM). We followed the methodology proposed by Chu et al. (2008) and Ortiz (2019) to estimate calcite heated temperatures. The results show three different groups of lime plaster floors, all of them composed by calcium carbonate ( $\text{CaCO}_3$ ). Group 1 is composed of calcium carbonate ( $\text{CaCO}_3$ ), heated at different temperatures from 0 to 752°C. Group 2 is composed of calcium carbonate ( $\text{CaCO}_3$ ), and a small proportion of muscovite ( $\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH},\text{F})_2$ ) in some samples, and heated at different temperatures from 0 to 843°C. Group 3 is composed of a lesser proportion of calcium carbonate ( $\text{CaCO}_3$ ), calcium aluminum-silicates ( $\text{Al}_2\text{Si}_2\text{O}_8$ ) and illite ( $\text{K}_{0.7}\text{Al}_2(\text{SiAl})_4\text{O}_{10}(\text{OH})_2$ ) and heated only at temperatures between 700 and 790°C. Groups 1 and 2 are located at different sites all over the region, while Group 3 is located only at the southeast corner of the region. We propose that the different chemical fingerprints respond to variations from diverse calcium carbonates obtained from several mines, as mines are abundant in the region. Group 3 could respond to the use of a particular calcium carbonate mine located at the southeast portion of the region. The changes in time respond to technological innovations, as different proportions would be used to aim variant physical properties of the lime plaster floors. Results show more variation in chemical composition and temperatures during the Classic period (250 - 1000 AD), indicating experimentation and innovation during that time. The samples with estimated heated temperature of 50°C indicates the use of geogenic calcites, a technology that reduces resources needed to produce lime plasters. This allows us to propose conservation plans based on unheated materials, such as *sascab*, a calcium carbonate sediment available in the region, for the Yucatán Peninsula archaeological sites. Work supported by CONACYT under contract CF 2019 No. 731762. Experimental work was possible thanks to the support of LANCIC-IF. S. Ortiz acknowledges the support granted by CONACYT by a postdoctoral fellowship.

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## Characterisation of natural stone materials employed in some historical monuments of Catania (Sicily): case study of the fabric-related degradation phenomena

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Keywords: building materials, petrophysics, eastern Sicily (Italy).

The late Baroque architecture of the Val di Noto towns in eastern Sicily (UNESCO World Heritage List) is characterised by a close relationship between stone building materials and geological context. The ancient centre of Catania is a representative example of such monumental architecture due to the employment of both sedimentary (Hyblean limestones) and magmatic (Etnean lavas) rocks, resulting in a characteristic bichromy (Punturo et al., 2005; 2006). Employed as building material, these stone materials are exposed to atmospheric agents (e.g. rain, wind, solar radiation, aggressive atmospheric pollutants, freeze-thaw cycles, crystallization of saline solutions, and growth of organisms) that, over time, cause deterioration of cultural heritage.

Among the various Hyblean limestone employed, we focused on Pietra di Noto (Palazzolo formation), widely used in most monuments. We carried out an investigation on its fabric-related petrophysical properties, in terms of petrography, porosity and seismic behaviour. The petrographic and mineralogical analysis of the cross-sections showed that Pietra di Noto is a bioclastic wackestone, i.e. a fine calcarenite with dominantly planktonic microfauna floating in the matrix, and the clastic grains are dominantly quartz with minor feldspar. Intergranular spaces are filled with micrite. Porosity, both interparticle and of vug type, is low and develops within fossils and matrix; 3D porosity was also assessed by X ray microtomography. Geochemical results showed that the Pietra di Noto is a marly limestone, based on CaO wt%, with a high Al<sub>2</sub>O<sub>3</sub> content related to its abundant terrigenous fraction.

Igneous rocks showed a porphyritic texture and a mineral composition mainly represented by plagioclase, pyroxene and olivine in a microcrystalline groundmass. Their porosity is low and represented by often isolated microvoids and microcracks.

We focused our attention on some of the numerous historical buildings located in the centre of Catania, showing different age of construction and purpose, and built employing the Pietra di Noto and the Etnean lavas. We carried out lithological survey and studied the various degradation phenomena affecting these monuments in different amounts (Punturo et al., 2006; Pappalardo et al., 2022).

Since the mineralogical composition of rocks, together with their physical properties (e.g. porosity), plays a key control in the kinetics of degradation processes, we compared the deterioration forms observed in the buildings with those ones obtained in the laboratory; results highlighted the close relationship between textural characteristics and damage and permitted to related them to the environmental context.

In conclusion, our archeometric study has succeeded in providing a basic tool, which may be useful either for conserving monuments of cultural heritage or for their restoration.

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## **Pore network impact on petrophysical characteristics of the asphaltic limestone used in the Late Baroque towns of the Val di Noto UNESCO site (south-eastern Sicily)**

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*Keywords:* pitchstone, geomaterial, Sicily.

Pitchstone is a bitumen-impregnated carbonate rock cropping out in the Hyblean Plateau (south-eastern Sicily). The area has been for decades the main target for both hydrocarbon and ornamental stone exploitation. The stones have been largely used in the monumental architecture of the late Baroque towns of the Val di Noto (UNESCO World Heritage Site) (Maniscalco et al., 2022; Punturo et al., 2023). Indeed, the brown-with-whitish-veins to almost black colour, resulting from the bituminous impregnation, favoured its use in combination with white calcarenites to obtain the typical bichromatic effect in architectural elements (Punturo et al., 2006, 2021, 2023). Besides, pitchstone was also used for road paving in several Italian and European towns such as Milan, Palermo, Berlin, Paris, Amsterdam, and London (Punturo et al., 2006, 2023). However, although this rock has long been used as a cutting stone, it has not been studied in detail before (Punturo et al., 2023).

In our study a multi-analytical investigation of two differently impregnated samples, representative of the main exploited and marketed pitchstone lithotypes, was carried out to provide a detailed knowledge of this geomaterial and its fabric-related properties. Petrographic analysis, X-ray computed microtomography surveys and 3D image analysis, ultrasonic testing, gas chromatographic analysis, thermogravimetry (TG-DTG) and differential scanning calorimetry (DSC) were performed.

The petrographic analysis of the cross-sections showed that the two samples consist of bioclasts, and carbonate grains in a predominantly micritic matrix (microcrystalline calcite) with a lower percentage of sparry calcite cement. In terms of seismic behaviour, the samples are characterised by comparable average P-wave propagation velocity values that can be interpreted as the effect of a similar fabric; nevertheless, since both lithotypes do not exhibit any observable fabric anisotropy, the noticed differences in seismic anisotropy may be due to the arrangement of pores and voids. C12-C40 hydrocarbon concentration change can be related to the higher impregnation revealed by X-ray microtomography. This, together with the coarser grain and pore size observed in PP1, allows us to conclude that the bitumen impregnations in pitchstone samples depend entirely on the pristine porosity properties.

In conclusion, our multi-analytical study has succeeded in highlighting the intrinsic properties of an important geomaterial, which is useful for the proper planning of monument restoration, as well as for monitoring available raw materials and planning their sustainable use in the context of the green transition. Pitchstone proves to be an excellent building material due to the presence of a bituminous impregnation, which confers excellent physical and mechanical properties, such as good insulation against rising damp, good resistance to erosion, malleability, and workability.

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## **Preliminary minero-petrographic characterization of archaeological ceramics from Pompei (Regio I, Insula 1). Pompei Archaeological Research Project: Porta Stabia (IV-I century B.C.)**

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*Keywords:* archaeometry, archaeological ceramics, Pompei.

This investigation deals with a preliminary archaeometric characterization of 24 ceramic samples (IV-I century B.C.) collected at the Pompeii Archaeological Park (southern Italy) as part of the "Pompeii Archaeological Research Project: Porta Stabia (PARP:PS)". The goals of the PARP:PS project have been "to reveal the structural and social relationships over time between Pompeian households of variable economic portfolios, to determine the role that sub-elites played in the shaping of Roman urban networks, and to register their response to city- and Mediterranean-wide historical, political, and economic developments. An additional and especially important aim has been to unravel the complex connections between urban infrastructure (especially waste management) and the making of long-lived, complex urban sites" (<https://classics.uc.edu/pompeii/>).

The ceramic sherds here examined came from Regio I (Insula 1) and consist of 7 beakers, 6 spacers, 3 skyphos, 2 basins, 2 thin walled, 2 bowls, 1 jar and 1 fragments of kiln floor.

After a macroscopic description, the fragments were characterized following a multi-analytical approach (OM, XRD, XRF, TG/DSC, FTIR) that allowed interesting considerations on the production technology and selection of raw materials used for the manufacturing of these artifacts.

According to XRD and OM observations, spacers were probably manufactured using CaO-rich marine clay (with rare occurrence of foraminifera residues), fired at an Estimated Fired Temperatures (ETFs) at least over 950°C in oxidizing atmosphere. Traces of analcime attributable to post-depositional alteration processes of amorphous fraction were observed as well.

The use of CaO-rich clay in the manufacturing of skyphos was also presumed by XRD analyses. These samples probably underwent to ETFs ranging from 950 to 1050°C due to the occurrence of rare gehlenite, once again in oxidizing conditions. This mineral was clearly observed, along with other newly-formed phases (i.e., pyroxene and feldspars), in bowls where the use of calcium-rich raw materials (up to 17 wt%) was confirmed by XRF. Aplastic components observed in thin section are generally composed by volcanic inclusions (e.g., clinopyroxene, leucite-bearing scoriae and garnet) from Somma-Vesuvius environs. In some cases (e.g., in the kiln floor fragments), these grains are arranged in a bimodal distribution in which coarse fraction was probably added as temper. Lastly, beakers and the remaining utilitarian common wares were manufactured using CaO-poor clayey raw materials and likely fired, in oxidizing conditions, between 850-950°C.

All the information gathered so far, also thanks to the presence of production indicators (e.g., spacers and overfired beakers), may be useful for significant comparisons with ceramic materials found in other archaeological sites of Campania region, and to better understand and describe the social context of the time.

## Archaeometric investigation on Roman fresco fragments from topsoil of Aquileia (Italy)

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Keywords: Roman fresco, tectoria, Aquileia.

The aim of this study is to develop a novel procedure that can help placing Roman fresco fragments in their original context. The proposed methodology aims to assign decontextualized and featureless fresco fragments to specific building phases based on the production technology and compositional properties of mortars and plasters. Additionally, the pigments used in the pictorial layers can provide clues about the association of the fragments to public or private contexts. Applying this approach to the vast amount of fresco fragments available in archaeological storages and never studied can open the possibility to recover a wealth of information.

The area surrounding ancient Aquileia, Italy, is rich in archaeological artifacts, some of which can be found just by surveying the top layer of agricultural soil during field walking surveys. Wall painting fragments found on the topsoil are in a fragmented state, and hardly any fresco fragment is found in situ. Complicating matters, the lack of preserved Roman-era buildings makes it challenging to accurately date fragments and determine their original architectural context, whether public or private (Salvadori et al., 2017; Dilaria et al., 2021): archaeometric research on tectoria has only provided characterization data on artifacts discovered in primary and well-defined excavation contexts, which are infrequent occurrences in Aquileia.

This study examines a selection of 21 fresco fragments from the Aquileian countryside using optical and electronic microscopies to analyse the petrographic and textural properties of the mortars and the composition of the pictorial layers. The results are then cross-referenced with existing literature data to validate the proposed protocol. The analyses carried out on the mortars highlight an aggregate fraction composed of angular calcite or marble grains in the “intonachino” layers and calcite, micritic limestone, quartz, flint, and phyllosilicates in the “arriccio” ones. Lime is identified as the main binder of the mortars in all the samples studied, as shown by the textural characteristics and chemical composition of both “arriccio” and “intonachino” layers (Pecchioni et al., 2014). Analysis of the layers of paint has revealed the presence of haematite and yellow ochre alongside Egyptian blue and cinnabar.

The results suggest that the fragments likely came from private residences that were probably dated to the Late Antiquity period. These preliminary findings highlight the potential of the proposed approach to reveal new information and to determine the period to which the fragments belong.

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## Promotion of Thassos and Naxos heritage ornamental stones

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*Keywords:* Thassos Crystallina, Naxos Crystallina, heritage stones.

Heritage stones have been widely used structural materials since Prehistoric times for a wide range of purposes, from tool manufacture for hunting to magnificent construction of monuments during the centuries. The beauty of historical stone constructions which have endured over time, document the importance of the heritage stones for the cultural heritage of societies. A historical synopsis of the main events that marked the history of the use of heritage stones is presented by Freire-Lista (2021). This paper examines the timelessness and importance of “Thassos Crystallina” and “Naxos Crystallina” heritage stones quarried in Thassos and Naxos islands, focusing on their physical - mechanical features, such as apparent density, open porosity, water absorption, compressive and flexural strength, abrasion resistance, etc, and their mineralogical characteristics, determined at “Lithos” Lab of HSGME in Greece. The oldest marble quarries in ancient Greece were in Thassos and Naxos Islands, operated around the 7<sup>th</sup> century BC. “Alykes quarry” was located on the southeastern side of Thassos island and produced a semi white calcitic marble. Thanks to its location, near to the sea, the marble transportation was very easy all over to the Mediterranean. Marble architectural decoration at various sites around the Mediterranean has been attributed to Alykes quarries on the basis of traditional art historical methods (Herrmann & Barbin, 1993). Furthermore, research on the Neolithic marble vases from Luminaria in Thassos showed clear connection between Thassos and Cyclades already in the Neolithic period (Maniatis et al., 2009). Today, there are ruins of “Alykes quarry”, partially submerged in the sea, semi-finished sculptures, huge marble blocks and columns, evidence of the ancient mining. Nowadays, “Thassos Crystallina” marble which is quarried in the central part of Thassos has almost the same features as those of the marble extracted in Alykes ancient quarries. It is a metamorphic rock belonging to the carbonate marbles of Rhodope Mass area, part of the region of East Macedonia and Thrace. “Naxos Crystallina” white marble was widely used even in prehistory and antiquity for religious purposes or for daily life objects (Cycladic civilization) and later for architectural purposes, in monuments and sculptures. During the centuries, these materials have played major role in culture, history, civilization of humankind, in the restoration of architectural heritage, and in the geoheritage in general. The physical - mechanical features of these marbles, on which their endurance through time and under mechanical stresses depends, as well as their aesthetics resulting from their mineralogical composition, render them attractive structural ornamental stones with a wide range of applications to-date, thus confirming and justifying the timelessness in their use. Their properties have crucial influence on their behaviour and have made them appropriate for use in any type of application both in local communities and all over Mediterranean.

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## Diagnostic investigation on a Sorel and Portland cement boiserie at Palazzo Fizzarotti (BA)

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*Keywords:* cemento Sorele, cemento Portland, Palazzo Fizzarotti.

This paper describes the results of the diagnostic investigation conducted on the “boiserie” of the Rococo Hall at Palazzo Fizzarotti (1850-1908) in Bari. The “boiserie” is an artifact made of faux marble with included “seminato” elements and characterized by the presence of assembly plastering. The study aimed to identify its constituent materials, reconstruct the production technique, and understand its conservation state to carry out a critical restoration work which respected the “boiserie” from a material, historical and aesthetic point of view.

Non-invasive analysis took place in situ by means of colorimetry, X-Ray Fluorescence (XRF) and UV Fluorescence (UVF) while a multi-technical approach was performed on 15 samples through micro-destructive analyses as Stereomicroscope observation (OM), petrographic microscope observation (POM) on thin sections, scanning electron microscopy combined with energy dispersive spectroscopy (SEM-EDS), Raman spectroscopy (RS) and X-Ray Powder Diffraction (XRPD).

The SEM-EDS investigation revealed the use of Sorel cement for the surface mortar layer in the faux marble elements (including the assemblage plastering) and the use of Portland cement in the “seminato” elements and the plastering depth layer. This technique and RS displayed hematite, carbon black, chromium oxide green and ultramarine blue as coloring agents.

Furthermore, SEM-EDS analysis shown an incorrect dosage of the Sorel cement mixing components, and two of its alteration products were identified (chrolartinite and hydromagnesite) by XRPD and RS. POM investigation and UVF revealed traces of a serial production technique, including the successive pouring of mortar layers in a fluid state into molds, the creation of original assemblage plastering and localized surface treatment application.

Based on the results, it was possible to carry out a critical and appropriate restoration work and limit the worsening of the “boiserie” conservation state.



## **Innovative and sustainable lime-metakaolin restoration mortars: development and applications**

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*Keywords:* restoration mortars, lime, metakaolin.

The Cultural Heritage Group of the CNR-ISSMC (former ISTECC) has been developing lime-based (putty lime CL90-S PL and natural hydraulic lime NHL; acronyms according UNI EN 459-1:2015) restoration mortars with different functions for about twenty years. Mortars compatible with the materials present in/on the artefacts of historical-artistic-architectural interest, prepared with binders and any admixtures obtained by low carbon emission firing, free of synthetic additives, with zero VOC (Volatile Organic Compounds) emissions, particularly durable, easy to apply and at costs not particularly high.

This work highlights the studies and applications relating to the development of lime mortars (CL90-S PL and NHL) and metakaolin (pozzolanic admixture obtained by the firing of kaolin) carried out on the occasion of two POR FESR projects of the Emilia-Romagna region and of a research collaboration with the Academy of Fine Arts of Naples. In all three studies the development of the mortars was preceded by the characterization, by means of different analytical techniques, of the raw materials. The first POR FESR project: "MITAI L4" highlighted the strong pozzolanic activity of metakaolin, through the evaluation by DTA-TGA analyses of its reactivity with calcium hydroxide present in the binders. In addition, the presence of metakaolin in high percentages gives the mortars high mechanical performance, making them suitable for use also in the building sector. The second POR FESRS project "MImeSIS" aimed to develop sensor-integrated smart systems to monitor the deterioration of traditional masonry buildings. The main task of CNR-ISTECC was to formulate lime-based mortars with low environmental impact and high durability to host sensors. Hemp fibres were used to achieve good thermo-hygrometric conditions sustainably. Several specimens were made, and physical and mechanical tests were carried out to identify the best admixtures. Finally, a prototype of a historical masonry structure decorated with a mosaic floor and fresco on the wall was created, and sensors (pH and chloride content) were successfully applied to it, demonstrating the suitability of these mortars for different functions in the conservation of the historical building heritage, and their environmental sustainability. The study, in collaboration with the Academy of Fine Arts of Naples, focuses on a new bedding system for mosaics that uses lime-based mortar mobile backings as an alternative to aluminium honeycomb panels. It resulted in a system that uses two types of mortars, one for the bedding of tesserae and one for backing, both of which contain metakaolin. The backing mortar also contains lightweight aggregates. Afterwards, the bedding-backing system was applied to two fragments of detached mosaics found in Ponticelli (NA). The system has been proven to be chemically, physically, and aesthetically compatible with the artifacts. The main advantage of this system is its affordability and ease of use.

## Roman settlement in Sardinia: archaeometric contribution to the excavation of Santa Filitica Villa (Sorso, Italy)

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*Keywords:* ceramics, slags, mortars.

The complex settlement of Santa Filitica, which is located in north-western Sardinia, consists of the remains of an imperial Roman villa (and its annexed thermal plant). The site was reutilized from late 5th-6th century A.D. until Byzantine period (Rovina, 2003). Its complexity therefore makes it a particularly interesting site for reconstructing the history of Sardinia during a poorly known time span. This work focuses on archaeometric investigations conducted on ceramics (pottery and bricks), slags and mortars in order to characterize their composition, structure, provenance and technology. The results obtained from a combination of techniques (thin section Optical Microscopy, X-Ray Diffraction, X-Ray Fluorescence, Scanning Electron Microscopy), in addition to the statistical analysis, allowed us to formulate hypotheses about the provenance of raw materials or of pottery and on manufacturing tradition of the workshops. Among the findings pottery, bricks, mortars and slags reveal an heavy use of local raw materials including marly clays and local lime, as major content of the mortars, and iron ore. Noteworthy are the textural and chemical features of the Santa Filitica slags that, contrary to what was thought, point to blooming and forging at the same location. The abundance of wüstite and the absence of tapping-derived features also suggests (Miller et al., 1995; Senn et al., 2010) a low-efficacy reducing process and low-efficacy iron extraction, and the limited skills of the local smelters, which work, although not episodic, aimed to satisfy only local needs (Mameli et al., 2014).

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## The use of corrosive sublimate (HgCl<sub>2</sub>) in the Herbaria of the University of Florence – state of the art and future research

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Keywords: mercury, herbaria, conservation.

Herbaria are collections of dried plant specimens associated with the related metadata (provenance, date of collection, etc.). Typically housed in Natural History museums, they are not only a precious part of our cultural heritage, but also a key resource for the study of global biodiversity through the centuries. However, the application of corrosive sublimate (HgCl<sub>2</sub>), frequently used in the past to protect the specimens from pests infestations, has led to a mercury (Hg) contamination issue, which now affects the accessibility of worldwide herbaria and the fruition of the collections.

In this context, the Central Italian Herbarium (Natural History Museum of the Museum System) and the Tropical Herbarium Studies Centre (Department of Biology), both part of the University of Florence (UNIFI), are the largest herbaria in Italy and among the oldest in the world, with samples dating back to the 16<sup>th</sup> century.

Several analytical campaigns have been conducted at the UNIFI herbaria in the last decade, in order to assess the extent, characteristics and consequent hazard of the Hg contamination. An overview of this research is provided in the present contribution. In particular, the study of historical documents and interviews with the curators allowed us to acquire information on the chronological period and the type of collections in which HgCl<sub>2</sub> was used. Moreover, the gaseous elemental mercury (GEM) concentration, distribution and seasonal variation (Cabassi et al., 2020), as well as the size and composition of the particulate containing Hg, were determined (Ciani et al., 2021). More recent, unpublished studies explored the difference between various types of herbaria (open and closed), the extent of the Hg contamination of the cabinets containing the plant specimens and the role of the cabinets themselves in the GEM emission.

This review of previous studies was crucial to plan future activities with specific reference to: 1) the mass digitisation of the collections which will take place in the near future in the framework of the National Recovery and Resilience Plan (PNRR); 2) the identification of possible remediation strategies.

*Acknowledgements:* The authors kindly acknowledge the curators of the Central Italian Herbarium. RM, VR and MB acknowledge the support of NBFC to the University of Florence, funded by the Italian Ministry of University and Research, PNRR, Missione 4 Componente 2, “Dalla ricerca all’impresa”, Investimento 1.4, Project CN00000033.

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## **Analysis and evaluation of abandoned modern concrete heritage: the case study of the “Marxer Pharmaceutical Laboratory and Research Institute” in the context of the Olivetti heritage in Ivrea**

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*Keywords:* industrial heritage, exposed concrete.

The case study is set in the context of the industrial and social history and of the Olivetti architectural heritage (Boltri et al., 1998). The Olivetti territorialism refers to the co-evolution of human life and work, and the industrial architecture acquires a high symbolic value. The recognition in 2018 of the Ivrea Olivetti heritage as an “outstanding model of industrial city” and UNESCO universal heritage site, has opened up opportunities for valorisation and new development.

The works by Galardi, Sgrelli and Zanuso bear witness to the Milanese school’s experimentation on exposed concrete, in accordance to international models. The Marxer complex is thus characterised by its technological quality and almost forty years of neglect. Designed by Alberto Galardi on a direct commission from Adriano Olivetti in 1959 and inaugurated in 1962, the Pharmaceutical Institute is designed by Antoine Marxer. The complex has two main orthogonal buildings: the office-research building and the factory (Naretto & Beltramo, 2019).

The first has two floors above ground and a basement, the second a single floor and a technical basement, surrounded by a park, according to the concept of a human-scale environment surrounded by nature. The linear modernist geometry is characterised by the “béton brut” of the façades with modular sun-shading baffles sloping 45 degrees with respect to the elevation line, forming a continuous grid spaced about 90 cm from the window and door frames on the larger façades, with stringcourses and gargoyles. The archive documents on the cement deposit (1960), signed by Antonio Migliasso, and on the test (1965) show the use of a cement type 680, dosed 300 kg/m<sup>3</sup>, with AQ.42 homogenous iron reinforcement, with a maximum project stress of 65 kg/cm<sup>2</sup> in the concrete and 1400 kg/cm<sup>2</sup> in the iron. The photographic documentation at the time of realisation highlights the good quality of the finishing.

Abandonment since 1990 has resulted in the aggression of the environment exacerbated by vandalism, with the destruction of all glazing and protection. Degradation, in the most critical cases, results in the expulsion of the iron covering, leaving the smooth reinforcement exposed, particularly on the sunbreaks and cornices. Widespread are chromatic alterations, efflorescence and localised damp stains, extensive biological patinas and vandalism graffiti in the lower blind areas (Locatelli, 2020; Maspoli, 2022).

The superficial decay of the concrete is more pronounced in very sunny areas (south-east) and close to weedy vegetation and in some corner areas, leading to the loss of thin layers up to the erosion with the detachment of flakes of incoherent material.

Eight samples were taken on the external fronts of the two buildings, in relation to orientation and exposure and representative of areas in various states of decay. A mineralogical-petrographic study and a study of the physical characteristics (water accessible porosity, bulk density) was carried out on these samples in order to determine their mix design and the way in which decay developed.

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Locatelli L. (2020) - Analisi, valutazione, recupero adattivo e riuso del patrimonio olivettiano industriale, terziario e di servizio. Il caso studio “Laboratorio Farmaceutico e Istituto di Ricerca Marxer” a Loranze, tesi di Laurea, Politecnico di Torino.

Maspoli R. (2022) - Modern and industrial: the new abandonment. The case of the Canavese area. In: Hadda L., Mecca S., Pancani G., Carta M., Fratini F., Galassi S., Pittaluga D. (eds.), Villages et quartiers à risque d’abandon: stratégies pour la connaissance, la valorisation et la restauration. Firenze University Press, 47-63.

Naretto M. & Beltramo G. (2019) - Dalla ricerca farmaceutica alla patologia: l’Istituto e Laboratorio Marxer a Loranze tra memoria e oblio. In: Canella G., Mellano P. (eds.), Il diritto alla tutela. Architettura d’autore del secondo Novecento, Franco Angeli, Milano, 336-345.

## 4D imaging synchrotron x-ray microtomography to investigate the dynamic of the consolidation process due to inorganic treatments on calcareous stone

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**Keywords:** consolidation process, diammonium hydrogenphosphate, synchrotron radiation x-ray microtomography.

A burning goal in Conservation Science is to study the diffusion of inorganic-mineral treatments inside stone materials and to understand how these treatments modify the microstructure of the substrate. Diammonium hydrogenphosphate (DAP,  $(\text{NH}_4)_2\text{HPO}_4$ ) solutions are commonly used in stone conservation to restore the mechanical and microstructural features of decayed carbonatic matrix (Matteini et al., 2011). These treatments act in a water-based solution and partially transform the original minerals of the carbonatic substrate in newly formed crystalline phases by a dissolution and recrystallization reaction nucleating on calcite grains (Sassoni, 2018). The kinetics of the reaction and the induced effects on the stone microstructural features are ruled by several variables i.e., treatment methodology, solution molarity, free ions availability, specific surface area, microstructural characteristics of the lithotype (Possenti et al., 2016). Therefore, the direct effects induced by the solution on the stone microstructure (e.g., pore morphology, connectivity, etc.) are still poorly understood and no information is available on the interaction between the calcite crystal and the DAP solutions during the reaction process (Possenti et al., 2019). Here, for the first-time, time-resolved (4D) high-resolution synchrotron X-ray microtomography was used to obtain real-time quantitative information on the structural evolutions induced by the treatment process on the Noto limestone, a porous carbonatic stone used as building stone since antiquity (Val di Noto - Siracusa, UNESCO's World Heritage List). The experimental setup developed allowed us to consider the intrinsic microstructural heterogeneity of the Noto limestone and, at the same time, to unambiguously attribute any specific microstructural variations during the treatment to the peculiar effect of the DAP treatments. With the aid of image analysis, microstructural modifications in terms of boundary morphology, porosity (both the total porosity and its components), interconnection and pore size distribution have been demonstrated in different stadia of the consolidation process. The quantitative analysis of the VOIs pointed out differences in the consolidation dynamic asserting the influence of molarity was asserted. This study paves the way to a deeper understanding of consolidation mechanisms and the effects induced to the 3D microstructural features of porous materials by inorganic treatment. Above all, this study supports the application of inorganic-mineral treatments in conservation worksites based on advanced knowledge of the dynamics of the consolidation process and effects induced by DAP conservation treatments.

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## Archaeometric study of ancient mortars and plasters from Palazzo Vecchio (Florence, Italy)

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**Keywords:** archaeometry, hydraulic index, partially calcined limestones.

Aim of this work is the archaeometric study of ancient mortars and plasters from the archaeological excavations of Palazzo Vecchio (Florence, Italy). The building raised on the ancient ruins of the Roman Florentia theatre dating between the 1<sup>st</sup> century BC and the 2<sup>nd</sup> century AD (Bruttini, 2013) and it is the result of several changes that took place from Roman times to the Renaissance.

The study is the one carried out on Roman mortars in Florence, but also included later periods. Samples were studied by polarized optical microscopy (OM) (including the modal analysis using JmicroVision software), X-ray powder-diffraction (XRPD), X-ray fluorescence (XRF) and Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDS).

The mineralogical and petrographic data showed a great compositional homogeneity among the samples, confirming that the raw materials used for their production are closely linked to the geology of the area. In fact, in the aggregate of all the samples the presence of “Pietraforte” (fine-grained sandstone with clayey matrix that is part of the Ligurian Tectonic Units, Calvana Supergroup; Pecchioni et al., 2020), “Pietra serena” (quartzfeldspar sandstone with medium-coarse grain, with clayey matrix that is part of the Macigno Formation which is part of the Tuscan Units; Fratini et al., 2014) and “Pietra alberese” (torbitidic marly limestone that is part of the Monte Morello Formation belonging to the Calvana Supergroup; Fratini et al., 2020) was highlighted.

However, it was possible to differentiate the mortars in three groups, corresponding to three different historical periods: Roman, Medieval and Renaissance, whose differences are mainly related to the aggregate sorting and to the presence and/or absence of partially calcined limestone fragments, both aspects related to the production technology of the mortars. Differences among these three groups were also confirmed by discriminant analysis performed on the modal and chemical data and by SEM-EDS that revealed, in the mortars of the medieval period, a high hydraulic index due the use of a mixture of lime and clay as raw materials in the production of the binder.

In addition, SEM-EDS analysis highlighted a difference in the binder composition between the plaster and the mortar samples, which allowed us to state that the mortars and the plasters were made with two different lime types: “calcina forte” for the mortars and “calcina debole” for the plasters, confirming what has been shown by previous studies (Fratini et al., 2020).

In general, the study allowed to verify the archaeologists’ hypotheses on the main construction phases of the building and showed how the technological processes, the raw materials used and the manufacture change over time, also defining the phases in which parts of the masonry, that was from unknown periods, were built.

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## **Discovering peoples, cultures, and technologies: toward a non-invasive approach for the study of archaeological ceramics from the Phoenician necropolis of Monte Sirai and Pani Loriga (Sardinia)**

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*Keywords:* archaeological ceramics, non-invasive protocol, mineralogy.

Archaeological ceramics are among the most investigated and studied samples in the field of archaeometry. The reason for this is that they hold a huge amount of information by means of which it is possible to reconstruct the cultural and technological context of the artifact's production. On the other hand, however, studying ceramic artifacts very often requires an invasive and destructive approach, compromising the study of all those artifacts that are musealized and of high archaeological and artistic value. In order to overcome these limitations, this study aims to provide a multi-analytical and non-invasive protocol to allow the full characterization of ceramic bodies. We selected two set of representative samples from locally produced amphorae, the first one dated back to the 6<sup>th</sup> BCE and coming from the Phoenician necropolis of Monte Sirai (Carbonia, Sardinia, Italy), and the second one from the Phoenician site of Pani Loriga (Santadi, Sardinia), dated back to the 8<sup>th</sup> and 7<sup>th</sup> BCE. The transition between invasive and non-invasive analysis requires a full awareness of the samples, in order to lay the roots for a reliable non-invasive ceramics analysis, this is why our ceramic samples were preliminary examined with conventional invasive analysis, such as petrographic thin-section observations under the polarised microscope, X-Ray powder diffraction with Rietveld full-profile fit and benchtop XRF.

Here, we present some preliminary data applied to the aforementioned class of materials obtained by non-invasive analytical protocols, such as XRD and pXRF, without any sample preparation, with the purpose to evaluate reliability and validity of the experimental data when compared with the results obtained applying invasive techniques on the same set of samples. It was also possible to apply, on those samples, analytical techniques with unconventional light sources such as  $\mu$ CT and XRD-CT, performed with synchrotron light radiation, paving the way for the study of archaeological ceramics with new micro- or non-invasive analytical methodologies.

The present work is part of a larger project aimed to consolidate the use of a multi-methodological approach to provide valuable information on production, trade and technology of ceramics in ancient societies, offering a valuable tool for archaeologist and conservation scientists to approach the past minimizing the manufactures damages.

## Heating temperatures in the Kilns: evidence on how the Maya pre-Hispanic society manufacturing their lime

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Keywords: pit-kiln, heating calibration curve, Maya area.

The Maya world was built with lime and the earliest archaeological evidence is dated to the Early Middle Preclassic period (1000 BCE-400 BCE) but how the Maya manufactured the lime was an incognito. For many years the researchers assumed that the lime was produced with a pyre method, but recent discoveries confirm the presence of pit-kilns (Seligson et al., 2019). We developed a model using the Fourier Transform Infrared Spectroscopy (FTIR-ATR) for the determination of heating temperatures that allowed us to describe and determinate the distribution and the temperature at which the limestone was exposed inside the heating structure (Ortiz et al., 2023). That provided insights on the lime industry and manufacturing process and allowed us to suggest how the kilns worked and how the Maya used and controlled the fire.

In this work we present the description and characterization of pit-kilns located in the northern Maya lowlands. We carried out a FTIR-ATR analysis for determining the heating temperature, TGA-DSC analysis and X-ray diffraction (XRD) for linking the structural changes made for the fire to the heating temperatures determinate by FTIR-ATR. This allowed us to determinate the heating process in the kiln that was used by the Maya people.

At the excavation the samples were differentiated by stratigraphy, which allowed us to calculate the temperatures for each layer, we have samples with low temperature and zones with high temperature, this suggest that the combustion process was imperfect but efficient.

The development and use of the heating calibration curve is the first step in the technological study of lime production in the Maya area. But for a better understanding of this production, we still need to comprehend how the Maya used the wood, how long was the heating time, as well as the heating ratio and the cooling process. In order to achieve that, we still need to study the slag production and the architectural materials.

Work supported by CONACYT under contract CF 2019 No. 731762. Experimental work was possible thanks to the support of LANCIC-IF. S. Ortiz acknowledges the support granted by CONACYT by a postdoctoral fellowship.

Ortiz Ruiz S., de Lucio O.G., Mitrani Viggiano A., Perez Castellanos N.A., Ruvalcaba Sil J.L., Barba Pingarrón L. & Goguitchaichvili A. (2023) - Mayan fire: valibration curve for the determination of heating temperatures of limestone, lime and related materials by FTIR measurements. *J. Archaeol. Sci. Rep.*, 49, 103966. <https://doi.org/10.1016/j.jasrep.2023.103966>.

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## On the origin of Italian maiolica: a compositional and lead isotopic study of maiolica glazes

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Keywords: archaeometry, lead isotope, maiolica.

Italian maiolica is one of the most representative vestiges of Medieval and Renaissance art, society and economy. The production technique was born in the Near East in the 8th century and spread rapidly in the Islamic world reaching the Iberian Peninsula in the 10th century. It is known that commercial trades between Spain and the Republic of Pisa played a fundamental role in the diffusion of these artifacts in the Tuscany region (Berti & Giorgio, 2010), allowing the development of large production centres such as Pisa itself in the 13th century and subsequently Montelupo Fiorentino in the 14th century.

The purpose of this project is to broaden the knowledge of maiolica production techniques and their evolution over the centuries through the comparison of important productions, such as that of Andalusian Spain, Pisa and Montelupo Fiorentino which were active over a large period of time between the 10th and 18th centuries. Furthermore, the origin of the raw materials used to produce the tin glazes typical of maiolica will also be investigated. Specifically, the origin of the lead, used as a flux in the production of the glazes (Piccolpasso, 1879), will be studied through the application of lead isotope geochemistry. Indeed, lead is a very common metal and easily available locally; however, previous studies have highlighted the existence of large-scale trade of this raw material (Chiarantini et al., 2015; Paghi, 2022).

The compositional investigation of the samples will be carried out by Scanning Electron Microscopy (SEM-EDS), while the isotopic analysis will be performed with mass spectrometry techniques such as TIMS and MC-ICP-MS.

This research, which is in its initial phase, represents an important opportunity to reconstruct the cultural and commercial exchanges of raw materials, artifacts and craftsmen in the Central European and circum-Mediterranean area, which have allowed the birth and development of numerous centres of maiolica production in Italy. Due to their long production history, their figurative evolution in line with foreign cultural influences and the need to procure raw materials (lead and tin) that are not easily available locally, Italian maiolica well represents the complexity of Medieval and Renaissance society.

The wealth of information which could be provided by the study of maiolica is still largely unexplored.

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Piccolpasso C. (1879) - *Li tre libri dell’arte del vasajo*. Nobili, Pesaro, 144 pp.

## Alkali-activated earthen mortars in the medieval site of San Giovanni Evangelista in Castelseprio (Varese)

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*Keywords:* alkaline activation, ancient mortars, magnesium silicate hydrate.

Modern society is dealing with global changes aimed to face exploitative practices of natural and local resources; among these new perspectives about everyday life, common goals touching both academics' and non-academics' interests may be highlighted: increasing environmental sustainability and energy efficiency and stimulating technological innovation with specific attention to economic resilience. The construction industry seems to be strongly connected to these issues, with its internal dynamics and constant evolution depending on large volumes of materials produced linked to the continuous growth of the global population; in recent decades public and private institutions involved in this field are trying to overcome the widespread construction practice based on the systematic use of Portland cement and concrete, energy-intensive and often not commensurate with the actual performance requirements of the buildings in which it is used. The careful application and re-introduction of ancient building practices constitutes a field of research with great advantages, to develop innovative heritage-inspired products with a low environmental impact.

In this work, an example of ancient and sustainable materials is presented, recently found during the archaeological and archaeometric investigation of the medieval church of San Giovanni Evangelista in Castelseprio. This archaeological site is a remarkable context in which local constructors have been involved in the building process through the pragmatic use of local resources: the local use of the so-called Ferretto deposits (clay-rich sediments) (Zuccoli, 2000), in association with lime, was crucial in the production process of the medieval mortars. The in-depth and multi-analytical study of the final mixtures indicated that the introduction of these lateritic soils as additives moved the reaction toward pozzolanic processes; this strategy allowed the double structuring of both a standard system of the calcium aluminosilicate hydrate (C-A-S-H) type, and a para-pozzolanic system with the precipitation of magnesium aluminosilicate hydrate (M-A-S-H) phases due to the strong occurrence of magnesian ions in solution (Secco et al., 2022). At the end of the production processes, these complex systems with threefold composition (aluminosilicate, calcic, and magnesian), obtained through the alkaline activation of Ferretto, gave large variability to the mortars employed in San Giovanni (Razzante, 2023).

Comparing these choices within contemporary architectural projects and in the field of conservation and restoration programs linked to architectural heritage, mortars and binders such as those presented here and mostly created by adding a specific portion of local geo-resources in the original mixture, could be a starting point to establish a new conception of noble re-use of simple and local geo-materials characterized by low environmental and energy impact.

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## The key to ancient Roman mortars hydraulicity: ceramic fragments or volcanic materials?

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Keywords: Roman mortars, hydraulic mortars, cocciopesto.

The manufacturing of mortars can be considered such an art that began in historical times and reached a particularly wide diffusion and innovation in the production technologies during the Roman Empire. Roman craftsmen guessed that the combination of lime with a specific volcanic sandy material, called pozzolana led mortars and concretes to become hydraulic, allowing underwater hardening and increasing their mechanical strength (Miriello et al., 2015; Lezzerini et al., 2018). Whether volcanic material was not available, ceramic fragments, having similar hydraulic properties as pozzolana, were used to produce the so-called "cocciopesto", in particular in water-bearing structures and to protect walls from moisture, typically in baths, canals, and aqueducts (Columbu et al., 2022). According to previous studies (Rispoli et al., 2021), ceramic fragments used to mortars production probably derive from recycled material, as they proved to be different from one another in terms of petrography, optical activity and texture, so they possibly represent the first example of reuse and recycling in history, which are also the most current research themes.

This research deals with mineralogical, petrographic, chemical, and microstructural characterization of raw materials from the Dragonara cave (Phlegraean Fields, Campania region, Italy) through Polarized light microscopy (PLM), X-ray Powder Diffraction (XRPD), Field Emission Scanning Electron Microscopy coupled with an Energy Dispersive Spectrometer (FESEM/EDS), Simultaneous Thermal Analysis (STA) and Mercury Intrusion Porosimetry (MIP).

The aim of this work was to establish provenance of raw materials, mortars recipe and hydraulic properties, with a particular focus on the reactions between ceramic aggregates and volcanic materials with binding matrix, to define their role in the mix design of mortars.

Results showed that hydraulicity of the analyzed mortars is mainly due to volcanic materials rather than ceramic fragments. In fact, reaction features such as Reaction Rims (RR), Interfacial Transition Zones (ITZ) and particularly Ca-rich rims were usually found at the matrix-volcanic fragments interface. Moreover, porosity tests evidence that bedding mortars, which contain mainly volcanic material and only sporadically ceramic fragments have a higher closed porosity of binder due to the good pozzolan reactivity.

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## New advances in stone Cultural Heritage conservation: the advantages of superhydrophobic and self-cleaning coatings

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*Keywords:* superhydrophobic coating, stone conservation, self-cleaning.

The mitigation of the effects caused by physical, chemical and microbiological agents on stone buildings and objects is a concern for public or private owners. In fact, the conservation requires high maintenance/restoration costs, and can also have a high environmental impact such as the use of large quantities of raw materials (e.g. replacement of degraded stones, mortars) and chemicals. The universally accepted strategy to stop or slow down stone degradation processes is to modify the wettability of the surface, thus reducing the effects caused by rainwater and air humidity, which are recognized as a direct and indirect degradation agent of stones. To achieve this purpose, the application of hydrophobic compounds on stone surfaces has been a widespread and commonly adopted practice since the second half of the 20<sup>th</sup> century. With the advance of science and technology, synthetic materials (e.g. acrylic polymers, silicon-based compounds, perfluorinated polymers) have completely replaced natural compounds (e.g. oils and waxes) in stone protection (Charola, 1995). From the beginning of the 21<sup>st</sup> century, some innovative materials have been tested. These materials are nature-inspired compounds with superhydrophobic (i.e. water contact angle: > 150°) and self-cleaning (i.e. sliding angle: < 10°) properties. They have been studied for many functional applications (Zhang et al., 2008), and have gained attention as stone protective agents (Cao et al., 2021; Karapanagiotis & Manoudis, 2022,). In this work, a new partially fluorinated amidosilane coating was easily synthesized in two steps: the one-step nucleophilic ring-opening reaction between the terminal amino groups of 3-aminopropyl(diethoxy) methylsilane and a perfluorinated epoxy derivative (3-perfluorohexyl-1,2-epoxypropane) was followed by the step-growth polymerization of the silane chain (hydrolysis of diethoxy groups and condensation). The partially fluorinated amidosilane, soluble in alcohols, was applied as hydro-alcoholic dispersion on Carrara marble (low porous and smooth surface) and Lecce stone (high porous and rough surface) samples for testing the coating performances as protective agent. In particular, superhydrophobicity and self-cleaning properties, robustness and environmental durability were systematically confirmed through several tests: water contact angle, sliding angle, water inhibition efficiency, vapor diffusivity, sun-like irradiation and rainfall simulation. Thus, this new partially fluorinated silane is ought to be proposed as protective coating material for stone heritage. As a matter of fact, its high performance, obtained with very low amounts (< 2 g/m<sup>2</sup>), favors the conditions for a sustainable mitigation of stone degradation in terms of reduction of maintenance/restoration costs (including materials and manpower), lower environmental impact, and better preservation of the original stone surface compared to the presently-known hydrophobic products.

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## Archaeometric analysis for the provenance of Roman amphorae of Cumae from North Africa: a preliminary assessment

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**Keywords:** Roman amphorae, Cumae, mineralogical-petrographic approach.

Aim of this work is the mineralogical-petrographic characterization of Roman amphorae from the ancient settlement of Cumae (Campania, Italy) through a strictly integrated interdisciplinary approach. The study focuses on a selection of amphorae ascribed to North African productions in order to determine their provenance from specific ateliers. The areas involved in amphorae production are the regions of Zeugitania and Byzacena (south-central Tunisia), Tripolitania (between southern Tunisia and western Libya), and Mauretania Caesarensis (between Morocco and Algeria), which also produced cooking ware and fine ware (Bonifay, 2004).

To this purpose, nineteen samples of the most common amphora types found at Cumae were studied, dated from the 2<sup>nd</sup> to the 6<sup>th</sup> centuries CE, when trade with North Africa became more intense and frequent, as a result of the crisis in local trade, which led to a change in the trading system: from the provinces to Rome (Rizzo, 2014; Capelli & Bonifay, 2016). North African amphorae are known to have carried liquid goods, such as high-quality oil, garum and fish sauces, with the occasional association of wine, which is restricted to a few defined types: Dressel 30 and Africana III (Bertoldi, 2012).

The archaeometric investigation was performed via mineralogical-petrographic techniques. Polarized light microscopy (PLM) highlights the presence of groups of samples and outliers characterized by different petrographic characteristics, which could be ascribed to different raw materials employed.

X-ray powder diffraction (XRPD) revealed quartz as the prevalent mineralogical phase along with calcite, feldspar, hematite and neoformed Ca-silicates that provided useful information about the EFTs (Equivalent Firing Temperatures) estimation.

The chemical analysis by X-ray fluorescence (XRF) shows that most samples have a high concentration of CaO (> 6%). The detected groups are broadly in line with the petrographic ones. In addition, various outliers can be identified.

Considering the archaeological evidence (kiln refuses, large number of fragments of the same ceramic class, mainly from the Tunisian coasts) from North African ateliers and local geological features, each group of samples could be ascribed to a specific atelier.

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## Geological and ore deposit collection of the Museum of Natural Sciences of Turin

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*Keywords:* ore deposit study, mining, mineralization.

Here, we intend to present a peculiar samples collection hosted in the “Museo Regionale di Scienze Naturali”, Torino. The collection, acquired in 2005 by the Geology and ore deposit collections of the Polytechnic of Turin, consists of specimens from mining districts and mineralized occurrences mostly located in Italian regions, with numerous representative specimens from different parts of the world.

The material comprehends both ore samples and ornamental stones of the first half of the twentieth century and partly to historical collections of the nineteenth century. At least 5000/6000 specimens of essentially scientific interest are estimated. However, historical paper catalogues do not support the samples.

The ore deposit collection comprehends many samples, mostly collected directly from mining sites and corresponding to the stratigraphic sequence typical of the mining locality. Concerning the Italian mineral deposits, those of Piedmont, Trentino Alto Adige, Tuscany, and Sardinia are mainly represented. For some of them, the type of barren rock, the mineralization paragenesis, and the superficial alteration mineralogy are catalogued. In addition to those above-described, the collection also comprehends some specimens derived from the exploration campaigns, not followed by extractive activities. Most of the samples are of high interest for ore deposits studies, whereas some are fascinating for petrographic and mineralogical purposes. Furthermore, a series of videos entitled “Sardinia between history and mining activity” was dedicated to Sardinia from which many ore samples derive. The videos comprehend thematic insights on the type of rocks, extractive history and social-cultural heritage of the mining activity in Sardinia (<http://www.mrsntorino.it/cms/il-museo/collezioni/mineralogia/item/189-la-collezione-giacimentologica>).

The material included in the ornamental and building stone collection comes from worldwide. The collection consists of stone slabs (over 600) of various sizes that integrate the one already present and catalogued in the Museum of Natural Sciences of Turin. Thin sections were obtained for some of these slabs for mineralogical and petrographic classification of the rocks.

Up to date, about 600 specimens have been selected based on typological and geographical representativeness and catalogued; these specimens have been codified and inserted into a dedicated database where geological, depositional, historical, iconographic and environmental recovery aspects are described.

## **The historical collection of minerals and rocks from Egypt preserved at the Regional Museum of Natural Sciences**

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*Keywords:* historical collections, heritage stones, Carlo Boreani.

A collection of minerals and rocks from Egypt, made up of about 700 specimens and preserved at the Museum of Natural Science in Turin, has been studied. No information about its constitution and the place of origin of the samples were available up to now. However, thanks to some ancient manuscripts and fragments reporting name of localities it was possible assume with reasonable certainty that the collection was assembled by the mining engineer Carlo Boreani, in the first half of the nineteenth century. It possibly occurred in collaboration with his secretary, the lawyer Giovanni Pollonera, who worked in Egypt at the service of the viceroy Muhammad Ali. The collection, petrographically widely studied and now accompanied by a digital catalog, has been often used for exhibitions in Italy and abroad. The study of this collection made it possible to enhance and deepen the enhancement of materials that represent a historical, scientific and cultural asset to be rediscovered with the help of the multimedia resources now available.



## Preliminary results of a multidisciplinary study on the anthropogenic vitrified rock structure of Serravuda (Acri, Calabria, Italia)

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*Keywords:* vitrification, bronze age, Magna Graecia.

A multidisciplinary (mineralogical, petrographic, chemical) study and preliminary TL investigations were carried out on vitrified rocks found on the top of the Serravuda hill near Acri (Calabria, Italy). The aim was to determine their origin and, in particular, to verify if they were formed by natural processes or are the results of ancient anthropogenic activities (Bertolani, 1972; Elmi et al., 2021).

The spatial distribution of the vitrified rocks suggests that they formed a sort of semi-circular 130-140 cm thick wall-like structure extending for some tens of metres (about 25 m long). Comparative mineralogical, chemical and isotope data on vitrified rock fragments and on bedrock rocks indicates an allochthonous nature for most of the material used to build the structure and possible transport by man starting from the flanks up to the top of the hill. The position of the vitrified structure placed on the top of the hill, its morphology and some chemical and mineralogical data on the materials (e.g. technological trace metals) rule out the hypothesis that it corresponds to the remains of ancient furnaces for the production of ceramics or for metallurgy activities. Rather, all these features suggest that originally it was built specifically for defensive purposes, similarly to other historic and proto-historic sites in southern Italy and elsewhere in various areas of the Mediterranean. The data also excludes the hypothesis that the cementing of the rock fragments obtained by in situ partial fusion is the result of natural processes (wild fires, lightning strikes, extra-terrestrial impacts). On the contrary, it seems that the vitrified structure was obtained by a heating event caused by the combustion of timber purposely inserted by man among the materials used for the construction, of which several moulds impressed on the vitreous matrix are still visible. Mineralogical data suggest that during rock heating relatively high temperatures were reached (up to 1100°C), capable of producing extensive fusion of the rocks, especially of those richer in phyllosilicates (biotitic gneiss).

Observations and comparisons suggest analogies between the Serravuda structure and vitrified forts of North Europe, whose construction is in general and recently placed in the first millennium AD. Differently, TL dating on Serravuda's heated materials (rock fragments and vitreous cements of the structure) gived ages variable on the range 1700-100 BC, i.e. from the Medium Bronze to the Roman age, although the construction of the structure as a whole is attributable to the Bronze age. The partial data collected (we are waiting for an archaeological investigation at the site) raises questions not only on the origin and function of this vitrification, but also on the identity of the builders of this structure, to date unique in Magna Graecia and not only, their socio-economic organization and on the modalities of occupation and control of their territory.

Bertolani M. (1972) - An enigmatic outcrop of vitrified rocks near Acri (Cosenza). *Boll. Soc. Geol. It.*, 91, 683-692.

Elmi C., Cipriani A., Lugli F. & Sighinolfi G.P. (2021) - Insights on the origin of vitrified rocks from Serravuda, Acri (Italy): rock fulgurite or anthropogenic activities? *Geosci.*, 11, 1-14.

## Differently Calenian: a multi-analytical study on coarse-grained pottery from the archaeological site of Cales (South Italy)

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*Keywords:* coarse-grained pottery, multi-analytical approach, local production.

For centuries the hallmark of Calenian production has been the black glazed pottery, a class of fine pottery widely distributed in the central and western Mediterranean. This kind of pottery was later replaced by the production of the so-called Terra sigillata, a class of fine red pottery with glossy slipped surfaces made in specific areas of the Roman Empire (Soricelli, 2004). In such an important manufacturing center, it is not surprising that the workshops also produced coarse-grained wares. This is evidenced by the presence of production indicators that have been investigated in this study for the first time to define the typical compositional features of these productions (Verde et al., 2023).

A selection of 46 ceramic fragments of coarse-grained ware including cookware, internal red slip ware, thin-walled pottery imitation, dolium and production indicators recovered at the archaeological site of Cales (located in southern Italy). All of these were characterized by a coarse-grained structure and subjected to a program of multi-analytical investigation, including PLM, FESEM/EDS, XRPD, TG-DSC, and XRF. Among the materials under study, the production indicators, represented by wastes of common cookware and supports, attest to local production.

Thin-section analysis shows that almost all samples have an optical active matrix except for the production indicators. The inclusions consist of feldspar, quartz, clinopyroxene, mica, lithic fragments of volcanic nature (fragments of trachyte) and juveniles (pumices and glass shards). The XRPD confirms the thin-section observation and also reveals the presence of neoformed Ca-silicates in the supports and dolium samples. Most of the samples show a Ca-poor composition and an extreme compositional homogeneity, which is in line with the chemical composition of the production indicators. The supports and the dolium, on the contrary, show a Ca-rich composition. The geochemical comparisons with some Ca-rich and Ca-poor Campanian clay materials show a good affinity with alluvial clay sediments of the Voltturnum river plain.

Soricelli G. (2004) - La produzione di terra sigillata in Campania. In: Poblome J., Talloen P., Brulet R. & Waelkens M. (eds.), Early Italian Sigillata. Proceedings of the First International ROCT Congress (Leuven, May 7-8, 1999), 299-307.

Verde M., De Bonis A., Tomeo A., Renson V., Germinario C., D'Uva F., Rispoli C. & Morra V. (2023) - Differently Calenian: a multi-analytical approach for the characterization of coarse ware from Cales (South Italy). *J. Archaeol. Sci. Rep.*, 49, 103941. <https://doi.org/10.1016/j.jasrep.2023.103941>.

## **S5.**

# **Geosciences and heritage in a time-lapse: origin, lifetime and future challenges**

*CONVENERS AND CHAIRPERSONS*

*Michela Botticelli (University of Glasgow)*

*Giulia Ricci (Università degli Studi di Padova)*

*Laura Medeghini (Sapienza Università di Roma)*

## **Biomineralization activity of bacteria for ornamental stones restoration**

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*Keywords:* biomineralization, calcium carbonate, biorestitution.

Microbially-induced calcium carbonate precipitation (MICCP) is a widespread biological process in which bacteria promote the production of calcium carbonate. This technology has been extensively explored in various environmentally friendly applications, such as biorestitution of ornamental limestones. However, while biomineralization is a common phenomenon among bacteria, not all species are suitable for such an application, due to their slow growth rate, and low conversion efficiency. Moreover, many of them not only precipitate but also dissolve calcium carbonate. In this work, a bacterial strain due to its high and fast carbonatogenic activity, isolated from the sculpture “Il Giovane di Mozia”, has been selected to evaluate the effectiveness of biorestitution treatment on three lithotypes. The three lithologies are characterized by the same mineral composition, however, they pertain to different depositional settings having different petrophysical properties. The chemical and physical properties of pre- and post-treatment samples have been studied for all the three lithologies by a multi-analytical approach. Preliminary results show clear differences on the measured parameters after the treatment, being this particularly evident for porous lithologies. These results allowed to shed light on the behavior of the carbonatogenic bacterium on different substrates in laboratory conditions to set up future in situ applications.

## Geoheritage and geoconservation, from theory to practice: the “ghost town” of Craco (Matera, Basilicata Region, Southern Italy)

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Keywords: geoconservation, geoheritage, Craco Italy.

Over the years, many studies have been devoted to the issues of geological heritage management and geoconservation, both from theoretical and practical-applicative points of view (Henriques et al., 2011; Geremia et al., 2015; Pescatore et al., 2019). The variability of natural and anthropic landscapes in which the geological heritage is included, as well as the problems related to its management makes these topics stimulating for scientific discussion which will be expected to outline the theoretical approach and the procedure of application. The work is aimed to a practical application of a flow process, based on previous scientific works, starting with the identification and basic description of multicultural interest sites (approaching with the geo and non-geo aspects) (Pescatore et al., 2023). Then, the work proceeds with the investigation of the area furnishing information based on different end users. The study area includes the well-known ‘ghost town’ of Craco, located in the Basilicata Region of southern Italy. The site is a characteristic and evocative place, internationally well-known, where it is possible to observe natural and anthropic landscapes. It was used as a set for some movie productions (e.g. scenes from the Passion of Christ by Mel Gibson). The BEGIN project, acronym of “abBandonno vErsus riGenerazIoNe” (abandonment versus regeneration) (POR FESR 2014-2020 interregional and transnational cooperation projects), is currently being implemented in that area. The BEGIN aims to develop a multilevel methodological-operational protocol with the purpose of increase the cultural acknowledgement of abandoned sites using high-tech services. The final goal will be the realization of a new memorandum on the geoconservation, regeneration, valorization, fruition, and management of “ghost towns” which will be repeatable in Regional, National, European and non-EU contexts. Here, a summary of the activity related to the geoconservation are discussed.

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## **The itinerary of Muro Lucano, in Basilicata: between geology, archeology and industrial archeology**

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*Keywords:* geoheritage, industrial archaeology, Muro Lucano.

The area of Muro Lucano contains a widespread geological heritage, made up of various geosites mainly of geological/archaeological/industrial interest (Palladino et al., 2013). Geosites are typical of the axial sector of the Southern Apennines, which is a Cenozoic fold and thrust belt formed by superposed NE-verging thrust sheets derived from different palaeogeographic domains. The Muro Lucano village is mainly located on Jurassic limestones of the Apennine platform (Patacca & Scandone, 2007), characterized by high fracture density, and representing an important aquifer. The Jurassic substratum is covered unconformably by the Castelvetero Formation (Serravallian-Tortonian) and the Ariano-Irpino Unit (Plio-Pleistocene). The studied area is affected by E-trending Cenozoic thrusts and Plio-Quaternary normal faults with E-W, NW-SE and NE-SW orientations. Lithologies and tectonic structures influence the local morphology. Karst phenomena and the tectonic structures condition the development of the surface drainage network. Within limestones, several engraved valleys sometimes give rise to deep gorges. These geological and geomorphological features strongly influenced human activities and the history of the local population. To illustrate that, we propose a geotouristic itinerary, which aims at raising the awareness in the local population on the geodiversity and history of the Muro Lucano area. The proposal of the itinerary would be the first step of sustainable valorization for this territory. The geotouristic itinerary consists of the following 5 stops:

- Stop 1 – Museo Archeologico Nazionale di Muro Lucano  
The museum is divided in 5 section and collects many artifacts found in the area (Ranaldi, 1976).
- Stop 2 – Le Ripe and water mills  
The Ripe path is one of the oldest roads in Muro Lucano (9<sup>th</sup> century). It crosses the gorge of the Rescio stream and the Pianello district, which is the first urban settlement with ancient water mills used for grinding cereals and for wool processing.
- Stop 3 – First urban settlement “Il Pianello” and “Ponte Pianello”  
“Il Pianello” is the oldest district of Muro Lucano. It was built on a concave limestone slope. The “Il Pianello” bridge was built in 1918 to connect Muro Lucano with the Capodigiano locality. It is the first reinforced concrete building in Basilicata.
- Stop 4 – Gorge of the Pascone stream  
The Pascone stream borders Muro Lucano to the north and east. In the northern segment, the steeper slopes expose most of the Jurassic carbonate sequence. The southernmost segment preserves scenic spots, where it is possible to observe geological and geo-archaeological elements.
- Stop 5 – “Diga San Pietro”, penstock, piezometric tower and hydroelectric plant  
The abandoned San Pietro arc dam was built in 1913, using reinforced concrete, with irrigation and hydroelectric purposes (Nardiello, 2010). It is still well preserved, together with the gallery containing the penstock, the piezometric tower and the hydroelectric plant.

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## **Exploring ancient mortars for the creation of innovative restoration materials: On-Tech Project**

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*Keywords:* conservation, mortars.

In the realm of conservation, a significant hurdle is developing restoration products that are both environmentally friendly and safe for those working with cultural heritage. Building materials, particularly mortars, require special attention because of the CO<sub>2</sub> emissions generated by the cement industry, which is the third-largest source of anthropogenic emissions. The aim of this project is to provide innovative, durable, and compatible mortars that minimize CO<sub>2</sub> emissions. The starting point for this study is the ancient Roman recipe used for the Traiano-Paolo Aqueduct, known for its high resistance and durability. The first phase of the project involves characterizing the raw materials that are compatible with ancient materials. Specifically, pozzolans from quarries around Bracciano Lake in Rome were sampled and analyzed using a multi-analytical approach to study their mineralogical-petrographic and chemical composition. Variations were observed in matrix, leucite crystals, phenocrystals, and porosity. For the experimental phase, vesicular pyroclastic materials with abundant crystals of leucite, clinopyroxenes, and high porosity were chosen as starting materials for new formulations, which were then characterized using OM, XRPD, FTIR, and SEM-EDS.

## Multiscale characterization of corrosion in archaeological artefacts from Motya (Sicily, Italy) through X-ray microscopy

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*Keywords:* corrosion, X-ray microscopy, alloys.

Here we presented a multi-analytical approach (Multiscale X-ray Microscopy, Micro-Raman, SEM, HR- FESEM- EDS and EMPA) to explore corrosion mechanisms in different type of metal artefacts from Motya (Sicily, Italy) to gain the maximum information with the minimum sampling. Indeed, the elemental analysis provides key information on the role of alloying elements in production technology and corrosion process, whereas the structure information from Multiscale Xray Microscopy (XRM) enables multilength scale visualization of whole objects and provides the spatial distribution of corrosion phases.

The results revealed the internal structure of the artefacts and the structural discontinuities which lead the corrosion, highlighting the compositional differences between the tip and the head of the iron nail (Bernabale et al., 2022). All copper-based artefacts were exposed to bronze disease corrosion induced by the presence of the reactive cuprous chloride (CuCl) located at the interface between external corrosion layers and the surviving metal core. In a Cu nail arsenic was forced outwards along inter-granular channels and it combined with Fe atoms at Cu grain boundaries, leading to the formation of copper-iron arsenate. Binary and ternary alloys revealed marked Cu and Sn selective corrosion and thicker patina compared with Cu metal due to the presence of Sn in chlorine-rich environment. The dissolution factor of copper in these alloys showed a great variability. In addition, the occurrence of cracks inside the bronze needle acted as new corrosion interfaces and involved the formation of complex and periodic stratified corrosion layers, leading to a complete mineralized structure (Bernabale et al. 2023).

Bernabale M., Cognigni F., Nigro L., Rossi M., de Caro T. & De Vito C. (2022) - A comprehensive strategy for exploring corrosion in iron-based artefacts through advanced Multiscale X-ray Microscopy. *Sci. Rep.*, 12(1), 6125.

Bernabale M., Cognigni F., Mura F., Nigro L., Montanari D., Rossi M. & De Vito C. (2023) - 3D imaging of micro-segregation and corrosion behavior of alloying elements in archaeological artefacts from Motya (Sicily, Italy). *Corros. Sci.*, 211, 110900.

## Reproduction of archaeological patinas on bronze coupons through 15 years of intentional burial in the soil of Tharros (Sardinia, Italy)

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**Keywords:** archaeological bronze patinas, bronze corrosion processes, metal cleaning.

Bronze archaeological artifacts are usually covered by alteration products (i.e., the patina) that result from the long-term interaction between the alloying elements and the soil in which they are buried (Tylecote, 1979; Scott, 2002; Ingo et al., 2019). Bronze corrosion patinas are composed of mineralogical compounds including, as the most common, copper(II) salts (carbonates, hydroxychlorides), copper(I) oxides, tin oxides or hydroxides and terrigenous species.

The intentional reproduction of corrosion patinas naturally grown during a long-term burial is a challenge for the scientific community. The major problem is related to the research time frame that is usually too short compared with that required for the development of archaeological corrosion layers. However, sacrificial substrates with composition and surface features like those of the archaeological finds are essential to test and validate new conservation materials.

In this study, bronze coupons were intentionally buried for 15 years in the soil of the archaeological site of Tharros (Western Sardinian coast, Italy), both in the laboratory and in situ, with the aim of reproducing corrosion patinas typical of a burial environment. The morphological, chemical and mineralogical features of the patinas were analysed and compared with those of an archaeological bronze recovered from the same site. The effect of the short-term intentional treatment in soil (for about 15 years) was evaluated with respect to that of the long-term burial (for about two thousand years) of the archaeological object. Results revealed that mechanisms controlling the corrosion of bronzes are the same for both short- and long-term interactions with soil. Time-dependent features are the thickness of the patina and the amount of cuprite (Cu<sub>2</sub>O), whereas the roughness is mainly affected by the surrounding environment.

Based on these results, a corrosion patina grown during the 15 years of burial in Tharros was selected and used as a sacrificial substrate to study the effect of a cleaning treatment performed using a polyvinyl alcohol (PVA)-based gel loaded with a chelating agent (Mastrangelo et al., 2020). The gel was effective in removing the disfiguring corrosion products (i.e., contaminants from the soil) and preserving the stable and protecting patina. Moreover, the depth of cleaning can be tuned based on the conservation needs by varying the time of application.

The present work was financially supported by the national PRIN 2017249YEF project and the GREENART project (Horizon Europe research and innovation program under GA no. 101060941).

Ingo G.M., Riccucci C., Guida G., Albini M., Giuliani C. & Di Carlo G. (2019) - Rebuilding of the burial environment from the chemical biography of archeological copper-based artifacts. ACS Omega, 4, 11103-11111. <https://doi.org/10.1021/acsomega.9b00569>.

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Tylecote R.F. (1979) - The effect of soil conditions on the long-term corrosion of buried tin-bronzes and copper. J. Archaeol. Sci., 6(4), 345-368. [https://doi.org/10.1016/0305-4403\(79\)90018-9](https://doi.org/10.1016/0305-4403(79)90018-9).

## Artificial reproduction of natural and artistic patinas on bronze mock-ups to be used as sacrificial substrates for the validation of new conservation materials

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*Keywords:* natural bronze patinas, artistic patination, cultural heritage conservation.

Modern, historical and artistic bronze sculptures frequently present a matt and colored surface rather than a pure metallic appearance. Color changes can be related to the occurrence of alteration phenomena or to an intentional patination designed by the artists. In the first case, bronze artworks, especially those exposed outdoor, naturally react with atmospheric pollutants, such as SO<sub>x</sub>, NO<sub>x</sub>, O<sub>3</sub>, airborne particulate matter (PM), to form green sulfate species (Chiavari et al., 2007), sometimes appreciated for the old-like appearance they provide to the object. On the contrary, artistic patinas are intentionally applied to the works of art to obtain special chromatic effects and emphasize textured surfaces with light and shade effects. Although recipes used by artists to artificially patinate modern sculptures are commonly kept secret, it is known that they are based on the use of reagents like “liver of sulfur” (K<sub>2</sub>S), copper nitrates or iron nitrates (Bongiorno et al., 2012; Crippa et al., 2019). In both cases, the surface reactivity significantly changes (Kosec et al., 2021), and tailored conservation practices are required to protect this type of materials from disfiguring degradation processes.

In this work, several existing methods to artificially patinate bronze substrates were tested and critically compared with the aim of developing an easy and comprehensive standard procedure to obtain bronze patinas with different colors, structure and minero-chemical composition, representative of both natural and artistic aged surfaces. Copper and iron nitrates, copper sulfates and potassium sulfide were selected as patinating agents for both immersion and hot-brushing treatments. The morphological, chemical and mineralogical features of the patinas were studied by a multianalytical approach, including optical microscopy (OM), field emission scanning electron microscopy coupled with energy dispersion spectroscopy (FE-SEM-EDS), Fourier transform infrared spectroscopy in attenuated total reflection mode (ATR-FTIR) and x-ray diffraction (XRD). Results pointed out that by properly varying the patination procedure a set of artificial patinas, representative of different typologies of bronze artifacts surfaces, are easily obtained. Therefore, these patinas can be used as sacrificial substrates to reliably validate new conservation materials.

The national PRIN 2017249YEF project and the GREENART project (Horizon Europe research and innovation program under GA no. 101060941) are gratefully acknowledged for financial support.

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## **Aqua Virgo: first characterization of mortars and plasters from the inner duct**

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*Keywords:* ancient Roman aqueduct, mortars and plasters, archaeometry.

Aqua Virgo is the ancient Roman aqueduct, inaugurated in 19 BC, that today still carries water to Fontana di Trevi. It is the only aqueduct built by ancient Romans for their capital that never stopped working, even when all the other aqueducts have been damaged during barbarian invasions (Pace, 2010). Two sectors of the inner underground duct of the aqueduct have been explored in this research: one still functioning area located under Pincian Hill, from San Sebastianello reservoir to the spiral staircase of Villa Medici, and one segment (now in disuse) between Via del Nazareno, Via dei Due Macelli and Via del Tritone. A total of 17 mortars and plasters samples have been collected from different parts of the inner duct (vault, lateral walls, inner part of walls, covering plasters) and 3 samples also from the cocciopesto of a duct that intersect Aqua Virgo just before Via del Nazareno, named “Y” (Baumgartner, 2017). A multi-analytical approach has been applied for the archaeometric characterization of the materials constituting the binder and the aggregate, and the reactions occurred between them: optical microscopy in thin section (OM), X-ray powder diffraction (XRPD), scanning electron microscopy (SEM-EDS), and thermogravimetric analysis on the binder fraction (TGA). As Aqua Virgo has a millenary working history, the aim of this work is to characterize what are supposed to be original materials from the Roman period and compare them with subsequent restorations; also, to compare the samples from aqueduct “Y”, whom attribution is still unknown (but it is supposed to be antecedent), with the ones of Aqua Virgo.

Baumgartner M. (2017) - Roma rinascete: la città antica tra Quirinale e Pincio. De Luca Editori d'Arte, 295 pp.

Pace P. (2010) - Acquedotti di Roma e il De aquaeductu di Frontino. Consiglio Nazionale delle Ricerche (CNR), 326 pp.



## Evaluation of the hydraulicity of ancient Roman mortars: the aqueducts of ancient Rome

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*Keywords:* ancient Roman mortars, hydraulicity, archaeometry.

The aqueducts built by ancient Romans are not only majestic archaeological ruins, but the tangible expression of the technological level reached in the hydraulic mortar production, as some of them are still in function. Beyond the characterization of the materials constituting the mortars, using techniques already consolidated in the field, such as optical microscopy (OM), X-ray powder diffraction (XRPD) and scanning electron microscopy (SEM-EDS), a relevant aspect is the evaluation of the hydraulicity of the mortar. Thermogravimetric analysis (TGA) has been applied at this purpose, as with this technique it is possible to evaluate the loss of carbonate phases (over 600°C) and the loss of water in hydraulic compounds (200-600°C) (Bakolas et al., 1998; Biscontin et al., 2002; Rizzo et al., 2008). The analysis has been applied on the sole binder fraction: each of the 76 mortar samples, collected from the inner duct of ancient Roman aqueducts in the surroundings of Rome, have been mechanically sieved, and only the fraction smaller than 63 µm (Maravelaki-Kalaitzaki et al., 2003), which is reported to be the most representative of the binder, has been investigated. Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) has been performed on each sample, before and after TGA. TGA analyses on powders have been carried out at ISTerre (Grenoble, France), with a TGA-DSC3+ Mettler Toledo instrument, burning the sample from 25 to 1000°C, under N<sub>2</sub>, with a heating rate of 10°C/min. The calculation of CO<sub>2</sub>/H<sub>2</sub>O ratio firstly allowed to highlight the hydraulic nature of all the samples analyzed. Moreover, it permitted to define which samples contains more hydraulic phases than others, and correlate the TGA data with the characterization performed with OM, XRPD and SEM-EDS. The samples showing higher hydraulicity are also the ones that present an amorphous binder at OM, do not contain calcite at XRPD and have a binder rich in Si and Al at SEM-EDS. Moreover, these samples are also the ones coming from the two still functioning Roman aqueducts: Aqua Virgo and Aqua Traiana.

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## **Provenance analysis and production technology of ancient ceramics from Battifratta cave, Italy**

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*Keywords:* pottery, archaeometry, provenance.

Ancient ceramic artifacts play a key role within archaeological contexts as they provide information on the production process, use and provenance. This information is essential to understand material culture, technological development, the origin of raw materials and to reconstruct ancient relationships and trade routes. For this reason, the present work focuses on the study of Neolithic and Bronze Age pottery from the cave of Battifratta in Sabina region (Central Italy) and of local clay deposits with the aim of understanding the origin of raw materials and the ceramic production technology. The archeometric analysis was carried out by a combined application of optical microscopy (OM) and Fourier transform infrared spectroscopy (FTIR) which allowed a minero-petrographic characterization of the samples (Whitbread, 2017). Finally, Principal Component Analysis (PCA) was applied on the FTIR data to define patterns useful to study the possible relationships between the pottery and the clay samples collected from the surroundings of the site (Medeghini et al., 2016). The results of the ceramic composition and their comparison with the clays specimens have allowed to evidence affinities, suggesting a local provenance for most of the materials studied. The mixtures are consistent with the mineralogical-petrographic characteristics of the geological context close to the site. These results confirm the attendance of the site and the important role of the Sabina region as connection point between the middle-Adriatic and the middle-Tyrrhenian areas during Prehistory and Protohistory.

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Whitbread I.K. (2017) - Fabric description of archaeological ceramics. In: Hunt A.M. (eds.), *The Oxford handbook of archaeological ceramic analysis*. Oxford University Press, 200-216.

## Preliminary investigation of geomaterials from the archaeological site of the Holy Sepulchre

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*Keywords:* holy sepulchre, geomaterials, archaeometry.

The Church of the Holy Sepulchre in Jerusalem is considered one of the most important religious sites of Christianity as, according to traditions, it is the place of Christ's death and resurrection. Indeed, the Church (dated back to the 4<sup>th</sup> century) incorporates both the Golgotha hill, the site of crucifixion, and the tomb of Christ located in the famous Rotunda containing the Holy Aedicula (Stasolla, 2022).

Archaeological excavations by Sapienza University of Rome have been conducted inside the Church of the Holy Sepulchre in Jerusalem, as part of a project to restore the floor of the religious complex wanted by the main Communities that have its custody.

The western area of the church, including part of the north aisle (the so-called Virgin's Arches), has brought to light a part of an ancient quarry and foundations of the Paleochristian walls. Archaeometric investigations have been performed on representative samples of mortars, soils and fragments of rocks by the GEOMLAB-Laboratory using a multi-analytical approach including Optical Microscopy (OM), Micro Fourier Transform Infrared Spectroscopy ( $\mu$ FTIR), X-ray powder diffraction (XRPD) and Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy (SEM-EDS) to define the mineralogical and petrographic composition of the geomaterials.

The results showed a mineralogical composition quite similar among the different groups of the analyzed geomaterials, with predominant calcite and minor amount or traces of quartz and clay minerals. Samples from the quarry and the wall slabs are defined as limestone ranging from biosparitic/fossiliferous limestone to rare biomicritic limestone which can be correlated to local late Cretaceous lithostratigraphic sequences of hard and permeable limestone and dolostone, interbedded with argillaceous impermeable layers. The archaeometric analysis confirmed that the construction material used for the closing wall of the complex was compatible with that of the quarry used along with reuse blocks.

Stasolla F.R. (2022) - Archaeological excavations in Jerusalem, Holy Sepulchre: a preliminary report. *Liber Annu.*, 72, 449-486.

## **Birth and rebirth of the mosaic in Rome: characterizing the revival of Roman recipes in the 16<sup>th</sup> century large-scale wall decorations of the Caetani Chapel, Santa Pudenziana**

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*Keywords:* 16<sup>th</sup> century Rome, mosaic, conservation science.

This work presents the results of the analytical campaign carried out to support the restoration of the architectural decoration of the Caetani Chapel in the Church of Santa Pudenziana in Rome. Paolo Rossetti produced the wall mosaic in two years (1593-1595), from a sketch by Cesare Roncalli. It represents one of the greatest examples of late 16<sup>th</sup> century art in Rome (Catalano et al., 2020). A micro-destructive investigation was carried out to characterise tesserae, mortars and stuccoes from the lunette and the three panels on the vault of the chapel entry. The use of optical microscopy (OM), scanning electron microscopy with energy dispersive X-ray analysis (SEM-EDX), X-ray diffraction (XRD) and thermogravimetric analysis (TGA) allowed a better understanding of the original materials and technique. Results proved that the mosaic layer has been directly mounted on an oil-based stucco layer, likely used to give the artist more time to complete the daily work. Cross-sections observed under OM showed that a paint layer often lies over the stucco. The wide range of materials used for the tesserae demonstrate the great mastery of the mosaic technique Rossetti had. Gold lamina tesserae alternate with a wide range of coloured glass pastes, their dimension changing to gain different visual effects. The vitreous tesserae are made of a silica-soda-lime glass with moderate-to-high lead content, opacified with tin compounds. Stone and terracotta are used to produce tesserae for the flesh tones. Limestone is also used with a great variety of shape, roughness and hue, that further contributes to the vibrant composition.

Catalano D., Gennari D., Massa V., Moro F., Ciabattini R., Conti L., Medeghini L., Rubino A., Sidoti G. & Torre M. (2020) - Restoration and conservation of the mosaics in the Caetani chapel, Church of Santa Pudenziana (Rome): first observations. In: Nardi R., Pugè i Dorcawhat M. (eds.), What comes to mind when you hear mosaic? Conserving mosaics from ancient to modern, proceedings of the 13<sup>th</sup> conference of the International Committee for the Conservation of Mosaics, Barcelona 15-20 October 2017. EDIFIR-Edizioni Firenze, 415-429.

## The gems of the Targioni Tozzetti 18<sup>th</sup> century naturalistic collections: a mineralogical study

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Keywords: gems, museum collection, micro-raman spectroscopy.

The Targioni Tozzetti Collection is one of the few examples of 18<sup>th</sup> century litho-mineralogical collections that survived to the present day. Giovanni Targioni Tozzetti (1712-1783) purchased the collection of his master, the naturalist Pier Antonio Micheli (1679-1737), after his death and enlarged it considerably. The catalog's collection consists of 12 volumes (n.1 and n.11 are related to the zoological collections, from n.2 to n.9 concern mineralogical samples, while n.12 is about the samples of his son Ottaviano (1755-1829) (Cipriani & Scarpellini, 2007). Actually, 2687 specimens, complete with original signs and tags, described by Giovanni Targioni (618 collected from the Micheli collection), are still preserved at the Museum of Natural History of the University of Florence.

The present work aims to characterize from the mineralogical point of view the specimens described in the volume 4 of the catalog, which contains mineralogical samples of gemological interest (Cipriani, 2007). Another purpose of this study is to obtain information on the personal cataloguing method followed by Giovanni Targioni Tozzetti.

After a historical/biographical study conducted on the information contained on Tomo 4, a total of 67 samples, referring to 37 inventory voices, undergone to a macroscopic analysis carried out with stereoscopic microscope and  $\mu$ -Raman spectroscopy investigation.

The analytical results allowed to discredit the mineralogical attribution operated by Giovanni for 19 samples out of 67; while for 46 samples the original attribution was confirmed. The identification of two samples was not achieved.

Hereafter are indicated the species recognized with, in brackets, the number of the corresponding specimens: analcime (2), beryl (var. emerald, 6), diamond (1), fluorite (3), garnet group minerals (pyrope, almandine etc., 30), quartz (vars. amethyst, citrine and chalcedony, 10), olivine group minerals (forsterite, 4), sphalerite (1), topaz (1) and zircon (7).

The evidence observed indicated that Giovanni made an incorrect attribution mainly when it was simply based on the colour of the specimens. On the other hand, when he was able to achieve more information from direct observations regarding physical properties, like habitus, brightness and hardness, or by means of indirect observations (e.g. from data collected by other scholars), the attribution was mostly correct from the mineralogical point of view.

Despite the limited number of samples selected, as compared with the total corpus of the collection, this work represents a pilot project that opens the way to the systematic study of the collection by means of modern techniques. It has therefore a remarkable importance in the museographic valorisation of the specimens and for the development of the knowledge on Italian mineralogy's history in the 18<sup>th</sup> century.

Cipriani C. (2007) - La collezione mineralogica Targioni Tozzetti: gemme e pietre dure. Rend. Lincei, 18(2), 67-87.

Cipriani C. & Scarpellini A. (2007) - Un contributo alla mineralogia settecentesca: la collezione di Giovanni Targioni Tozzetti. L.S. Olschki, Firenze, 200 pp.

## The ingots from the archaic Giglio-Campese wreck: chemical and isotopic study

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Keywords: copper metallurgy, Pb isotopes, archaic ingots.

For a long time, archaeologists have debated the origin of the ship sunk a few hundred meters off the island of Giglio (Tuscan Archipelago, Italy), at about 50 m depth: the Giglio-Campese A wreck. The cargo of this wreck contained both Greek and Etruscan artifacts. In particular, the cargo consists of a series of luxury and functional artefacts: including, for the first, fine or decorated ceramics, and carved woods; for the latter, trade amphorae, metal ingots and weapons. These artifacts allowed to date the wreck to the early 6<sup>th</sup> century B.C.E.

The identification of the provenance of the ancient metal found in the cargo, could give several issues to reconstruct the origin of this ship and improve the knowledge of technical and social aspects involved with this wreck. In fact, it is possible to locate the mining districts that supplied the ore and spread light among the ancient metal trade routes used in the archaic period.

With this aim, five Cu ingots, and ten Pb ingots have been analysed in order to investigate the origin of the ore material used.

The copper ingots, one of which was recovered from a recent seizure, are of the B2.2 and B2.3 types, according to Brown classification (Brown, 2011). The lead ingots are of the A3 type (Brown, 2011) and have a roughly triangular section.

The methodological approach was based on optical microscope analysis, followed by SEM-EDS analysis to determine their chemical composition and morphology. Trace element composition was determined through ICP-OES, whereas lead isotopic composition (<sup>206</sup>Pb/<sup>204</sup>Pb, <sup>207</sup>Pb/<sup>204</sup>Pb and <sup>208</sup>Pb/<sup>204</sup>Pb) was measured by TIMS (Thermal Ionization Mass Spectrometry) to investigate the metal provenance.

The composition of Cu ingots has Cu contents between 87 wt% and 98 wt%, however, the analyses show an extensive corrosion, characterized by compounds of Cl and Ca, present in veins and porosity. In unaltered areas the Cu content rises. Different concentration of S, As, Pb and Ag suggests the use of different mineral charge.

Sn is revealed in trace in all the Cu ingots analyzed (in the range 111 to 623 ppm). Noteworthy it is the diffuse presence of circular areas of few  $\mu\text{m}$  enriched in Bi. Nevertheless, it is attested a metallogenic separation between the majority of Sn and Cu deposits (Sillitoe & Lehmann, 2022). For this reason, it is possible to hypothesize a reuse of secondary material for the realization of this of ingots. The evidence is also supported by the isotopic data that reveals a signal scattered between the Greek and Italic areas.

Concerning the Pb ingots, the Pb content is around 85 wt%, with minor content of Cu and Al. The presence of small quantities of S and several primary galena fragments, suggest that the ingots are the result of raw smelting from lead ores, without the reusing of other metal materials. The evidence is confirmed by isotopic data, which show a very similar Pb isotope composition and indicate a compatibility well centered on the Aegean area.

Brown H.G. (2011) - A study of lead ingot cargoes from ancient Mediterranean shipwrecks. Master's thesis, Texas A&M University. <https://hdl.handle.net/1969.1/ETD-TAMU-2011-08-10126>.

Sillitoe R.H. & Lehmann B. (2022) - Copper-rich tin deposits. *Miner. Deposita*, 57, 1-11. <https://doi.org/10.1007/s00126-021-01078-9>.



## Study for the production of a new sustainable additive for restoration mortars

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*Keywords:* mortar, conservation, sustainability.

The strong demand for innovative and sustainable materials for the conservation and the restoration of cultural goods represent a fundamental point in current research in the cultural heritage field. In this context, the NYMPHA project propose a new solution for the restoration and conservation of works of art made of different materials, through the use of a mixture of polysaccharides extracted from microalgae cells (Masi et al., 2021). To this aim, a sustainable protocol for the extraction and purification of polysaccharides has been designed using the unicellular microalga *Chlamydomonas reinhardtii*. The final product has been characterized from a chemical (FT-IR, Raman and quantitative essays) and biological point of view (antioxidant tests and analysis of resistance to biological attack). From the laboratory characterization, it was possible to compare the polysaccharides composition and the total sugar concentration present in the polysaccharide mixture extracted from *Chlamydomonas reinhardtii* with other commercial polysaccharides widely used in the restoration sector.

Experiments based on polysaccharide extracts applications on several materials were performed to evaluate their efficacy as consolidant. First of all, tests were carried out on organic (wood and paper) and inorganic surfaces (white marble). Then, the polysaccharide extract was added in restoration mortar. The aim was to contribute to the needs of heritage buildings conservation activities by providing an economical, sustainable, and non-toxic additive with a great level of compatibility with ancient materials.

Several samples were realized to evaluate the efficacy of NYMPHA product as additive: samples with two different extract concentration, samples with Primal B60 (acrylic resin) as typical restoration additive and sample without additives as reference. Physical properties of the samples were tested before and after the artificial ageing period in climate chamber and UV chamber, to evaluate differences in mechanical resistance, surface wettability, capillary ability, variation in porosity and to estimate the preservation of the aesthetic characteristics, with colorimetry test. Moreover minero-petrographic and chemical analyses, such as optical microscopy, XRPD, SEM-EDS and FT-IR were realized in order to evaluate changes in the mortar texture, as well as the enhancement of the carbonatation process and, consequently, the consolidation property of the product here proposed.

Masi A., Medeghini L., Masi A., Sadori L., Leonelli F., Favero G. & Antonacci A. (2021) - Natural polysaccharides from microalgae for the protection of cultural heritage. SMART eLAB, 16, 24. <https://doi.org/10.30441/smartelab.v16i.127>.

## Diet and mobility in Medieval Florence: a multi-isotopic approach

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Keywords: isotopes, bioarchaeology.

We have employed a multi-isotopic approach ( $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ , and  $\delta^{34}\text{S}$ ), for the first time in high medieval Italy, with the aim of reconstructing possible mobility patterns and diet of a population from Florence (11<sup>th</sup>-13<sup>th</sup> century CE). The individuals were recovered from the Uffizi complex in the cloister arcade of the former church of San Pier Scheraggio. The type of burial and its position in the church suggests the individuals had a relevant social status. Historical sources suggest that between the Early and Late Middle Ages, is evident an increasing disparity between social classes often resulted in the differential consumption of particular cereals and meats. During this period the Church's influence became more severe, also for what concerns diet. This is reflected in the imposition of fish in substitution for meat on several days per year. Regarding mobility, no isotopic studies have focused on medieval Tuscany. There needs to be more direct evidence that inquires into the diet of medieval Florence. All of this highlights the necessity for an isotopic study.

Our analysis suggests that the dietary patterns of the population buried at San Pier Scheraggio are consistent with those observed in other medieval communities in Italy. However, our results reveal a higher proportion of animal products in this population's diet than in other groups. Our results also show that, at least in our samples, during medieval times in Florence, there were no dietary differences in relation to age or sex. Ultimately, thanks to the sulphur isotopes it was possible to propose mobility for at least one individual buried at the site.

## **Non-destructive monitoring of an outdoor stone monument for analyzing the evolution of degradation phenomena in 25 years**

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*Keywords:* natural degradation, planned sustainable conservation, multitemporal analysis.

The study of the degradation of monuments and artifacts exposed outdoors is a complex problem due to the multiplicity of the phenomena involved, from the environmental conditions in which the cultural structures are located to the great variety of materials that compose them. Times and methods of impact differ both according to the type of material and the physical-chemical and biological agents involved.

Most of the experiments that study the interactions between materials, atmospheric and topographical factors, were conducted on quarry samples while studies on real monuments are rarer because the definition of the state of conservation of outdoor monuments is complicated by the summation of the degradation factors. These studies are different all over the world according to different atmospheric conditions (Gulotta & Toniolo, 2019; Urbina Leonor et al., 2023).

This paper aims to analyze with non-invasive methodologies, the evolution of the deterioration of a monument exposed outdoors in the city of Potenza (Southern Italy at 800 m asl), the Tempietto di San Gerardo, built at the end of the 1800s with different geomaterials, natural and artificial, treated with organic compounds during the last restoration in 1997.

In 2008 a study aimed at starting a process of preventive planned conservation has been drafted for the Tempietto (Grano, 2011) through the drafting of detailed descriptive reports of the state of conservation and of the major risks to be kept under control, to slow down the progress of degradation by a careful organization of maintenance periodic activities (Della Torre, 2021). The detailed reports, made for every single element of which the monument is composed, are methodologically predisposed to be enriched and contain information detected from numerous investigations: historical analysis, visual examination, photographic documentation (and macro-photographic documentation on some sample areas), the minero-petrographic characterization of the materials and the definition of the forms of alteration and degradation of the materials, reported on a graphic survey.

15 years after the drafting of the conservation plan, through recourse to the same non-invasive methodologies, any transformations that have taken place will be assessed, both those envisaged in the 2008 reports and the unexpected ones, in order to better understand the mechanisms of the degradation for natural aging of materials exposed to atmospheric, topographical and characteristic factors of the constitutive materials.

The meticulous observation of the characteristics of the materials and their modification over the years can be validated by the comparison of the laser scanner surveys carried out after 15 years, to perform a change detection analysis due to erosion or other material loss phenomena. Results stimulate the discussion on the study of the evolution of degradation phenomena through non invasive methodologies, the identification of uncharted risk factors and the development of a planned conservation approaches in a sustainable way. In this context, geosciences allow to study artworks and their life cycle, but also to ensure their preservation for future generations.

Della Torre S. (2021) - Italian perspective on the planned preventive conservation of architectural heritage. *Front. Archit. Res.*, 10, 108e116.

Gulotta D. & Toniolo L. (2019) - Conservation of the built heritage: Pilot site approach to design a sustainable process. *Herit.*, 2, 797-812.

Grano M.C. (2011) - Quaderno di conservazione programmata del Tempietto di S. Gerardo a Potenza. *Ricerca storica, analisi minero-petrografiche e proposta di una metodologia conservativa*, Quaderni della Regione Basilicata. Consiglio Regionale della Basilicata, Potenza.

Urbina Leonor L.M., Sosa Echeverría R., Perez N.A., Vega E., Kahl J.D.W., Solano Murillo M. & Soto Ayala R. (2023) - Importance of atmospheric sciences in stone heritage conservation study in Italy and Mexico. *Sustainability*, 15, 5321.

## Microbiological survey in hypogeal environments, assessing the bacterial and fungal metabolic role in biodegradation

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**Keywords:** biodegradation, metabolic pathways, porous stone.

In recent years, the knowledge of the biodeterioration potential of the microbial community on works of art has assumed great relevance. Hypogeal confined environments, such as the Etruscan tombs in Tarquinia (Italy), are characterised by the presence of microorganisms (i.e. bacteria and fungi) which deeply interact with porous stone materials (Paiva et al., 2022). Changes of the environmental conditions could lead to biodeterioration phenomena on the mural paintings, resulting in losses of pictorial layer or damages of the aesthetic properties. Besides the identification of the species inhabiting the surfaces, the evaluation of their metabolic potential is essential to assess the “health” condition of the tomb. A unique characteristic of the Etruscan tombs in Tarquinia is the presence of the moonmilk, nanofibers of calcium carbonate, which protected the paint layers without damaging them (Cirigliano et al., 2021). These environments are characterized by the co-presence of carbonate-producing and carbonate-dissolving organisms in dynamic equilibrium within the tomb (Cirigliano et al., 2018; Tomassetti et al., 2017). Unfortunately, in the Tomba degli Scudi, dark spots have been observed on the mural paintings, indicating the presence of black fungi. Here, the fungal pigment production is investigated to perform a targeted action against the fungal bio-deteriorative activity on mural paintings. The use of functionalised plates to evaluate specific metabolic pathways and/or enzyme production is fundamental to reveal the hazard of the selected species (Trovão & Portugal, 2021). These characteristics could guide restores during the evaluation of the appropriate method for conservation treatments, safeguarding artworks from worthless and dangerous practices.

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## New prospective in the use of inorganic consolidants for mortars: the case of the urban mural “Ama il tuo sogno” by Jorit Agoch in Matera

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*Keywords:* mural painting salt damage, inorganic consolidants, mortars.

The urban mural painting “Ama il tuo sogno” was created in 2019 in the city of Matera (Italy) by the contemporary artist Jorit Agoch. It is placed in an outdoor context, on a masonry wall set against a filler ground.

The mural painting consists of pictorial layers which were applied on preparatory layers executed with cement mortars applied on the wall. The artist combined the use of aerosol spray with the traditional painting technique, not only spraying the colour on the surface but also applying it in brushstrokes, using different types of spray cans.

Since few months after its creation to nowadays, some areas of the painting started to be affected by several degradation forms, due to the constant phenomena of wetting of the surface, evaporation of water, and crystallization of soluble salts in the mortars and on the pictorial film.

Within the conservation project (Logiodice, 2022), the application of new sustainable materials was planned to consolidate the mortars affected by salt damage. Therefore, an experimental part was focused on the use and comparison of inorganic products such as barium hydroxide and strontium hydroxide. They may address both consolidating action and the ability to block the low-soluble sulphates into the insoluble ones (Baglioni et al., 2021; Licchelli et al., 2014). At first, the treatments with these products were tested on mortar sample mocks in order to preliminary assess their compatibility and effectiveness. The surface distribution of the consolidants and the penetration depth were evaluated by SEM-EDS. Changes in the mortar microstructure due to the application of the products were evaluated by Ultrasonic Pulse Velocity measurement and a micro drilling test was performed to assess the surface hardness increase on the treated mortar samples. The effects of both treatments on the mortar behaviour against water transfer were verified by vapour permeability and capillarity absorption tests, while Ion Chromatography was used to evaluate the effectiveness in blocking soluble sulphates. Finally, the resistance of the treated samples against salt crystallization was also investigated through accelerated salt ageing tests.

The comparison of the overall results highlighted the performance of the Ba hydroxide product compared to Strontium hydroxide. Nevertheless, also strontium hydroxide has shown good performance in the consolidation of the mortars and future research could be continued on traditional mortar-based plasters.

Baglioni M., Poggi G., Chelazzi D. & Baglioni P. (2021) - Advanced materials in cultural heritage conservation. *Molecules*, 26, 3967. <https://doi.org/10.3390/molecules26133967>.

Licchelli M., Malagodi M., Weththimuni M. & Zanchi C. (2014) - Nanoparticles for conservation of bio-calcarene stone. *Appl. Phys. A*, 114, 673-683. <https://doi.org/10.1007/s00339-013-7973-z>.

Logiodice A.L. (2022) - “Ama il tuo sogno” di Jorit Agoch: studio sperimentale per la riconversione dei sottoprodotti di degrado, pronto intervento di restauro conservativo di un'area campione di un dipinto murale urbano. Master Thesis in Conservation and restoration of Cultural Heritage at the Istituto Centrale per il restauro, Matera.

## **Amber jewelry from pre-roman Apulia between 6<sup>th</sup> and 5<sup>th</sup> century BC the case of Rutigliano**

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*Keywords:* preroman ambers, funerary assemblages, prestige goods.

The excavations carried out at the necropolis of the contrada Purgatorio in Rutigliano have brought to light burials of great importance, dating between the 6<sup>th</sup> and the first decades of the 4<sup>th</sup> century BC, which are distinguished by the existence of funerary assemblages referable to small family groups placed at the top of the community. Within these families, the presence of important people is affirmed, who have returned funerary assemblages of great value. They included Attic red-figure and black-paint vases, Greek and Etruscan bronze vessels, glass balsam jars of oriental origin, personal ornaments in precious material, such as necklaces, pendants and silver fibulae, but above all amber artifacts of great value, often shaped like a human figure, as a sign of prestige and an expression of high status.

The high number of these amber jewels found in the necropolis compared to what was observed in the other necropolises of pre-Roman Apulia leads us to think of a possible presence of a local workshop in which craftsmen of consummate experience and great technical skills worked. These rich complexes attest the central role also assumed by the indigenous aristocratic women within the community, capable of acquiring prestigious goods from various sources, their high standard of living, the intensity of trafficking and the extensive relationships entertained by Peucetian customers with the different areas of the Mediterranean.

The purpose of the contribution is to offer some reflections on these precious artifacts, belonging to funerary assemblages for the most part still unpublished and examined by the writer almost fifty years after the discovery, to outline the productions, styles, as well as behaviors in the funerary field of the people who inhabited this important settlement.



## **Direct study of natural stone materials of historical architecture in the context of the deposit for rubble of cultural interest in seismic emergency**

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*Keywords:* earthquake, rubble, cultural heritage.

The study of natural stone materials in the field of cultural heritage is of strategic importance for the preservation of historic architecture. The interest of the scientific community concerns the entire process, from quarrying, processing, construction, aging, degradation and conservation needs. Usually, the direct study of the material is possible in the preliminary stages and during the restoration. In some exceptional cases, it is possible to have a lot of material and for a long time, as happens for example following a seismic event. With the MiBACT Directive 12/09/16, "Procedures for the removal and recovery of the rubble of protected and historic buildings", temporary deposits were established for the first time, to set aside the rubble deriving from the collapses. As they are currently organized, the deposits for the rubble are places of orderly storage of materials of cultural interest, assigned to their custody, in the time that elapses between their removal and their possible relocation on site. The materials arriving in the rubble deposit are not particularly perishable and do not need thorough checks on their state of conservation. However, the diagnostic study in the rubble deposits represents a procedural improvement for its intrinsic knowledge value and for the subsequent activities of restoration, on site relocation of the materials or their musealization. As already happened for the reconstruction of the Cathedral of Venzone, following the earthquake that struck Friuli in 1976, the preparatory study of the individual stone elements, including archaeometric data such as morphology, metric data, petrographic data and the characterization of degradation, proved to be fundamental for the post-emergency conservative phases (Doglioni, 2008). This contribution illustrates some operational proposals for the scientific study of natural stone materials from collapses of historic buildings, to be carried out inside the deposits and shows the results of a coherent experimentation conducted at the deposit for the rubble in Rieti on some remains from the church of Sant'Agostino in Amatrice (Porrovecchio, 2020). Specifically, the study was conducted on the pieces of the portal and the rose window and led to the acquisition of significant data regarding the construction and conservation history of the two elements. The diagnostic investigations conducted on site were: the characterization of the materials by digital optical microscopy, the study of the traces of processing of the materials by photographic shooting in grazing light, the study of the residual traces of painting by colorimetric tests, the observation of materials in UV light. From the cross-reading of the diagnostic data it was possible to discern the original materials of the portal from restoration ones, also estimating the different resistance of both materials and the resistance of the anchoring system of the restoration elements. Those characteristics determined distinct responses to seismic stress. About the rose window, dated from historical documentation to 1933, the analysis of the stone elements has identified 17 elements belonging to an older rose window, thus documenting a case of reuse of ancient decorative stone materials, previously unknown.

Doglioni F. (2008) - Nel restauro: progetti per le architetture del passato. Marsilio Editore, 367 pp.

Porrovecchio C. (2020) - La diagnostica per gli edifici storici nell'emergenza sismica: una proposta di metodo finalizzata alla conoscenza e alla definizione di buone pratiche operative. Tesi di Dottorato in Storia, Disegno e Restauro dell'Architettura, Sezione Restauro, Ciclo XXXII. Sapienza Università di Roma, 458 pp.

## Protection of dinosaur footprints in carbonate deposits: the case of Sezze (Latium, central Italy) ichnosite

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*Keywords:* dinosaur footprints, ichnosite, conservation.

More than 200 dinosaur footprints were found on three stratigraphic surfaces in the abandoned quarry “Cava Petrianni”, about 70 km south of Rome, nearby the town of Sezze (Latium, central Italy). The ichnosite is located in the westernmost sector of the Lepini Mts., with an exposed carbonate succession belonging to the Lepini-Ausoni-Aurunci Unit. Three distinct trampled surfaces were recognised in a 250-m-thick succession referred to the “Laziale-Abruzzese-Campano domain” deposited in a persistent shallow carbonate platform setting from the Late Triassic to the Late Cretaceous. The footprints, preserved on carbonate platform limestones, are exposed to natural environment degradation (especially karst processes), that can irreversibly modify track morphology, resulting in the loss of details in a site of unique paleontological and paleobiogeographic value (Antonelli et al., 2023). The aim of the present project is to find an appropriate solution in the long-term preservation of dinosaur footprints produced in carbonate deposits from the environmental degradation naturally occurring in paleoichnological and geological sites. The final purpose is both enhancing this palaeontological heritage and proposing a possible solution applicable to other ichnosites with similar conditions. Several consolidants have been tested on the trampled surfaces to evaluate the better in terms of application, costs and results. In particular, a mineral consolidant based on the sol-gel technology (SIOX-5 RE50), a nano-sized silicon dioxide fixative/consolidant in colloidal aqueous dispersion (Nano ESTEL) and TEOS with chitosan were applied. In addition, a bioconsolidation process was tested, applying several bacterial strains, taking advantage from the natural bacterial ability to induce carbonate precipitation (Nigro et al., 2022).

Antonelli M., Romano M., De Sario F., Pignatti J., Sacco E. & Petti F.M. (2023) - Inferred oviraptorosaur footprints in the Apenninic Carbonate Platform: New tools for the identification of trackmakers from the Sezze ichnosite (lower-middle Cenomanian; central Italy). *Cretaceous Res.*, 141, 105362. <https://doi.org/10.1016/j.cretres.2022.105362>.  
Nigro L., Mura F., Toti M.P., Cirigliano A. & Rinaldi T. (2022) - Carbonatogenic bacteria on the ‘Motya Charioteer’ sculpture. *J. Cult. Herit.*, 57, 256-264. <https://doi.org/10.1016/j.culher.2022.09.009>.

## **Back to Ancient Neolithic: archaeometric investigation of pottery sherds from Rio Tana (Abruzzo, central Italy)**

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*Keywords:* archaeometry, neolithic ceramics, pottery manufacturing techniques.

This work describes a research project that investigates the pottery complex found at Rio Tana, a neolithic settlement in Abruzzo (Central Italy). The primary objective of this study is to analyze the characteristics of the pottery production at the site, including the shapes, decoration, and manufacturing techniques (Petrinelli Pannocchia et al., 2022).

The preliminary findings suggest that the pottery at Rio Tana is closely related to the Middle-Adriatic Impressed Ware, (Bagolini & Von Eles, 1978). The pottery production at Rio Tana is characterized by a predominance of coarse and simple open-shaped vessels with a limited use of decoration: primarily engraved lines, digital and instrumental impressions, with occasional plastic elements.

A multi-analytical approach to examine samples of sherds from various levels and areas of the site has been performed. The techniques used include optical microscopy (OM) in thin section, X-ray powder diffraction (XRPD), Fourier Transform Infrared (FTIR) spectroscopy, Scanning Electron microscopy with microanalyses (SEM-EDS) and portable X-ray Fluorescence (pXRF).

The results of the analysis revealed the existence of several pottery productions at Rio Tana, reflecting different manufacturing techniques, functional objectives, and cultural traditions. This suggests that pottery played an essential role in the social and economic life of the neolithic community under study.

Bagolini B. & Von Eles P. (1978) - L'insediamento neolitico di Imola e la corrente culturale della ceramica impressa nel medio e alto Adriatico. *Preist. Alp.*, 14, 33-63.

Petrinelli Pannocchia C., Vassanelli A., Naime Y., Terranova A., Sani S., Spadacini L. & Ceccaroni E. (2022) - Le nuove ricerche sul sito neolitico di Rio Tana (Lecce nei Marsi, AQ). In: *Il Fucino e le aree limitrofe nell'antichità. Atti del IV Convegno di Archeologia (Avezzano 2021)*.

## Minero-petrographic characterization of historical mortars from Aquileia

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Keywords: mortars, mosaics of Aquileia, characterisation.

Mosaics are complex systems composed of several layers (Pasqualucci, 2004) of finer and coarser mortar. This stratification makes them interesting case studies for evaluating the properties of different mixtures. Maintaining the stability of these layers is a fundamental aspect of conserving a mosaic. The durability of mortars is considered one of the fascinating mysteries that has spanned centuries of research in construction engineering. The mechanical characteristics and strength of mortars are due to the pozzolanic reaction, a chemical process that is strictly related to its composition. Given these premises, a clear understanding of the nature of ancient mixtures is essential to preserving the layered mortar systems that compose mosaics and developing compatible conservation materials.

In this research, 40 samples of mortars collected from fragments of mosaics were analyzed. The archaeological material studied was gathered during a field walking survey of the peripheral areas surrounding ancient Aquileia, Italy, which is well known for its famous mosaics. There are several works in literature that focus on the study of the mortars used to produce them (Secco et al., 2018; Dilaria et al., 2022). A mineral-petrographic characterization was carried out using a multi-analytical approach that allowed for a thorough description of the investigated material. Specimens were observed under a Polarized Light Microscope (PLM) to explore the main textural and compositional features of both binder and aggregate fractions. Among the selected materials, five remarkably well-conserved specimens were analyzed with Scanning Electron Microscopy coupled with X-ray probe (SEM-EDX). These specimens served as reference materials for comparison with samples taken from other less-conserved stratifications. Mortars detached from the specimens were analyzed using X-ray diffraction (XRD), enabling the identification of the crystalline phase and mineralogical content. Furthermore, Thermogravimetric analysis coupled with an Infrared spectrometer (TGA-IR) was used to identify specific regions of decomposition indicators of the presence of different materials. Moreover, one fragment with a complete stratification of mortars still attached to tesserae was analyzed with X-ray Fluorescence (XRF), allowing for the elemental mapping of the material. Thus, it was possible to obtain a complete characterization of the mortar according to its stratifications (Boschetti et al., 2021). The extensive dataset acquired through the analysis of a significant number of samples in this research has facilitated a better understanding of the mortar technology used in the production of Aquileian mosaics.

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## **S6.**

# **The new era of remote sensing and 3D modelling in digital geological mapping**

*CONVENERS AND CHAIRPERSONS*

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## The “il Casone-Monte delle Fate” mega-olistostrome in the Eastern External Ligurian Unit

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*Keywords:* mega-olistostrome, middle Eocene, external ligurian unit.

In northern Latium, the allochthonous External Ligurian Unit (Tolfa Unit) tectonically overlies the Mesozoic succession of the Tuscan nappe. NE of Santa Severa (RM), the “il Casone” and “Monte delle Fate” area shows some Mesozoic carbonate rocks, with Tuscan affinities, surrounded by a sedimentary succession pertaining to the Flysch della Tolfa (Eastern External Ligurian Unit). Previous Authors (Fazzini et al., 1972; de Rita et al., 1989) considered these carbonate rocks as part of the autochthonous Tuscan succession cropping out in tectonic windows below the overlying allochthonous Tolfa Unit. Cipollari et al. (2023) consider the carbonate rocks with Tuscan affinities as part of a huge middle Eocene sedimentary mélange called “il Casone-Monte delle Fate” Olistostrome, also containing Flysch della Tolfa olistoliths.

Recently, fieldwork for the geological survey of the CARG Project 364-Bracciano, carried out in the area between Bagni di Stigliano, Rota, and Vejano, using FieldMove software and high-resolution satellite imagery, allowed us to significantly extend the outcropping area of the “il Casone-Monte delle Fate” Olistostrome, defining the occurrence of a mega sedimentary mélange.

In the study area, the stratigraphical and geometrical evidence observed in the field, together with the results of the calcareous nannofossils biostratigraphic analysis, constrain the sedimentary mélange of “il Casone-Monte delle Fate” to a Bartonian age (middle Eocene). The fieldwork clearly reveals that this mega-olistostrome is placed in the uppermost part of the Mignone clays (Auctt.).

According to these results, we propose a new stratigraphic architecture for the highest portion of the Tolfa Unit. Above the Fosso Anitrella member (FYT2, Flysch della Tolfa), the Mignone clays are considered a formation instead of a lithofacies, as in the 354-Tarquinia geological map (ISPRA, 2020). In conclusion, the “il Casone-Monte delle Fate” mega-olistostrome records a tectono-sedimentary event occurred at the Adria passive margin during the sedimentation of the Mignone clays (Auctt.).

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## **The Mesorif unconformity: new stratigraphical constraints from a late Serravallian wedge-top basin in the Tamda tectonic window (Northern Morocco)**

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*Keywords:* mesorif, calcareous nannofossils biostratigraphy, wedge-top basin.

During the Tertiary evolution of the Western Mediterranean subduction system, the orogenic accretion on the Maghrebian margin resulted in stacking three main tectonic domains of the Rif fold-and-thrust belt: 1) the Internal Domain, 2) the Maghrebian Flysch Basin, and 3) the External Domain.

We report new stratigraphic data on Middle Miocene deposits exposed in the Mesorif subdomain, which is part of the External Rif Domain. We studied stratigraphic sections and stratigraphic relationships between pre-orogenic and late-orogenic deposits in an area close to the Tamda village, 50 km east of Taounate City. In this region, a thick succession of conglomerates, marls, and marly-limestones with intercalations of calcarenites unconformably overlies a continuous Late Jurassic-?Aquitanian pre-orogenic succession. This latter mainly consists of silty-clay marls, marly-limestones, and limestones.

Geological field mapping by using FieldMove software and high-resolution satellite imagery, combined with measuring of detailed stratigraphic sections, allow us to reconstruct the major tectonostratigraphic features of the study area. A strong angular unconformity defines the base of the studied succession (Mesorif unconformity). The succession above the unconformity (Tamda section) is slightly affected by compressional deformation (late-orogenic succession) and unconformably overlies a stratigraphic succession highly affected by compressional deformation (pre-orogenic succession).

The lower part of the late-orogenic succession resting above the Mesorif unconformity consists mainly of a thick-bedded polygenic conglomerate with thin intercalations of marls and marly-limestones. Moving upward, the succession consists mainly of calcarenites, marls, and marly-limestones, which show several slumping horizons.

Quantitative biostratigraphic analyses on calcareous nannofossils assemblages from fine-grained samples of the Tamda late-orogenic deposits yielded a late Serravallian age for the Mesorif unconformity, previously considered to be Oligocene.

Our results on the age of the Mesorif unconformity provide significant constraints on the tectonic phase responsible for the orogenic deformation of the Mesorif. Moreover, the tectonostratigraphic features detected from the Tamda succession suggest deposition in a wedge-top basin for the succession above the Mesorif unconformity. According to the age provided by our biostratigraphic analysis, the studied area records the involvement of the Mesorif Domain in the Rif fold-and-thrust belt during the late Serravallian (~12 Ma). At that time, the leading edge of the Rif Chain was represented by the basal thrust of the Mesorif, while the Prerif sub-domain was still in a foreland setting.

## Reservoir-scale structural architecture of high-angle basin-bounding faults in Mesozoic platform carbonates

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*Keywords:* basin-bounding faults, fractured reservoirs, Mesozoic platform carbonates.

High-angle basin-bounding faults (BBFs) play a critical role in the geometry and distribution of geofluid reservoirs. In platform carbonate settings, BBFs have complex architectures due to the modalities of rock diagenesis and tectonic evolution. In fact, the interplay between these two processes, and the scales of observation provide a complex puzzle to precisely assess the control exerted by BBFs on the fractured reservoirs at depth. For this reason, we investigate the multi-scale structural architecture of high-angle transtensional fault zones crosscutting Mesozoic platform carbonates, and bounding the Agri Valley, southern Italy. By integrating the results of field and digital outcrop analyses, we focus on the fault array exposed at the Viggiano Mt and pertaining to the East Agri Fault System (EAFS, Cello et al., 2000). The specific goals of this work are the assessment of the variation of both geometry and distribution of mesoscale fractures and larger scale faults according to (i) the host rock lithology, and (ii) distance from the basin-bounding faults. Moreover, for all the study outcrops, we (iii) compute the multiscale dimension of single fault and fracture sets.

Four individual carbonate units are studied. Field data are gathered by mean of linear and circular scanline techniques, and elaborated to assess the geometry, distribution, and dimension of single fracture sets, 6 cm - 3 m in height. In the field, we also acquire high-resolution images using a drone to later build 3D digital outcrop models. A minimum of 280 high resolution digital images are collected with a >75% overlap. The 3D models are generated for the study outcrops using the Agisoft Metashape® software. Structural data are then extracted using the Open plot® software (Tavani et al., 2011), and finally processed with FracpaQ® (Healy et al., 2017). The digitally extracted planes are 2.5 m - 45 m in height.

In terms of lithology, the results are consistent with the finer grained carbonates being characterized by the highest values of both fracture density (P20) and intensity (P21). According to the scales of observation, we document a scale-variant geometry of the fracture and fault arrays in all four carbonate units. In detail, we show similar trends of P20 and P21 at all scales. However, we note that the field-related structural analysis is needed in order to precisely assess the P20 values due to a lack of resolution at larger scales. Finally, as expected, high peaks of both P20 and P21 are found for the faulted outcrops exposing the damage zones of the main basin-bounding faults. In conclusion, the outcomes of this work can be of interest to the geoscientists dealing with the forecast of the fluid transport and storage properties of fractured platform carbonates flanking sedimentary basins.

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## **PZero: a new open-source Python geomodelling platform**

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*Keywords:* 3D modelling, open source, structural geology.

Commercial 3D geomodelling software has been available for decades and has reached a very high level of development. However commercial packages can be not suitable for many applications, since (i) they are very specialized for industrial applications in oil and gas reservoirs or mineral deposits, and (ii) because of the cost of licenses, that is too high in many smaller-scale projects and is a barrier to a wider diffusion of 3D geomodelling.

In the last decade, some very interesting and fast-growing geomodelling libraries have been developed with the combined goal of testing new modelling paradigms and providing open-source tools to the community. However, limited computer science skills and technical difficulties are making it difficult for many geologists to use these libraries in their projects.

With PZero we have developed a Qt GUI (Graphical User Interface) in Python, providing a system that is able to manage all the typical objects of a geomodelling project, such as points, lines, and surfaces with a geological modelling role, geological cross-sections and maps, wells and well logs, digital elevation models, geophysical datasets, structured and unstructured volumetric meshes, fluid or hydrogeological contacts, etc. All these objects are stored and visualized leveraging the VTK library (in some case with some help from the PyVista library), that ensures great visualization performances also on cheap laptops (and in theory could be scaled up to supercomputers).

PZero projects are centered around a geological legend, implemented in such a way to be very intuitive for a geologist, and consistent with implicit modelling algorithms since it includes a generalized geological time and cross-cutting relationships between structures. Other properties can be visualized and analyzed in a multi-window system, using VTK- or Matplotlib-based plotting.

To facilitate the transition to 3D modelling for all geologists, PZero includes tools to draw and analyze standard 2D cross-sections, tools for orientation analysis (e.g. stereoplots), etc. Some tools are particularly dedicated to 3D modelling from high-resolution surface geological data, such as very efficient tools to visualize and interpret Digital Outcrop Models (either textured surfaces or point clouds with several million points).

First-order uncertainty is considered in terms of alternative scenarios that can be transparently traced in a project and activated/deactivated in 2D and 3D views.

Since most object properties are available as Numpy arrays, implementing or linking different modelling libraries is straightforward, and we are working to include methods from the largest number of open-source geomodelling libraries. Thanks to this approach, PZero can be seen as a convenient platform to develop and test new modelling algorithms.

Since we know that in a fast-developing field like geomodelling nothing is forever, we are also trying to keep PZero as modular as possible. For instance, at the moment VTK is the cornerstone of PZero for object storage and visualization, but if in the future a new or different library should be considered more efficient, thanks to a smart organization of the code we could rather easily rebuild the project using a different library for these functions.

At this stage of the project, our aim is to share our work with colleagues, collect useful suggestions, and keep it growing!

## Use of UAS survey method to monitor, analyze geological hazards and morphological changes on the Santa Barbara mud volcano of Caltanissetta (Central Sicily, Italy)

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*Keywords:* UAS, statistical approach, deformation monitoring and analysis.

The effects of surface deformation could be uplift, subsidence and shear discontinuities) and are strictly related to the source parameters and geomechanical properties of the surrounding rocks. In the last two decades, remote sensing has been a key tool for assessing and monitoring deformation and the resulting natural hazards.

The use of Unmanned Aerial System (UAS) for monitoring natural hazards can be simplified into three main phases:

- data acquisition before and after the event;
- monitoring;
- risk assessment.

The Santa Barbara mud volcano in Central Sicily (Italy) is an example of a potentially dangerous site, because on 11 August 2008 a paroxysmal event caused severe damage to nearby infrastructure within a radius of about 2 km. The main precursors of paroxysmal mud volcano events are uplift and/or subsidence with the development of structural features ranging in size from centimetres to decimeters (Kopf, 2002; Antonielli et al., 2014).

Here we present a methodology to monitor deformation processes that may be precursors of paroxysmal events in the Santa Barbara Mud Volcano. This methodology is based on (i) data collection, (ii) the structure-from-motion (SfM) processing chain, and (iii) the M3C2-PM (James et al., 2017; Lague et al., 2013) algorithm for point cloud comparison and uncertainty analysis using a statistical approach.

The objective of this methodology is to detect precursor activity by monitoring deformation processes and morphological changes with centimetre-scale precision.

Antonielli B., Monserrat O., Bonini M., Righini G., Sani F., Luzi G., Feyzullayev A.A. & Aliyev C.S (2014) - Pre-eruptive ground deformation of Azerbaijan mud volcanoes detected through satellite radar interferometry (DInSAR). *Tectonophysics*, 637, 163-177. <https://doi.org/10.1016/j.tecto.2014.10.005>.

James M.R., Robson S. & Smith M.W (2017) - 3-D uncertainty-based topographic change detection with structure-from-motion photogrammetry: precision maps for ground control and directly georeferenced surveys. *Earth Surf. Proc. Land.*, 42, 1769-1788. <https://doi.org/10.1002/esp.4125>.

Kopf A.J. (2002) - Significance of mud volcanism. *Rev. Geophys.*, 40, 1005. <https://doi.org/10.1029/2000RG000093>.

Lague D., Brodu N. & Leroux J. (2013) - Accurate 3D comparison of complex topography with terrestrial laser scanner: application to the Rangitikei canyon (N-Z). *ISPRS J. Photogramm.*, 82, 10-26. <https://doi.org/10.1016/j.isprsjprs.2013.04.009>.

## **Integration of DInSAR and geological data to infer lithology and tectonic structures controlling coseismic deformation**

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*Keywords:* 2016-17 Central Italy earthquake sequence, DInSAR data, coseismic ground deformation.

Large seismic events ( $M_w > 5.5$ ) can trigger surface deformations, which in turn are controlled by the location, geometry and size of active faults as well as by the lithologies distribution within the struck area.

In 2016-2017, a long earthquake sequence struck the Central Italy Apennines, producing impressive surface ruptures generated by the 24 August Mw 6.0 and 30 October Mw 6.5 main-shocks. These ruptures were mapped by field geologists soon after the earthquakes, as well as during the following years along with remote sensing data.

Following Carboni et al. (2022), we present detailed maps of the surface deformation pattern produced by the M. Vettore Fault System (VFS) during the October 2016 earthquakes. The DInSAR analysis have been retrieved from ALOS-2 SAR data, via the Parallel Small Baseline Subsets (P-SBAS) algorithm. We also draw 5 geological cross sections to investigate the coseismic vertical displacement in comparison with the lithologies distribution and the tectonic structures of the area (i.e., thrust, normal faults); on these sections we also project the seismicity distribution recorded during October 2016.

We recognized an important lithological control in the overall distribution of the deformation. It is maximum in correspondence of the carbonatic multilayer and minimum within the clastic succession. The deformation field gradually reduces northwards, where the tip of the VFS is located within outcropping marly lithologies.

We also observe that further deformation, as well as shallow seismicity, is localized at the footwall of the VFS, mainly in the surroundings of the Mt. Bove, corresponding to the hangingwall block of an important thrust fault.

Our results demonstrate that the integration of surface geology, seismicity distribution and remote sensing data, can lead to a better understanding of the influence of geological structures on the distribution of the deformation at the surface associated with earthquakes.

Carboni F., Porreca M., Valerio E., Manzo M., De Luca C., Azzaro S., Ercoli M. & Barchi M.R. (2022) - Surface ruptures and off-fault deformation of the October 2016 central Italy earthquakes from DInSAR data. *Sci. Rep.*, 12, 3172. <https://doi.org/10.1038/s41598-022-07068-9>.

## **A new digital era for geological mapping in the CARG Project at 1:50,000 scale: the case of the Sheet n. 313 “Camerino”**

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Fabbi S.<sup>1-4</sup>, Fiorenza D.<sup>1</sup>, Frezza V.<sup>1</sup>, Garzarella A.<sup>1</sup>, Lo Faro S.<sup>1</sup>, Muraro C.<sup>1</sup>, Nocentini M.<sup>1</sup>,  
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*Keywords:* Carg project, digital geological mapping, GIS.

The development and accessibility of digital technologies such as smartphones, tablets, and apps/software packages are inevitably involving geological mapping. The acquisition of raw field data through digital instruments accessorised with GPS, digital cameras and GIS permits to enhance the collection of more accurate, organised, and still georeferenced, information, also reducing the time-consuming nature of traditional methods for geological map production. In addition, the collection of new field data may be accompanied by the consultation of existing geologic data (i.e., previous geological maps, scientific publications, borehole data, stratigraphic sections, etc.) or other data.

The Servizio Geologico d’Italia promotes in the CARG Project a significant digital transition of the field survey activities producing a geopackage based on the CARG Database (CARG DB - [https://progetto-carg.isprambiente.it/quaderno15&oggettigitali/BD\\_CARG\\_v2\\_maggio2023\\_geopackage.zip](https://progetto-carg.isprambiente.it/quaderno15&oggettigitali/BD_CARG_v2_maggio2023_geopackage.zip)) structure that includes a “CARG symbols library” (available at <https://progetto-carg.isprambiente.it/quaderno15&oggettigitali/Simboli%20CARG.zip>), thus complying also with the policy of the European Commission.

Benefitting from the experience started with Sheet n. 121 “Brescia” of the Geological Map of Italy at 1:50,000 scale (CARG Project) (Gencarelli et al., 2022), the Sheet n. 313 “Camerino” adopted the use of a digital geological field survey for the realisation of the map and related database.

For this purpose, and following the “Open Science” principles, the open-source software QGis (<https://qgis.org>) is used and combined with the open-source app QField (<https://qfield.org/>), installed on field geologists tablet devices. A GIS project based on the up-to-date structure of the CARG DB informative strata (for the last updates see Quaderni del Servizio Geologico d’Italia, serie III, vol. 15 – Vita et al., 2022) has been realised to collect organised and validated geometrical features (points, polylines, and polygons).

Despite the attribute fields reflect the layers occurring in the CARG DB, the preliminary legend of the Camerino sheet geological units, with predefined colours, and personalized fields have been added to facilitate the post-field survey elaboration phases and the joining of contributions of the different field geologists collaborating to the mapping.

The promotion, by the Servizio Geologico d’Italia, of digital geological mapping in the CARG Project will significantly improve and accelerate the field data collection, the map elaboration, and the database creation, facilitating the re-use of data as well. The realisation and dissemination of open and ready-to-use geopackage and symbol library, compliant with CARG standards, allow easy apply the here-presented methodology to all the geological sheets of the CARG Project, and to all the CARG-compliant cartographic projects.

Gencarelli C.N., Voltolina D., Hammouti M., Zazzeri M. & Sterlacchini S. (2022) - Geospatial information technologies for mobile collaborative geological mapping: The Italian CARG Project Case Study. *ISPRS Int. J. Geo-Inf.*, 11, 192. <https://doi.org/10.3390/ijgi11030192>.

Vita L., Battaglini L., Cipriani A., Consorti L., Falcetti S., Fiorentino A., Fiorenza D., Muraro C., Orefice S., Pieruccioni D., Radeff G., Silvestri S. & Troccoli A. (2022) - Aggiornamento e integrazioni delle linee guida per la realizzazione della Carta Geologica d’Italia alla scala 1:50.000 Progetto CARG. Modifiche ed integrazioni ai quaderni n. 1/1992, n. 2/1996, n. 6/1997 e n. 12/2009. Quaderni del Servizio Geologico d’Italia, serie III, 15, 261 pp. [https://progetto-carg.isprambiente.it/quaderno15&oggettigitali/Quaderno\\_N\\_15.pdf](https://progetto-carg.isprambiente.it/quaderno15&oggettigitali/Quaderno_N_15.pdf).



**The Cala Viola-Torre del Porticciolo coastal area:  
a unique tectono-stratigraphic site to unravel the polyphase tectonics in NW Sardinia**

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*Keywords:* geological mapping, structural geology, Permian-Triassic.

Along the coast between Cala Viola and Cala del Turco (NW Sardinia), an upper Palaeozoic to lower Mesozoic continental sedimentary succession is wonderfully exposed. Such deposits were intensively studied in the last decade also for their exceptional tetrapod body fossils and footprints that allowed to shed a light on the early-middle Permian and Middle Triassic of Sardinia. The new palaeontological age constraints have improved the definition of the stratigraphic framework of this area and the here-presented new field data resulted pivotal in reconstructing its polyphase tectonics. A detailed geological mapping performed between Cala Viola and Cala del Vino, coupled with facies analysis and collection of meso-structural data, has allowed to better define the Permo-Triassic stratigraphy and structural setting of this sector of Nurra region. Field activity was coupled with drone-based aerial photogrammetry resulting in the recognition and characterisation of the main fault sets of the area. The analysis of topology and cross cutting relationship of fault networks suggests that these structures were produced during different deformation phases which can be related to at least 8 tectonic events. These new data make it possible to reconstruct the complex tectonic history affecting the NW Sardinia from the deposition of the middle Permian deposits to Holocene.

## Determining the age of fault surface in a seismic gap area of Northern Calabria (Southern Italy), using UAV photogrammetry, high-resolution topography, and pedological analyses

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**Keywords:** UAV photogrammetry, high-resolution topography, pedological data-analyses.

The study of faults in a seismic gap area is crucial for assessing the potential for future seismic activity and developing strategies for mitigating its impact. In this study, we used a combination of geomorphological, aerophotogrammetry, high-resolution topography, and pedological analyses to estimate the age(s) of tectonically exposed fault surfaces in a seismic gap area. Our study focused on the Firmo Fault in the northern Calabria region (Brozzetti et al., 2017), which can be considered a significant regional tectonic structure for seismic hazards.

We conducted a field survey to collect soil samples from the fault surface, which were analyzed to determine the age of the fault. We also used high-resolution topography and aerophotogrammetry to create a detailed 3D virtual outcrop model of the fault surface, which was analyzed to identify features such as fault scarps and offsets (*sensu* Cirillo, 2020). Our results showed recent activity on the fault surface, suggesting that the Firmo Fault may pose a significant seismic hazard. Pedological analyses indicated that the fault surface is relatively young, with an estimated tectonic activity from the Middle-Upper Pleistocene. The high-resolution topography and aerophotogrammetry analysis revealed evidence of active tectonic deformation, indicating that the area is at risk of future seismic activity. Our study demonstrates the importance of integrating multiple techniques for studying fault surfaces in seismic gap areas. The combination of geomorphological analysis, aerophotogrammetry, high-resolution topography, and soil analysis provides a comprehensive understanding of the structure and behaviour of faults, which can help to assess the potential for future seismic activity and to develop strategies for mitigating its impact.

Brozzetti F., Cirillo D., Liberi F., Piluso E., Faraca E., De Nardis R. & Lavecchia G. (2017) - Structural style of Quaternary extension in the Crati Valley (Calabrian Arc): Evidence in support of an east-dipping detachment fault. *Ital. J. Geosci.*, 136, 434-453. <https://doi.org/10.3301/IJG.2017.11>.

Cirillo D. (2020) - Digital field mapping and drone-aided survey for structural geological data collection and seismic hazard assessment: case of the 2016 central Italy earthquakes. *Appl. Sci.*, 10, 5233. <https://doi.org/10.3390/app10155233>.

## Structural-geological analysis through Integration of PPK-UAV photogrammetry and digital field mapping

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*Keywords:* post processing kinematic, structure-from-motion, digital field mapping.

The Roccamanico Conglomerate (RCC) is a prominent calcareous-clastic mega-bed intercalated within the Late Messinian-Early Pliocene pelitic succession of the La Queglia and Maiella flysch units in the central Apennines. In this study, we focused on studying some exposures of the RCC in the overturned limb of a kilometric-scale syncline. The outcrops present a complex array of fractures, including multiple systems of closely spaced cleavages, joints, and mesoscopic faults, which record the progressive deformation associated with Late Pliocene thrusting.

Given the extent of the investigated sites and the large amount of data collected, we employed a multi-methodology survey technique that integrated unmanned aerial vehicle (UAV) technologies and field digital mapping. Our primary goal was to reconstruct the 3D-digital outcrop model of the RCC and define the 3D pattern of fractures and their time-space relationships.

The field survey played a critical role in determining the various sets of structures, their kinematics, the associated displacements and relative chronology. In addition, the methodology allows for evaluating the reliability of the applied remote survey techniques (i.e., using UAV) compared to those based on the direct measurements of structures using classic devices.

Our approach demonstrates that the multi-methodology survey technique can be applied to understand the tectonic evolution of remote/discussed areas with complex structural settings by producing 3D virtual outcrop models and digital mapping of all geological features (Cirillo et al., 2022).

In addition to our primary goal, we also proposed two alternative working methods and discussed their different fields of application. The first method involves using UAVs for photogrammetric surveys and ground-based instruments for direct measurements, while the second method entails using UAV-based image acquisition for high-resolution mapping of outcrops using Post Processing Kinematic (PPK) methods. These alternative methods have the potential to improve the accuracy of the data collected and expand the range of geological features that can be mapped.

Cirillo D., Cerritelli F., Agostini S., Bello S., Lavecchia G. & Brozzetti F. (2022) - Integrating Post-Processing Kinematic (PPK)–Structure-from-Motion (SfM) with Unmanned Aerial Vehicle (UAV) Photogrammetry and Digital Field Mapping for Structural Geological Analysis. *ISPRS Int. J. Geo-Inf.*, 11, 437. <https://doi.org/10.3390/ijgi11080437>.

## **The CARG Project toward 3D geology: the new “dimension” of the Geological map of Italy 1:50,000 scale**

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*Keywords:* 3D geological models, geological maps, CARG project.

Geological Survey Organizations are facing a growing demand, from decision-makers, private companies, and citizens, for independent, up-to-date, high-quality, and policy-relevant subsurface geological information. To answer this need, the Servizio Geologico d'Italia (SGdI) has promoted an acceleration in the production of 3D geological models, in the outline of the CARG Project (Geological map of Italy at 1: 50,000 scale). Therefore, in the next years, more than 35 geological 3D models will pair the production of traditional geological sheets and subsurface geological maps, improving knowledge of the subsurface geological structure, both for applicative purposes and scientific studies.

These 3D geological models will possibly cover the entire area (about 570 km<sup>2</sup>) of the corresponding sheet of the CARG Project, hence describing different geological settings from the Alps to wide plain areas, from the Apennines chain to intramountain basins and coastal regions, down to hundreds or thousands of meters deep depending on the availability of input data and the addressed topic.

Considering the variability of the geological settings, different types of input data will be used as constraints, mainly derived from geological field surveys in mountain and hilly regions, or from boreholes and geophysical investigations (e.g., seismic lines, curve logs, Time-Depth tables, gravimetric and aeromagnetic data) in plain areas. The geophysical data are mainly provided by ENI, as dedicated support for the realization of 3D modeling activities in the CARG Project, or derived from public national and regional databases. Many upcoming 3D geological models will focus on stratigraphic and structural architecture, however several of them will face more applicative topics such as urban geology, hydrostratigraphy, seismogenic faults, and contaminated sites.

To comply with Findability, Accessibility, Interoperability, Reusability - FAIR data principles and fulfills its institutional mandate the SGdI is engaged in the implementation of the “Geological 3D subsurface models database” and the development of a 3D web viewer. The database will include both CARG-related 3D geological models and those built in other projects by the SGdI.

Dedicated ISO-compliant metadata, defined in collaboration with AgID, and DOI persistent identifier will guarantee the findability, the use of OGC standard download services the accessibility, the adoption of an INSPIRE Geology-based extended data model and eventually geopackage encoding (developed in the GO-PEG project) the interoperability, and CC-BY open license the reusability.

Finally, the development of a dedicated 3D web viewer will allow also non-geologists to navigate and interact with the 3D geological models through tools for user-defined spatial queries (i.e., cross-section, map, and virtual borehole).

## Exploiting PlanetScope imagery for volcano deposits mapping

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*Keywords:* remote sensing, volcanic tephra, planetoscope.

In the period between 2021 and 2022, several lava fountain episodes occurred at Mt. Etna (Italy). Most of them produced abundant tephra fallout which caused several diseases to people living mainly in the eastern and south-eastern volcano flank. One of the ways to estimate the impact from tephra fallout is going to the field after an eruptive event but, in general, this is not always possible. In this work we try to identify the area covered by the tephra fallout after some eruptive events, which involved the eastern part of the volcano. We estimated the values of the visible (RGB) and near infrared (NIR) bands analyzing pre- and post-eruptive data in a specific area. For this purpose, we used the Google Earth Engine computing platform and PlanetScope satellite of which images have a high spatial resolution (~3 m pixel size) and high cadence (24 h). PlanetScope images are analyzed also for the calculation of the Normalized Difference Vegetation Index (NDVI), already used for other volcanoes worldwide. In detail, this calculation has provided negative values of the index in areas characterized by the presence of volcanic tephra.

Mainly for the high frequency of similar episodes occurring in the last decades, this work could have important implications for identifying areas affected by tephra fallout in near real time during a volcanic eruption, in the context of short-term volcanic hazard assessments for the whole region.

## **Geo-petro-structural digital mapping of crystalline basements and 3D Virtual Outcrop Model**

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*Keywords:* UAV, crystalline basement, VOM.

Geological-structural features of crystalline basement rocks can be inferred from digital survey of VOM (Virtual Outcrop Model) reconstructed by means of structure from motion techniques. A combination of aerial/field surveys with digital geological mapping using a LiDAR sensor is here presented. The combined aerial survey using UAVs (Uncrewed Aerial Vehicles) and terrestrial survey with portable LiDAR using Sfm (Structure from motion) technology allows the capture of both general and detailed geometric relationships of geological structures in metamorphic rock outcrops. Above all, the orientations of the main foliation or compositional layering, axes, and axial surfaces of folds with wavelengths of at least centimetres can be easily deduced. Lineations (e.g., mineral or stretching lineations) are generally more difficult to derive from 3D models, unless surfaces where they are clearly visible in outcrop, have been acquired with greater care and accuracy. The comparison of the spatial orientations of structural data acquired classically with the geological compass with those derived from a virtual structural survey (using the 3D model reconstructed with aerophotogrammetric techniques) is very good, as they are comparable and almost superimposable, with a deviation of less than 5° in azimuth and/or dip. The good correspondence of the data taken manually on the ground with those derived virtually from the VOM, therefore, allows the first data to be further supplemented with new structural measurements on the one hand and on the other to obtain information even for those areas that are difficult to reach (e.g., vertical cliffs) whose survey would otherwise require greater time and increased risk for operators. The method proposed here is an excellent solution to mitigate the risks for operators in inaccessible environments and still obtain good-quality structural data from the VOM.



## **Tectonic and paleo-morphologic influence on surface and ground water flows revealed by field-mapping and 3D modelling: the Florida basin (Siracusa, Italy) case study**

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*Keywords:* CARG, field mapping, 3D model.

Within the framework of the CARG Project (Siracusa 646 sheet), new field survey was conducted in the area of the Florida basin that represents the main water reservoir supplying the city of Siracusa. The basin infill mostly consists of Quaternary marly clays, with thin levels of basal calcarenites, unconformably overlying Miocene reef carbonates. The reservoir is internally divided into a shallow and a deep aquifer due to the occurrence of Quaternary clays interbedded between basal limestones and top marine terraced calcarenites.

An integrated set of field and wells data were managed on a GIS-based software (ArcMap ESRI) and, then, interpolated within the MOVE geomodelling package (Petex) using common algorithms (Kriging, IDW). This led to the 3D reconstruction of the top of Miocene limestones bedrock and Quaternary covers and related isopach maps.

The model revealed the morphological pattern of limestone bedrock, suggesting how the basin shaping was structurally controlled by bounding and internal faults. The obtained geometry of the top-basement well fits with the deep groundwater preferred pathways, reconstructed according to the available groundwater data. Conversely, the current surface water drainage follows different pathways, locally affected by sharp bends related to recent faulting. This evidence allows redefining of the tectonic and structural control of the Florida basin evolution and relative water flow.

The achieved subsurface model provides a precious tool for the assessment of the spatial distribution of geologic and water volumes and, therefore, it can be useful to enhance the efficiency in the management and protection of water resources.

## The 2023 Turkey earthquakes: a 3D geological model reconstruction of fault surfaces using the move software

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Keywords: earthquakes, 3D fault model, move software.

In 2023, two powerful earthquakes with magnitudes of 7.8 and 7.6 struck Turkey, resulting in significant coseismic ruptures on the ground surface, widespread destruction and a significant loss of life. In addition, these earthquakes activated two fault segments of the Eastern Anatolian Fault. This study allowed us to achieve a 3D geological model using the Move software, integrating geological, seismological, and InSAR data. In-depth, the Eastern Anatolian Fault were reconstructed using a database of over 17,000 relocated earthquakes from February to March 2023 by Anthony Lomax, while at the surface, we used coseismic displacements InSAR from Sentinel 1 and 2 data (Ou et al., 2023).

The construction of 3D geological models enables a better understanding of the subsurface structure and fault systems in earthquake-prone regions (Cirillo et al. 2022; de Nardis et al. 2022). The role of geologists and seismologists is crucial in developing 3D geological models of the affected area, reconstructing faults, and understanding the mechanisms that led to the earthquakes. These models are also analyzed to identify each fault segment’s seismic potential activity and develop earthquake prediction methods.

The reconstruction of faults through 3D geological models is a crucial step towards improving our knowledge of earthquake behaviour and defining the seismic potential of regions such as Turkey. In conclusion, the earthquake relocalizations and seismological cross-sections allowed the reconstruction of the fault surfaces activated during the 2023 Eastern Anatolian earthquakes in Turkey. This study provides valuable insights that can be used to develop more effective earthquake preparedness plans and improve earthquake safety and resilience in earthquake-prone regions.

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## Multidisciplinary study of the Tramutola oil field in the High Agri Valley, integrating geophysical and well data to the surface geological survey

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*Keywords:* Southern Apennines, subsurface investigation, digital geological survey.

The presence of natural oil spills in the Tramutola area (High Agri Valley, Southern Apennines) was known since the 19<sup>th</sup> century. This led to exploration the oil field during the first part of the last century and to the discovery of hypothermal waters, which circulate in deep aquifers. In the area, now decommissioned, 47 wells reaching depths of few hundreds of meters, have been drilled between the years '30 and '40 of the last century. A further well (Tramutola45), reaching a depth of 2000 m, was drilled in the years 1958-1959.

The abundance of subsurface data in the area represents a good opportunity for studying the geometry of the tectonic structures on the axial zone of the Southern Apennines fold and thrust belt (ftb) by means of a multidisciplinary approach. The area is located in the western side of the High Agri Valley (HAV), where low- and high-angle normal faults displace pre-existing contractional structures (Olita et al., 2023). The main high-angle fault set belongs to the Monti della Maddalena Fault System, oriented about N140E (Maschio et al., 2005).

The study area, extending for about 11 km<sup>2</sup>, includes an almost complete section of the tectonic Units of the Southern Apennines. With the aim of better understanding the geometry of the rock bodies and the trend of the tectonic structures at depth, the study was focused on a detailed geological survey with the creation of a geological map on a 1:10,000 scale, combined with the analysis well logs obtained during hydrocarbon exploration. Surface data were collected in the field with the Geopaparazzi© smartphone application and processed with the free QGis© software. Furthermore, two DERTs (Deep Electrical Resistivity Tomography) perpendicular to each other and up to 1 km deep, allowed to interpret the tectonic setting in the studied area.

Field and subsurface data have been synthetized in 2D geological-structural sections which represent geometry of the tectonic structures affecting the Apennine Units in the subsurface of the study area. Different sets of high-angle normal faults offset the previous low-angle structures resulting from the contractional phase, followed by horizontal stretching associated with the development of medium- and low-angle normal faults. The latter produced a significant tectonic thinning with respect to the normal pile of tectonic units exposed in the Southern Apennines, causing a boudinaging of the carbonates of the Apennine platform along the tectonic boundary between the Liguride Complex and the Lagonegro Units. DERTs suggest the presence of deep aquifers bounded by shallow and steeply inclined tectonic contacts. Summarizing, the circulation and upwelling of deep hypothermal fluids and hydrocarbons is connected to the polyphase tectonic evolution recognized in the study area, resulting in the intersection of fault sets with different dip-angles and orientations.

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## **Integration of field and 3D high-resolution digital outcrop model data for the study of a km-scale fault zone in the Ligurian Alps: a case from the Albenga sheet (CARG Project)**

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*Keywords:* fault zone, digital outcrop model, riedel shears.

We report the study of a newly discovered 15 km long fault zone crosscutting the metamorphic units of the Ligurian Alps and that was named “Horse Head Fault Zone”. The fault zone is up to 250 m thick and involves brecciated damage zones as thick as tens to hundreds of meters, while the ~1-3 m-thick fault core involves gouge and cataclasite. The presence of dilation breccia and large calcite crystals and aggregates attest evidence of dilation in the damage zone (Woodcock et al., 2007). Numerous polished surfaces with multiple sets of slickenlines have also been discovered. Most striations indicate strike-slip kinematics, and some of them are overprinted by slickenlines indicating down-dip slip. The main sets of faults are NW-SE right-lateral faults with a minor normal component and NE-SW left-lateral steep faults, consistent with a km-size dextral NW-SE-striking Riedel shear zone, in turn representing an antithetic R' of the regional sinistral shear zone constituted by the Ligurian Alps after the nappe stacking. Since the “Horse Head Fault Zone” is sealed by the sedimentary deposits of the Finale Ligure Basin, it accommodated km-scale displacement before the Early Miocene, earlier than the Corsica-Sardinia drifting (Collombet et al., 2002). The results of this research constraint the bending of the Ligurian Alps as part of the Western Alpine arc as accomplished through two consecutive, Late Oligocene and Early Miocene, stages driven by the combination of Adria rotation and the rollback of the Apennine subduction. The structural analysis integrates the traditional field survey with the Unmanned Aerial Vehicle (UAV)-based Digital Outcrop Model. We carried out a Digital Outcrop Model on the largest outcrop of faulted rocks in a quarry where a fault network is well exposed and hardly accessible. In fact, field surveying allows characterizing only small outcrop portions, whereas photogrammetry may perform high-resolution DOMs of large, even inaccessible areas supporting the collection of large dataset (Bellian et al., 2005).

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## Combining multisensor and multiresolution data for stratigraphical analysis on Mars

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*Keywords:* planetary geology, planetary mapping, Mars.

The availability of different types of satellite data at different resolutions and the ingestion in a GIS environment, provide an impressive suite of tools to develop geological analysis on Mars. The martian data coverage is extremely large covering the visible and infrared regions and with high-resolution in correspondence of small areas (e.g., basins or landing sites) making the mapping process more significant. This approach can allow to distinguish the deposits on the base of their objectively defined characters (i.e., tone, texture, absence/presence of sedimentary structure, compositional hints) from the genetic interpretation provided by the morphological characters. However, the different spatial resolutions make this approach more complex and requires to simultaneously work at different scale.

A clear distinction between descriptive and interpretative units is specifically envisaged when geomorphological interpretation is particularly controversial. Stratigraphy represents another concept that needs to be included within map information. Unlike on Earth, sedimentary (and not only) systems preserve their morphological assemblages down to the deep stratigraphic record, making the identification of unconformities and stratigraphic relations a pre-requisite to a correct interpretation of Martian units.

We present some examples of stratigraphic reconstruction in areas where the past presence of water was inferred from several observations.

## Geological 3D survey with iOS LiDAR: quantitative and qualitative comparative assessment

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Keywords: iOS LiDAR, SfM, geological survey.

Real life is in 3D and every day, there is a strongest demand for spatial data to represent the real shape of the World. In the last decades, different sources of 3D numerical data can be easily gathered, making a virtual 3D world available to a growing number of Earth scientists. In the digital millennium, the main contribution to the geological field survey derived from the GNSS (Global Navigation Satellite System) geolocalization, probably the best geological tool after the compass. The main step to the 3D world derives from the terrestrial and airborne LiDAR (Light Detection and Ranging), the recent SLAM (Simultaneous Localization And Mapping) technologies and computational photography through the use of fly platforms like UAVs (Unmanned Aerial Vehicles), which permit to collect large amounts of spatial data. Computer vision algorithms like “Structure from Motion” (SfM) allow obtaining 3D spatial geolocalized points cloud with centimetres accuracy. Today these data are efficiently used in different disciplines of the geosciences, from structural geology, sedimentology to geomechanics.

In the last few years miniaturized LiDAR technology is also available in smartphones and tablets. The Apple@ iPad Pro and the iPhone Pro are the first handle devices integrated with a new LiDAR sensor. These devices permit close-range scanning of targets ranging from a few centimetres to meters limited to a few meters of distance from the objects and are extendible reasonably for tens of meters. Several iOS applications offer the possibility to immediately elaborate the data and generate georeferenced points cloud, taking advantage of the high computational capacity of the devices.

An evaluation of different acquisition methods is here proposed using a decametric outcrop of layered and fractured Jurassic carbonate in the Northern Apennines. Points clouds have been generated with different acquisition methods: (a) classical terrestrial Lidar, (b) SLAM LiDAR, (c) total station and SfM digital camera at 36MPixel, (d) UAV with a digital camera at 24MPixel, (e) iOS LiDAR from phone (f) and tablet (g), iOS SfM from phone(h) and tablet (i). The results in terms of sensitivity, precision, and accuracy, are good and acceptable but strongly influenced by the acquisition procedure and by the elaboration methods. The small iOS devices have an acceptable spatial georeferenced position (<1 m) for many geological applications. The LiDAR sensor has good spatial-tracking capabilities and permits the production of well-scaled and oriented points clouds with decimeter precision where surface planar attitude can be extracted for structural analysis with acceptable precision (>5°). Mostly, the main advantages of iOS technology are its simplicity and the opportunity to get a 3D model of a geological object directly in the field, without any previous planning. Diversely from conventional LiDAR, SLAM and SfM, methods, the iOS smartphone and tablet LiDAR can be easily processed with onboard software, with the final possibility to record and share data across different platforms.



## **Subsurface Map and 3D model of CARG Ragusa Sheet 648 (Hyblean Plateau, SE Sicily, Italy)**

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*Keywords:* 3D geological models, seismic, Hyblean plateau.

3D geological models are useful tools for mapping lithological units and main tectonic structures in the subsurface, using seismic, and borehole data. Recently, the CARG Project has started to promote subsurface mapping and 3D geological modelling of geological sheets at 1:50,000 scale to provide a better geological framework and a high-impact applicative tool. The CARG Ragusa Sheet 648 at 1:50,000 map scale, covers part of the Hyblean Plateau in SE Sicily. It represents a culmination of the Mesozoic-Cenozoic carbonate sedimentary succession, part of a larger crustal sector known as Pelagian Block, representing the northernmost margin of the African Plate. Since the 1950s, the Hyblean Plateau has been an area of great interest for hydrocarbon exploration. Exploration focussed in the Ragusa area, where the Ragusa Oil and Gas field has been discovered on 1954. Therefore, an important research activity has been carried out through several seismic surveys and drilled wells by ENI for over half a century. A large amount of subsurface data (wells and seismics) is available and has been kindly provided by ENI S.p.A. However, vintage seismic data are made available in analog (paper, raster) format. The vectorization of these data then constitutes an essential first step. Scanned images of stacked reflection seismic data need to be digitised, in order to work with modern tools. The geophysics logs permit correlation of lithological units and sonic logs are used to create a velocity model. This will serve to convert seismic data from time to depth.

Subsurface data will be later integrated with surface mapping, geological sections and biostratigraphic data, to obtain a comprehensive view of the area, with focus on active tectonic structures and natural resources.

## **Multidisciplinary analyses for a 3D modeling of Quaternary clastic infill of the High Agri Valley**

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*Keywords:* high Agri valley, modern acquisition tools, 3D modelling.

During Pleistocene, transtensional to extensional faulting affected the axial sector of the Southern Apennines fold and thrust belt, allowing the formation of NW-trending fault-related intermontane basins, filled by continental Quaternary deposits (Giano et al., 2000). Among them, the High Agri Valley (HAV) has a great importance, due to the presence of natural resources. The Quaternary clastic infill of the HAV (Carbone & Giano, 2015) was formed during the activity of two main systems of NW-trending basin-bounding faults: the East Agri Fault System to the NE and Monti della Maddalena Fault System to the SW.

With the aim to better understand the geometry of the clastic infill succession of the HAV, the study was focused on the realisation of a 3D static model in MOVE©, based on the acquisition of surface and subsurface data. Surface data, synthesised into a detailed geological map at a 1:25,000 scale, were collected in the field with the Geopaparazzi© smartphone application, and processed with the QGIS© free software. Field data were combined with stratigraphic information coming from shallow wells, pre-existing Shallow and Deep Electrical Resistivity Tomographies (Colella et al., 2004; Rizzo et al., 2004), and five newly acquired (5) deep electrical resistivity investigation down to 1000 m depth. By identifying levels with different resistivity and joining them with the information of well logs, has been possible to create 15 geological cross-sections reaching about 1000 m depth.

The 3D model allowed to construct in detail the bottom buried surface of the clastic infill deposits. The surface was processed to obtain an elevation map, which allowed the identification of three main depocenters and two threshold zones, partially corresponding to those already recognized by Colella et al. (2004). The difference in elevation between the bottom of clastic deposits and the surface topography allowed the creation of an isopach map, showing the depocentral areas with greater detail, reaching about 450 m of thickness. The geometry of depocenters is connected to the control played by NW-trending Quaternary faults, mainly characterized by dip-slip kinematics. The depocenters are bounded by thresholds, probably due to the activity of NE-trending transverse faults, with a possible strike-slip kinematics.

In conclusion, the integration of geological mapping, the geophysical data and the analysis of shallow well logs into a static 3D model, has provided a more detailed image of the buried HAV basin, that might be useful for hydrogeological studies and the interpretation of the Quaternary evolution of the whole area.

We are very grateful to Eni SpA and Shell Italia E&P for providing necessary data and authorizing their publication. We would like also to thank their technical teams for the fruitful discussions.

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## **Semi-automatic textural characterization of a massive rock failure deposit: the Rock avalanche of Sant'Eufemia a Maiella (Abruzzo, Italy)**

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*Keywords:* uav photogrammetry, rock avalanches analysis, Maiella (Abruzzo Italy).

In the Sant'Eufemia a Maiella area, a chaotic rock avalanche deposit, middle Pleistocene in age, has been recently recognized (Brozzetti et al., 2018).

Its mapping was performed during a 1: 10,000 scale geological survey of the upper Orta valley, aimed at a master's degree thesis (Cerritelli, 2016), during which the possible source area, located on the slope east of the Morrone massif (M. Le Mucchia), was also identified.

In the early stages of work, the textural characterization of the rock avalanche deposit was very rough due to the limited number of exposures useful for granulometric evaluations, fabrics assessments, and compositional analyses. The most extensive outcrop was found in correspondence with a sub-vertical scarp, about 20 m high, which, due to the poor coherence of the deposit, is inaccessible and highly unstable. The height and the frequent rockfalls make it impossible to work on this outcrop directly.

To overcome these problems, a photogrammetric survey of the scarp was carried out using UAV DJI Mavic 2 Professional with installed Antenna rover GNSS (L1/L2 RTK/PPK) and to collect the Ground Control Points Emlid Reach RS2 (GNSS/RTK L1, L2, L5) was used, in total we acquired 300 high-resolution images. Their subsequent processing with the Agisoft Metashape software made it possible to create an orthomosaic from which four images were exported representing the "sections" of the outcrop with different perspectives: a plan view of the entire area and three fronts of the scarp, having NW-SE, N-S, and NE-SW directions.

The binary version of the images (white elements = clasts > 1 cm, in a black matrix) was obtained manually using the CorelDRAW graphics software. Subsequently, the following tools were applied: 1) FabricS (Moreno Chávez et al., 2018) to obtain a rose diagram of the fabric of the deposit, 2) Rosiwal to process the granulometric statistical information, and 3) 3DVCV (Moreno Chávez et al., 2018) to integrate the rose diagrams relating to the various sections, obtaining an absolute orientation.

In order to verify the reliability of the results obtained through the semi-automatic procedure, these were compared, in the final phase of the work, with those acquired by applying the traditional field measurements in the few reachable outcrops. Based on this check, the pros and cons of the methodology used are discussed, and an estimate of the errors is carried out with respect to the results achieved through direct evaluation.

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## **Field survey using technological devices: an example from CARG geological mapping projects in Umbria (Northern Apennines, Italy)**

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*Keywords:* digital field mapping, geological map, database GIS.

In the last decades, the advent of innovative technologies in geosciences has led to developing new methods for more accurate geological surveying. Digital devices equipped with GPS systems helped make considerable progresses both in the collection of data and in the mapping of geological elements. Moreover, it is possible to work with high-resolution georeferenced maps, vintage and preliminary data of the interested study area.

This study aims to show the workflow and the preliminary results of the investigation of Sheet n. 300 “Gubbio” in Umbria (Italy), in the context of the national geological mapping CARG projects. This area is characterized by extensive outcrops of Miocene foredeep turbidite successions (Marnoso Arenacea Formation).

We performed a geological-structural mapping on a 1:10,000 scale integrated by photo-interpretation, through the use of anaglyphs and 3D glasses, useful for morpho-structural analysis.

The fieldwork was carried out using mainly digital methods, which increased the quality and detail of the study itself, integrating them with analogical methods to test the reliability of the collected data. The digital mapping was based on an App (FieldMove Pro, Petroleum Experts Limited) with a digital compass-clinometer for portable devices, a tool that allows direct measurement of georeferenced planar and linear elements.

During the survey, the above-mentioned tool showed its usefulness in determining the geology characteristics of an outcrop. It has been possible to reconstruct different stratigraphic logs, through a precise localization of the outcrops, accompanied by notes, sketches, and photographs of each survey site.

The numerous data collected during the surveys have been transferred to a GIS-managed project, which allowed different functions, such as the creation of a geological map, stereographic projections, and a GIS database.

We present a map and the related GIS-based database of the surveyed area which takes into account the revision of the stratigraphy and the newly acquired stratigraphic data-sets.

Finally, different applications will be compared to define the advantages and limitations they present.

## UAV photogrammetry for geomorphological and stratigraphical application in active tectonics perspective: the case of the Fornaca fan system (central Italian Apennines)

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Keywords: UAV photogrammetry, Gran Sasso fault system, active tectonics.

The geomorphological and chronostratigraphical reconstruction of the Quaternary successions in the Apennine intramontane basins is a key factor in defining the seismogenic behavior of the fault systems that determined the opening and evolution of these basins. A new tool that can support the classical study techniques of Quaternary geology and active tectonics is the processing of 3D morphological data derived from photogrammetric reconstructions made by Unmanned Aerial Vehicles (UAV) photographs acquisition and Post-Processing Kinematic analysis (PPK).

Our study area is located in the Campo Imperatore basin, at the base of the Gran Sasso Massif, whose evolution over time is closely related to the activity of the homonymous active fault system (Galli et al., 2022). In particular, the photogrammetric survey focuses along the Fornaca polyphasic alluvial fan, which piled up during the late Middle Pleistocene-Upper Pleistocene, in the eastern part of the basin for a length of 3 km in a N-S direction. We acquired aerial photos using a DJI Phantom 4 RTK drone (L1/L2 RTK/PPK rover antenna) in PPK acquisition mode (e.g. in Cirillo et al., 2022), using an Emlid Reach RS2 system (GNSS/RTK L1, L2, L5) as a base station. To ensure the accuracy of the 3D model, we placed Ground Control Points (GCPs) whose positions were acquired using the Reach RS2 GNSS sensor. We carried out photogrammetric processing using the Agisoft Metashape Pro software, which resulted in a very accurate 3D model of the investigated fan. In addition, chronological constraints of the fan succession were also acquired thanks to new radiometric dating of paleosols embedded in the alluvial fan succession, besides previous data collected by Giraudi (2003, and references therein).

The high-resolution topography obtained with the UAV enhanced our geomorphological analysis of the Fornaca polyphasic fan. This, complemented by chronological data on paleosols, has improved our knowledge of the repeated erosional and depositional phases of the alluvial fan, which were governed by the interaction between the Gran Sasso fault activity (Carraro & Giardino, 1992; Galli et al., 2022) and fluvio-glacial phenomena occurred since Middle Pleistocene (Giraudi, 2003 and references therein).

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## Evaluation of an innovative approach for the stability analysis of critical rock cliff based on UAV-based Digital Outcrop Model. A case from the 245-Albenga sheet (CARG Project)

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*Keywords:* uav, digital outcrop model, slope stability.

We present the stability analysis of a 100 m high 300 m wide carbonate rock slope (Finale Ligure, SV - Italy), whose stability is critical to project a new railway tunnel portal. The studied rock cliff is structured on the southern portion of a km-sized recumbent non-cylindrical fold, which involves a Mesozoic carbonate sequence. The rock slope shows pervasive sets of discontinuity (e.g., bedding planes, fractures and faults) combined with karst features. To achieve the stability analysis, we performed a preliminary field survey in the framework of the 1:10.000 scale mapping of the 245-Albenga Sheet (CARG project) and we developed a Digital Outcrop Model (DOM) from an Unmanned Aerial Vehicle (UAV) image dataset. The DOM was used to map and to analyse the discontinuity network. In particular, we use both manual (CloudCompare software) and automatic methods (DSE – Riquelme et al., 2014) acquiring 1265 and 202 371 discontinuity planes, respectively. The comparison of the two results shows that, significant incongruities affect the automatic method, including: i) poor detection of the discontinuities perpendicular to the slope wall (as bedding planes); ii) less representativity of discontinuities in correspondence of shadows zone derived from the camera orientations; iii) the 25% of the collected surfaces are <10 cm; iv) the slope surfaces are considered as discontinuities. Such ambiguity clearly affects the kinematic analysis of potential mechanisms controlling the rock slope failure. Due to these problems, the discontinuity dataset acquired through the automatic method was not used for the stability analysis. On the other hand, the manual detection of rock discontinuities from the DOM allowed us to discriminate their geological meaning, preserving a statistically significant collection of data. Moreover, the integration with the field survey and geotechnical boreholes data guarantees a correct rock slope characterization. The acquired discontinuity dataset was then analysed using the ROck Slope Kinematic Analysis (ROKA) algorithm allowing to identify the true potentially critical combination of the discontinuities and the orientation of the slope (Menegoni et al., 2021) and to precisely identify and visualize the critical rock volumes on the DOM. We show how results from this approach are more accurate and useful for geo-engineering purposes than the classic approach based on poorly characterized rock slope, particularly in complex structural and stratigraphic settings.

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## **Crustal deformation at the Himalaya region and South Tibet: a 3D structural model from a multidisciplinary perspective**

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*Keywords:* geodesy, geomodelling, seismotectonics.

One of the most reliable techniques for defining deformation rates is GNSS technology, which can provide an accuracy of less than 1 mm. In addition, significant progress has been made in 3D modelling to evaluate and connect seismogenic faults and seismicity distribution (De Nardis et al., 2022). Our primary objective is to integrate all available GNSS measurements in the literature (Wang et al., 2020) and combine them with our processing results for the Himalayan region and its surrounding areas in order to understand the long-term velocities and deformation rates of Quaternary active faults. The region is characterized by a long history of seismicity (Dasgupta et al., 2021), providing abundant data which are useful to construct a highly detailed 3D structure accommodating active compressional and extensional deformations.

To better estimate the geometry of the Main Himalayan Thrust, its splays (Main Frontal Thrust, Main Central Thrust, and South Tibetan Detachment) and other high-angle normal faults, we collect a large number of crustal-scale geological and tomographic cross-sections, from the literature, in a 3D environment using ArcGIS and MOVE software.

Contextualizing the strain calculated from continuous measurements of permanent GNSS stations to the reconstructed 3D surface fault model will be the major challenge of this work. This could allow us to answer major questions about lithospheric deformation, such as the compression-distension coupling in the Himalayan-Tibetan region. Furthermore, it could help us to identify areas of deep detachment or high-angle faults, where a particularly high strain rate is detected along with a lack of released seismicity (Sparacino et al., 2020).

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## **Deformation and rockfall processes on Ischia Island (Italy) by integrating satellite measurements and UAS platform data**

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*Keywords:* remote sensing, deformation, land mapping.

This paper will focus on the integration of satellite measurements and UAS platform data, aiming to show both the long-term dynamics that characterize the volcano-tectonic nature of the island and the local instability phenomena such as the rockfall processes. In particular, the main phenomena of deformation (such as the subsidence that characterizes the northern slope of Mount Epomeo), interspersed with seismic activity, such as the earthquake that struck the village of Casamicciola on 21<sup>st</sup> August 2017, will be shown. As regards the phenomena of local gravitational instability we will present a survey carried out using optical sensors (photogrammetry) and LiDAR mounted on UAS platforms; the processing of the acquired images provided the necessary information for the development of high-precision digital terrain models that can be used as a basis for the subsequent modeling of the stability analysis of collapse phenomena with a three-dimensional rockfall simulation model (STONE). These surveys allowed us to localize the possible detachment sources and the inclusion of scenario-based seismic shaking as a trigger for rockfalls.

The subsidence that characterizes a portion of the island has been analysed and monitored thanks to the use of sensors mounted on both first generation satellite platforms (such as ERS and Envisat), and second and third generation, such as the COSMO-SkyMed and Sentinel constellations. Furthermore, the geological, structural knowledge of the island and our capability to model the causative source has allowed us to identify the seismogenic structure responsible for the 2017 earthquake and probably also responsible for the oldest seismic activity of Casamicciola in the 19<sup>th</sup> century

For what concern the use of UAS platforms, the areas filmed fall almost exclusively along the north-western slope of Mt. Epomeo and more precisely in the areas identified as locality Falanga and locality Frassitelli in the Municipality of Forio and only marginally in the Municipality of Serrara Fontana. The slope surveyed has two distinct morphologies: 1) the north-west oriented sector delimited by extremely steep walls and by cliffs with variable vertical development, at the base of which there is a large sub-flat area delimited to the north by a new sudden jump in slope; 2) in the west sector the slope is instead more rounded; this side is characterized by the presence of numerous tuff blocks, which have stopped at various altitudes after having detached themselves from the overlying sub-vertical walls.

In conclusion, we try to show how the joint use of remote-sensing instruments, but from different heights, can lead to a better knowledge of the dynamic characteristics of the island, long- and short- term deformation phenomena and land mapping.

### 3D geological modelling generated from structure from motion, fieldmove and move software

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Keywords: fieldmove app, 3D geomodelling, aerophotogrammetry.

Technological advancement has replaced 20th-century field tools with smartphones, tablets, handheld Global Navigation Satellite Systems (GNSS), iPads, and drones. Last-generation tablets offer various functionalities, including a digital hand compass, taking pictures, acting as a notebook and mapping device, and gathering precise location data. They can also be equipped with Geographic Information System (GIS) software. In addition, technology development has significantly improved field mapping techniques and digital mapping using devices like tablets with dedicated software. In some cases, the acquisition of images by drones can now supplement the “classical” geological survey.

This study presents a multidisciplinary approach to realise a 3D geological model integrating UAV Photogrammetry and digital devices for field mapping.

The procedures used are the following listed:

- 1) Acquisition of high-resolution images from UAV
- 2) Analysis of the images with Agisoft Metashape
- 3) Creation of georeferenced Orthomosaic
- 4) Importing of georeferenced Orthomosaic on the Fieldmove app
- 5) Digital field mapping
- 6) Creation of a 3D geological model.

The geological mapping was performed using a combination of traditional survey techniques using a geologic compass-clinometer, and digital mapping techniques based on a digital compass-clinometer app for portable devices. The Fieldmove app, developed by Midland Valley & Petroleum Experts, was used for georeferenced measurements of planar and linear elements accompanied by written notes, sketches, and editable photographs of each survey site. The app was installed on an iOS Apple iPad device with an internal A-GPS GLONASS/GNSS. For the reconstruction of a virtual outcrop model we used a DJI Mavic 2 Professional drone with an antenna rover, and a Emlid Reach RS2 GNSS to measure the GCPs positioned on the ground.

In this work, we explored the advantage, conditions of applicability, and limits of the proposed novel approach to map and construct a 3D Geological Model through the integration of digital field survey and aerophotogrammetry.

## **GIS application for the analysis of the geological risk along the coastal area included in the 1:50.000 Siracusa Geological Map (CARG Project)**

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*Keywords:* geological risk, GIS, southeastern Sicily.

Southeastern Sicily is one of the most seismically active areas of the central Mediterranean, marked by a high level of crustal seismicity producing earthquakes with MCS intensities of up to XI-XII and M 7 (e.g., the 1169 and 1693 events). Several earthquake-generated tsunamis struck the Ionian coast of southeastern Sicily in historical times (e.g., the 1169, 1693, 1908 events). The most important tectonic domains of this area are the Hyblean Plateau and the Malta escarpment. The latter is a Mesozoic boundary separating the continental domain from the oceanic crust of the Ionian basin, reactivated by normal faulting during the Quaternary. Due to geodynamic processes, during the Late Quaternary this area has been affected by regional uplifting with rates decreasing toward the southeastern corner of Sicily. In fact, archaeological and borehole evidence along the Ionian coastal area show vertical land stability or weak uplift during the late Holocene. On the other hand, levelling surveys performed since 1970 and more recent GNSS data and InSAR analysis, highlighted a diffuse and interseismic low-rate land subsidence, which is in contrast with the weak long-term geological uplift of this region. So, the geodynamic processes also influence the sea level rise, increasing the effects of coastal retreat, flooding, and storms surges. Effects of several tsunamis have been reconstructed from the analyses of boulder accumulation, high-energy deposits and cores performed inside lagoons. The analysed area experienced the effects of several storms and Medicanes occurred over the last decades, mainly represented by boulders dislocation along the coastal area. This is particularly important considering that in a sea level rise scenario the effects of the extreme marine events will probably impact on the coastal landscapes currently emerged. As these natural events cannot be avoided, the study of the evidence of their destructive effects due to past event can be very useful in drawing up hazard and vulnerability maps that may help to estimate the recurrence times and to calculate the maximum inland penetration of impacting waves: these factors are very important for establishing evacuation/intervention plans and for locating appropriate shelter locations. The aim of this work is to generate a geo-database for the coastal area included in the 1:50.000 Siracusa Geological Map (CARG Project) in southeastern Sicily (Italy), including sea level rise scenarios for the next 50-100 years and geomorphological evidence of past tsunami and storm generated waves impact as well as: geodetic data, detailed topographical and morphological data (DEM 2x2, Ortophoto, TLS, DGPS), ondametric wave parameters dataset (RON, RMN), marine geophysical data (SBES, MBES, SSS, SPBP), infrastructural data (industrial areas, road, railway, shelters, etc...) together with the dataset provided from geoportal SITR (Sistema Informativo Territoriale Regionale - <http://www.sitr.regione.sicilia.it/>), to provide through GIS applications maps of vulnerability for the coasts of southeastern Sicily to sea level rise, tsunami and storm generated waves impact and to furnish the background of possible monitoring development.

## **Digital outcrop modeling as tool for geological field mapping in hard-to-reach areas: examples from “Sheet 370 Guardiagrele” CARG-project (Geological map of Italy at 1: 50.000 scale)**

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*Keywords:* 3D modeling, cartography, digital outcrop reconstruction.

3D modeling has arisen as an important tool to tackle the quantitative study of geological bodies and depositional systems at different scales with a huge field of applications spanning from field mapping to carbonate sedimentology and structural geology or reservoir characterization and analogue and sub-surface modeling. The widespread and faster development of technologies for 3D acquisition and visualization (drones, photogrammetry, 3D modelling software, mobile devices with GIS-apps and LIDAR-technology dedicated) are now able to provide an invaluable, easily accessible quantitative 3D-information for the geological objects at different scales. Geological field-based analyses, still representing the starting point for any geological reconstruction, can strongly benefit from the 3D perspective. The integration between the classical geological field survey and the 3D digitalization and visualization of geological maps can help to overcome the existing limitations inheriting in traditional methods of map production. The digital photogrammetry and its implementation in user-friendly software suites (Agisoft Metashape, VGRS-Virtual Reality Geological Studio, Pix4D), has emerged as an important source of data in many fields of geosciences allowing the reconstruction of georeferenced high-resolution 3D models avoiding the use the more expensive and time-consuming LiDAR acquisitions and processing. Drones and photogrammetric models by using a digital camera with a GPS have intrinsic advantages in collecting data in inaccessible areas or from different angles of view. The use of 3D digital photorealistic models allows also to enhance in more detail features of small outcrops developed in narrow and limited area (few km<sup>2</sup>). The 3D digital model obtained can be integrated with several numerical modelling software packages, becoming a powerful tool for merging raw field data, deriving from the geological field-mapping, and 3D digital outcrop models to better characterize the geological bodies, depositional geometries and to catch the complexity of the facies heterogeneities distributions in potential reservoirs. At this purpose, the geological sheet “370 Guardiagrele” part of the CARG-project (Geological map of Italy at 1: 50,000 scale) offers a good example to apply the digital photogrammetry and virtual outcrop reconstruction because of the occurrence of several inaccessible outcrops (vertical cliff, caves, and/or deep ditches) and geological bodies (clinostratified breccias) characterized by complex lateral and vertical relationships not often easily mapped on the field. The resulting digital outcrop models (DOMs) represent a georeferenced 3D view of the outcrop that can include topographical data at various scales (from millimeter to kilometer), offering the opportunity to better constrain the cartographic representation of a geological sheet and bringing the geological field mapping towards a new and smart facing.

## **S7.**

# **From magma degassing to gas-water-rock interaction: the role of fluids in understanding natural processes**

*CONVENERS AND CHAIRPERSONS*

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## Nitrogen, Helium, and Argon reveal the magmatic signature of fumarole gases and episodes of outgassing from upper-crustal magma reservoirs: the case of the Nisyros caldera (Aegean Arc, Greece)

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*Keywords:* noble gases, mixing modeling, magmatic degassing.

The chemical composition of gases emitted by active volcanoes reflects both magma degassing and shallower processes, such as fluid-rock hydrothermal interaction and mixing with atmospheric-derived fluids. Untangling the magmatic fluid endmember within surface gas emission is therefore challenging, even with the use of well-known magma degassing tracers such as noble gases. Here, we investigate the deep magmatic fluid composition at the Nisyros caldera (Aegean Arc, Greece) by measuring nitrogen and noble gas abundances and isotopes in naturally degassing fumaroles. Gas samples were collected from 32 fumarolic vents at water-boiling temperature between 2018 and 2021. These fumaroles are admixtures of magmatic fluids typical of subduction zones, groundwater (or air saturated water, ASW), and air. The N<sub>2</sub>, He, and Ar composition of the magmatic endmember is calculated by reverse mixing modeling and shows N<sub>2</sub>/He = 31.8 ± 4.5, N<sub>2</sub>/Ar = 281.6, δ<sup>15</sup>N = +7 ± 3‰, <sup>3</sup>He/<sup>4</sup>He = 6.2 Ra (where Ra is air <sup>3</sup>He/<sup>4</sup>He), and <sup>40</sup>Ar/<sup>36</sup>Ar = 551.6 ± 19.8. Although N<sub>2</sub>/He is significantly low with respect to typical values for arc volcanoes (1,000-10,000), the contribution of subducted sediments to the Aegean Arc magma generation is reflected by the positive δ<sup>15</sup>N values of Nisyros fumaroles. The low N<sub>2</sub>/He ratio indicates N<sub>2</sub>-depletion due to solubility-controlled differential degassing of an upper-crustal silicic (dacitic/rhyodacitic) melt in a high-crystallinity reservoir. We compare our 2018-2021 data with N<sub>2</sub>, He, and Ar values collected from the same fumaroles during a hydrothermal unrest following the seismic crisis in 1996-1997. Results show additions of both magmatic fluid and ASW during this unrest. In the same period, fumarolic vents display an increase in magmatic species relative to hydrothermal gas, such as CO<sub>2</sub>/CH<sub>4</sub> and He/CH<sub>4</sub> ratios, an increase of ~50°C in the equilibrium temperature of the hydrothermal system (up to 325°C), and greater amounts of vapor separation. These variations reflect an episode of magmatic fluid expulsion during the seismic crisis. The excess of heat and mass supplied by the magmatic fluid injection is then dissipated through boiling of deeper and peripheral parts of the hydrothermal system. Reverse mixing modeling of fumarolic N<sub>2</sub>-He-Ar has therefore important ramifications not only to disentangle the magmatic signature from gases emitted during periods of dormancy, but also to trace episodes of magmatic outgassing and better understand the state of the upper crustal reservoir.

## **New insights into the recent volcanic unrest at Campi Flegrei caldera (Italy) from geochemical and petrological evidence**

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*Keywords:* volcanic degassing, volcanic unrest, Campi Flegrei caldera.

The Campi Flegrei caldera is considered the most dangerous volcano in Europe and, starting from 2005, is currently in a new phase of an unrest that has persisted intermittently for several decades (main crisis occurred from 1950 to 1952, 1970-1972, and 1982-1984). The unrest phases are characterized by increasing ground uplift, seismicity and fumarolic activity. Particularly, CO<sub>2</sub> fluxes at the Solfatara-Pisciarelli hydrothermal site have been progressively growing up to 4000–5000 t/d during the ongoing unrest phase, a value that ranks this caldera among the main volcanic CO<sub>2</sub> emitters on Earth. Here, by combining the geochemical and petrological data collected in recent decades with numerical simulations of magma degassing, we place new constraints on the source(s) of the current dynamics of the volcano. We show that the measured N<sub>2</sub>-He-CO<sub>2</sub> geochemical variations at the Solfatara fumaroles are the result of massive (about 3 km<sup>3</sup>) magma degassing in the deep portion ( $\geq 200$  MPa, 8 km of depth) of the plumbing system. This degassing mechanism would be able to flood the overlying hydrothermal system with hot gas, thus heating and fracturing the upper crust inducing shallow seismicity and deformation. This implies that the deep magma transfer process ( $\geq 8$  km) has been decoupled from the source of deformation and seismicity, localized in the first kilometers (0-4 km) of caldera-filling rocks. Moreover, we show that the intense physical-chemical perturbation of the hydrothermal system during the current unrest phase is driving the decarbonation of hydrothermal calcite stored in reservoir rocks, providing non-magmatic CO<sub>2</sub> that can contribute up to 20%–40% of the total fumarolic CO<sub>2</sub>. These insights on depth and nature of fluid sources can have important implications for defining the best monitoring strategies and for forecasting a future eruption.

## Groundwater geochemistry in the Pesaro-Urbino province (Marche Region, central-eastern Italy) and stable isotope application to infer water-rock interactions and hydrological pathways

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**Keywords:** stable isotopes, hydrogeochemistry, water-rock interactions.

Spring and well waters occurring in the province of Pesaro-Urbino (Marche Region, central-eastern Italy) are characterized by a wide geochemical variability, pertaining to four compositional groups: (i) low salinity Ca-HCO<sub>3</sub>, (ii) Ca-HCO<sub>3</sub>-SO<sub>4</sub>, (iii) alkaline Na-HCO<sub>3</sub> and (iv) medium-high TDS Ca-SO<sub>4</sub>. Moreover, a few samples show a mixed composition in terms of major components (e.g., SO<sub>4</sub><sup>2-</sup> = Cl<sup>-</sup> or Ca<sup>2+</sup> = Na<sup>+</sup>, in meq/L). As far as the dissolved gases are concerned, two compositional clusters are observed: (a) N<sub>2</sub>-dominated, detected for springs and wells, and (b) CO<sub>2</sub>- and/or CH<sub>4</sub>-rich (up to 40% v/v), associated with sulfur and high TDS springs, gases.

The Na-HCO<sub>3</sub> waters mostly characterize the sulfur springs interacting with the Marnoso Arenacea Formation, which is consisting of sandstones and marls. They show an alkaline pH (>8.8), negative Eh values (<-180 meV), and a strong depletion in Ca (and Mg), being likely related to long-lasting interactions with Na-rich silicates in saturation/oversaturation conditions for carbonate mineral phases. The Ca-SO<sub>4</sub> composition is shown by mineral springs emerging from Miocene gypsum-rich formations with SO<sub>4</sub><sup>2-</sup> contents up to 1,950 mg/L and low to high contents in chloride up to 1,280 mg/L, whereas the Ca-HCO<sub>3</sub>-SO<sub>4</sub> waters have SO<sub>4</sub> concentrations up to 220 mg/L. Such a high sulfate content is possibly due to interaction with the Triassic Burano Formation (anhydrites, dolostones, and limestones), which do not outcrop in the study area though recognized in stratigraphic logs of deep wells (i.e., Burano well) drilled during hydrocarbons prospecting in the 1950's. The Ca-HCO<sub>3</sub> waters are likely produced by dissolution of carbonate rocks at a relatively shallow depths, as supported by the N<sub>2</sub>-dominated composition of their dissolved gases with a N<sub>2</sub>/Ar ratio approaching that air saturated water (ASW).

Analyses of δ<sup>13</sup>C-TDIC (Total Dissolved Inorganic Carbon), δ<sup>34</sup>S-SO<sub>4</sub> and δ<sup>18</sup>O-SO<sub>4</sub>, and δ<sup>13</sup>C in both dissolved CO<sub>2</sub> and CH<sub>4</sub> are planned to be carried out on a selected number of samples in order to provide new insights into the origin the major solutes, the main hydrogeological pathways and the possible interplay between deep-originated fluids and the shallow aquifers.

## **Distribution of chemical and physical parameters of the water column of Lago Piccolo, Mount Vulture hydro-mineral basin (southern Italy)**

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*Keywords:* chemical parameters, Vulture mount basin, water column.

Mount Vulture is a Pleistocene stratovolcano located in the northeastern sector of the Basilicata region (southern Italy) well known for the presence of two crater lakes: Lago Piccolo and Lago Grande. The volcanic products are unsaturated with alkaline-potassium composition reflecting the lithospheric setting near the Vulture area (Schiattarella et al., 2005). The magmas are evidence of partial melting of the “Apulian” upper mantle. For this work, physical-chemical parameters (temperature, electrical conductivity, Eh, pH), ion and trace element concentrations and the behavior of elements and mineral phases along the water column of Lago Piccolo were determined. The temperature of the lake shows a clear stratification into epilimnion, metalimnion, and hypolimnion; in the hypolimnion there is an atypical increase of the temperature (+2.44°C) probably due to a heat input from the bottom of the lake in accordance with the most recent literature (Paternoster et al., 2016). The pH of the water ranges between 8.1 (epilimnion) and 6.5 (hypolimnion) while the electrical conductivity values vary from 0.18 to 0.93 mS/cm, according with the chemical stratification of the lake. Mn and Fe concentrations increase with depth, similarly to the major ions which reach extremely high values in the hypolimnion. The saturation index of the Fe and Mn oxyhydroxides indicates these minerals are oversaturated, according with the Fe and Mn Eh-pH diagrams. Among the carbonates, siderite is oversaturated in the deepest part of the lake, where the iron concentration is particularly high. As for silicates, saturation indices suggest these mineral phases are generally supersaturated, except at medium depth (24 m). In order to fully understand the mechanisms of precipitation at the water-bottom interface it would be necessary to perform a sediment analysis in a future study.

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## Geochemical characterization of the karstic waters of Crete (Greece)

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*Keywords:* karstic aquifers, hydrogeochemistry, trace elements, stable isotopes.

Karst hydrosystems represent a worldwide drinking water resource thanks to their storing capacity of large amounts of good quality freshwater. At the same time, they are extremely vulnerable to chemical and microbial contamination and overexploitation. On the island of Crete, karst aquifers represent an important resource. The main aim of this study is to evaluate the chemical status of the big karst hydrosystems of Crete and to discriminate the possible geogenic and anthropogenic sources of contamination. In June 2022, 30 samples were collected from the major karst springs of the island. The samples were analysed for their major ion and trace element contents, dissolved gases and C, O and H isotopes.

Based on the chemical composition of waters, the karst springs are subdivided into three groups with different geochemical compositions. Group (a) is characterized by Ca-HCO<sub>3</sub> composition and low saline content (TDS <500 mg/L), showing the typical composition of groundwater circulating in carbonate aquifers. Group (b) is characterized by Na-Cl composition and higher saline content (TDS up to 6100 mg/L) showing important seawater contamination due to their coastal location and the overexploitation of their aquifers. Lastly, group (c) is characterized by Ca-SO<sub>4</sub> composition and intermediate saline content (TDS up to 725 mg/L) due to gypsum dissolution processes.

Trace elements display generally low values only rarely exceeding the European limit for drinking water. Also nitrate, often associated to anthropogenic contamination, displays low values (< 15 mg/L).

Water stable isotopes (O and H) indicate sometimes high mean recharge altitudes (up to 1800 m) and long hydrologic circuits. Dissolved gases analyses show very low CO<sub>2</sub> contents and together with negative d<sup>13</sup>C-TDIC values exclude significant geogenic gas input in the aquifers.

Generally, the Cretan karst aquifers show a good quality of their waters. In few cases deterioration is due to the intrusion of seawater within the karst aquifers or localised metal contaminations.

## **The hydrothermal area of Levante Bay hit by magmatic fluids during the 2021-23 unrest of La Fossa volcano (Vulcano Island, Aeolian Archipelago): clues from fumarole composition and submarine gas emissions**

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*Keywords:* Vulcano island, Baia di Levante, fumarole composition.

In September 2021, the La Fossa volcano in Vulcano Island entered a new phase of unrest. The main set of the crisis was the central hydrothermal system, deeply affected by the input of heat and chemicals from the magmatic source (Federico et al., 2023). The most intense variations were observed in the high-temperature fumarolic field in the crater area, but an anomalous CO<sub>2</sub> degassing was also recorded at the base of the active cone. The effects of the magmatic-hydrothermal unrest were also observed in the thermal area located northwest of the La Fossa edifice, the so-called Baia di Levante where, during fifties in the last century, some explorative drillings tapped a hydrothermal aquifer, with temperature in the range 100-200°C. The hydrothermal vapour is emitted from several low-temperature (100°C) fumaroles along the beach and in the near offshore, where some thermal springs and gas vents also exist. The composition of the gas is typical of hydrothermal systems and indicates equilibrium at a temperature close to 200°C. By the onset of the crisis, in September 2021, the composition of the gas emitted from these fumaroles showed a smooth trend of increasing contribution of the magmatic gas. In May 2022, a sudden release of gas occurred in Baia di Levante, which was testified by the whitening of the seawater in the bay, due to the formation of sulfur flakes, and by the appearance of typical pockmark structures on the seafloor. The drastic increase of the gas flux from the underwater gas vents, coupled with the presence of the pockmarks, suggested that an explosive emission of gas occurred in May 2022. The chemical and isotopic composition (He and C isotopes) of the gas emitted from the fumaroles in the Baia di Levante area revealed the prevailing presence of the magmatic component, closely approaching the composition of the gas emitted from the crater fumaroles. The gas composition changed according to a higher contribution of CO<sub>2</sub>-rich and more oxidizing gas species of magmatic over the typical hydrothermal end-member. This episode drove the attention of the scientific community to this area, currently affected by a significant input of the magmatic vapor, because of the risk related to the huge gas emission and the eventual overpressurization of the local hydrothermal aquifer.

Federico C., Cocina O., Gambino S., Paonita A., Branca S., Coltelli M., Italiano F., Bruno V., Caltabiano T., Camarda M., Capasso G., De Gregorio S., Diliberto I.S., Di Martino R.M.R., Falsaperla S., Greco F., Pecoraino G., Salerno G., Sciotto M., Bellomo S., Di Grazia G., Ferrari F., Gattuso A., La Pica L., Mattia M., Pisciotta A.F., Pruiti L. & Sortino F. (2023) - Inferences on the 2021 Ongoing Volcanic Unrest at Vulcano Island (Italy) through a Comprehensive Multidisciplinary Surveillance Network. *Remote Sens.*, 15(5), 1405.



## Hexavalent chromium in groundwaters interacting with serpentinite rocks outcropping in Pollino Massif: geochemical characterization and treatment

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*Keywords:* chromium, waters, membrane processes.

Chromium (Cr) is a dangerous element that strongly impacts ecosystem and human health. Geogenic Cr mainly occurs in rocks, soils and groundwaters of worldwide ophiolitic areas, where ultramafic rocks or sedimentary sequences produced by their erosion are present. Therefore, the ophiolitic sequence of Southern Italy outcropping in Pollino Massif, mainly its serpentinites part, represents an environmental issue for humans that live in the surrounding areas, considering different aspects like the potential presence of fibers in the air or into the water resources as well as the possible Cr enrichment into groundwaters

The pollutant can be present in several oxidation states in environment, but only Cr(III) and Cr(VI) forms are stable in common natural conditions. However, previous studies highlighted that Mg-HCO<sub>3</sub> Cr(VI)-rich water type represents the typical composition of groundwater interacting with serpentines rocks (Fuoco et al., 2020, Paternoster et al., 2021).

The WHO has fixed to 50 µg/L the threshold for total Cr in drinking water. However, considering the new knowledge concerning the Cr(VI) toxicity, the Italian government has set the total Cr limit value to 25 µg/L (D.M. 30/06/2021, which modifies the Italian Law D.Lgs 31/2001). Considering the increasing need for drinking water and the stringent concentration became mandatory the development of efficient remediation systems based on strong-geochemical considerations, to improve and give safe and unpolluted waters to the consumers for their uses. Within the scope of the PNRR project (CUP B83C22003980006), a multidisciplinary study was started to map the geochemical characteristic of groundwaters discharged from ophiolite sequence of Pollino Massif area, coupling suitable technologies to remove Cr(VI) from waters. Several on-site and off-site treatment technologies, conventional (e.g. precipitation, ion-exchange, adsorption onto different media) and advanced (membrane processes) were studied for Cr removal from waters. The cited conventional methods are often unable to lower the concentration of pollutants down to the stringent limit set for drinking waters. In contrast, membrane technologies can be viewed as innovative and interesting alternative methods, due to their many benefits, like the good product quality without using chemicals and the possible coupling with renewable energies (Figoli et al., 2016; Figoli & Criscuoli, 2017). This study will provide information from geological/geochemical point of view in the study area as well as will give a chance to fill the current gap in knowledge on the treatment of natural Cr(VI)-contaminated groundwater by using membrane processes, providing useful data for future scientific and application developments.

*Acknowledgements:* The work has been supported by the project “Tech4You - Technologies for climate change adaptation and quality of life improvement”, in the context “5. Climate, Energy and Sustainable Mobility”. MISSION 4 COMPONENT 2, “From research to enterprise” INVESTMENT 1.5 - CUP B83C22003980006.

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## Assessing the suitability of geothermal water for irrigation in arid areas: a comparative study using SVM and CART algorithms based on the Irrigation Geothermal Water Quality Index (IGWQI) in the EL Hamma Aquifer, Southeastern Tunisia

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*Keywords:* groundwater, geothermal water, irrigation, water resources management.

Groundwater is an essential resource for agriculture and sustaining life in arid regions. Therefore, monitoring the quality of aquifers is crucial to ensure effective groundwater control and water provision. This study evaluated the suitability of geothermal water for irrigation using the Irrigation Geothermal Water Quality Index (IGWQI). The study utilized conventional methods and machine learning algorithms like the support vector machine (SVM) and the classification and regression trees (CART) to analyze six variables (EC, SAR, Cl<sup>-</sup>, Na<sup>+</sup>, HCO<sub>3</sub><sup>-</sup> and Temperature) for 41 groundwater samples from the EL Hamma aquifer.

The SVM and CART models were developed and validated to determine the suitability of geothermal water for irrigation. The models demonstrated excellent agreement with the measured IGWQI, with R<sup>2</sup> values close to 1 (0.91 and 0.99, respectively), thus providing confidence in their practicality. The study identified three categories of groundwater quality, with 12% classified as good, 56% as satisfactory, and 32% as unsuitable for irrigation. The poor-quality water was found in the eastern areas, which corresponded to high water temperatures. The latter were controlled by a detachment fault, which in turn linked the deep compartments of the system with the shallow aquifer.

The study's findings are of great importance to agricultural regions, particularly in arid areas where groundwater is the sole source of water for crops and sustaining life. The study provides insights into the suitability of geothermal water for irrigation, which is crucial in ensuring sustainable and effective groundwater management. The SVM and CART algorithms developed in this study provided a more accurate identification of unsuitable groundwater areas while reducing estimation bias, particularly for limited datasets. This information is critical in supporting decision-making for groundwater planning and use, and the mapping and delineation of the IGWQI proved to be a valuable tool for safeguarding groundwater resources.

The study's findings can also contribute to the development of policies and strategies aimed at protecting and preserving groundwater resources, which are crucial for ensuring food security and sustaining livelihoods in arid regions. Overall, this study highlights the importance of aquifer quality monitoring and scoping in supporting effective groundwater management and underscores the critical role of computer models and conventional methods in evaluating the suitability of geothermal water for irrigation.

## **Linking dissipative Earth systems with their probability distributions**

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*Keywords:* thermodynamics, dissipative systems, distributions.

Many variables of Earth systems show typical distribution functions, such as the common normal, lognormal or power-law distributions. These variables often also reflect systems in thermodynamic disequilibrium, with processes aiming to reestablish equilibrium. How can we link these two perspectives together, so that we can infer the dissipative behaviour from their probability distributions? In this talk, we aim to link these two perspectives. We start with a general description of how thermodynamic disequilibrium is generated and dissipated within Earth systems, and how random perturbations can then result in different distribution functions, depending on how close the system is in thermodynamic equilibrium. We then use an example from the geochemical composition of river water from the Arno River basin to demonstrate this perspective.

## **The geochemistry of magmatic solicitations on volcanic-hydrothermal systems: the long-standing unrest of La Soufrière de Guadeloupe dissected via non-condensable gases**

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*Keywords:* inert gases, andesitic volcanism, hydrothermal-magmatic unrest.

At volcanoes in unrest, the interpretation of geochemical time-series is a major issue for decrypting volcano dynamics and forecast eruptive scenarios. However, interpretation cannot be purely observational and demands the assessment of the main physicochemical features of the hydrothermal system. In the case of La Soufrière de Guadeloupe (FWI) andesitic volcano, a careful analysis of different techniques adopted historically for gas sampling and analysis by the local observatory has allowed us to model degassing and assess gas indicators from non-condensable species in the H<sub>2</sub>-N<sub>2</sub>-CH<sub>4</sub>-He-Ar system available since 2006. Here we report on the nature of discharged gases, resulting from the mixing of atmospheric component and a magmatic-hydrothermal gas evolving along a lineage connecting MORB-like upper mantle and arc-volcano components. We show that along this lineage we can track the hydrothermal build-up of pressure and temperature modulated by magmatic variations, particularly decompression. A careful analysis of inert gas fractionation allows recognizing two main regimes: one is about hydrothermal degassing conditions perturbed by the deep impulsive gas infiltration after magma refilling in a 4 to 8 km deep chamber; the other is determined by the progressive gas stripping due to crystallization of a shallow magma batch. We also show that this second interpretation is preferred to open-system magma decompression, which would instead imply a very different hazard scenario. Although the intrinsic ambiguity in the interpretation of fractionation patterns cannot be fully solved on a pure geochemical basis, data are convergent in showing the role played by shallow magma exhaustion. Further changes of the bulk permeability structure in the hydrothermal reservoir due to fracture sealing and clogging effect may exacerbate observed evolutions but do not represent the primary control of the degassing process. We also show that gas ratios in the H<sub>2</sub>-He-CH<sub>4</sub> subsystem can effectively discriminate and anticipate such tendencies and, particularly, they can be turned into reliable precursors of magma-derived solicitations and set possible thresholds for next crises. The main test is made with reference to the 2013-2014 and 2018 episodes of seismic unrest. Besides, our method reveals that in 2007-09 an unrest phase similar to the 2018 one occurred, although not marked by the same seismic activity likely because the volcanic system was more sealed and less fractured before the magmatic upward excursion of the 2013-14 phase. Our results and conclusions are suitable for all those volcanic systems at the hydrothermal stage and allow a better definition of unrest scenarios whenever sampling frequency of fumarolic fluids is compatible with the expected transit times of magmatic fluids from magma chambers to surface.

## **The 2021-22 unrest of La Fossa volcano (Vulcano, Aeolian Archipelago): the amazing geochemistry of fumaroles**

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*Keywords:* geochemistry, magma, fumaroles.

In September 2021, the La Fossa volcano entered a new phase of unrest. The monitoring system, operating in the island since late '80s, recorded a sudden variation in seismicity, ground deformation, fumarole temperatures, soil and plume degassing (Federico et al., 2023). At the same time, the chemistry of high-temperature fumaroles at La Fossa crater showed clear-cut variations, related to the dominant contribution of the magmatic gas over the hydrothermal one. The CO<sub>2</sub> content and the helium isotope composition of the magmatic source revealed the appearance of a more primitive magma, compared to that feeding the fumaroles in the previous period, during the climax of the unrest. By the onset of the crisis, the composition of the gas emitted from Levante Bay, a thermal area located northwest of the La Fossa edifice, showed a smooth trend of increasing contribution of the magmatic gas. The chemical and isotopic composition (He and C isotopes) of the gas emitted from Levante Bay revealed the prevailing presence of the magmatic component, closely approaching the composition of the gas emitted from crater fumaroles.

The signs of the enhanced contribution of magmatic gases was already evident in La Fossa crater fumarolic gases since 2018, so the 2021 unrest appears to have been the outcome of a long lasting preparatory phase. When considering data before 2015, we revealed an end-member with very high Ar\* (namely, corrected for air), not peculiar He and N<sub>2</sub> contents and the typical magmatic C isotope marker of Vulcano. When including data from 2016, it is evident a new trend toward low Ar\* and N<sub>2</sub>, especially for data of 2022-23, while data from the crisis acme (October-November 2021) are in the typical local magmatic range of the deep latite reservoir or deeper (Paonita et al., 2013). The new endmembers cannot be explained by degassing processes produced by decompression starting from the magmatic end-member. Despite, we observe that the trend toward low Ar\* and N<sub>2</sub> points to a typical continental crustal end-member, here represented by the KTB deep wells in Germany, while the Ar\*-rich data point to a Sicilian crustal end-member, here represented by the gas collected in CH<sub>4</sub>-dominated vents nearby Mt Etna. Gneiss and metabasite rocks, drilled in the KTB deep wells, could be representative for the lower and upper crust below Vulcano, so as to locate the low-Ar\* endmember at great depth. In contrast, the high-Ar\* at shallow levels would derive from both Calabrial metapelite and volcanic and sedimentary cover. In this context, the occurrence of these crustal gases would be strictly linked to the tectonic stress. The appearance of the deep crustal gases could be linked to the magma and/or fluid transfer from depth, that produced the massive degassing of the crisis.

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## Introduction and prospects for the study of reactions between polymineralic-supercritical fluids systems

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*Keywords:* water-rock interaction, CCS, supercritical CO<sub>2</sub>.

Over the last few years, carbon capture and storage (CCS) appears to be an increasingly studied and applied technology to reduce CO<sub>2</sub> concentrations in the atmosphere. Among the various technologies studied, one that is very promising is mineral carbonation, usually consisting of the interaction between Ca-Mg-Fe bearing basaltic rocks and CO<sub>2</sub> in order to store it in the rocks via the crystallization of carbonate minerals (e.g., CarbFix project in Iceland). Although progress has been made in recent years on the study of CCS in basaltic reservoirs, the physicochemical relationships between water, dissolved ions and growing crystals in complex multicomponent systems are not well understood at the atomic- and nanoscale. During the last years the researchers have focused on the study of forsterite-magnesite systems (Kwak at al., 2011). Forsterite dissolution and magnesite precipitation are well described and there are works that investigate their combination (e.g., Raza et al., 2018). A variant of this method that will be explored in this study involves the application of supercritical CO<sub>2</sub>, which is reached above the critical temperature and pressure of 30.97°C and 73.773 bar. Under these conditions the behavior of CO<sub>2</sub> is both liquid and gaseous. Some experiments concerning the reaction between CO<sub>2sc</sub>, water and natural forsterite have shown not precipitation but dissolution, this due to the formation of passivation layers. Taking into consideration the works on synthetic minerals, the carbonation of forsterite and the following precipitation of Mg-carbonates and silica was observed (Kwak et al., 2011; Felmy et al., 2012). During laboratory investigations of multi-component solutions, numerous uncertainties arise when certain parameters are modified, like CO<sub>2</sub> pressure and temperature specific ions (such as Mg<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>, and PO<sub>4</sub><sup>3-</sup>), salinity, and pH. These uncertainties have a tendency to escalate as the parameters in question become increasingly variable. Based on the available literature, there is a dearth of references pertaining to these parameters. Therefore, the primary aim of this project is to investigate whether manipulating certain parameters can yield enhanced reaction rates to facilitate the precipitation of C-bearing phases.

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## The crystallisation of CaCO<sub>3</sub> from solution at ambient temperature in the presence of rare earth elements

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*Keywords:* carbonates, crystallisation, REEs.

The rare earth elements (REEs) are a group of 17 elements of great importance in modern world because of their wide range of hi-tech industry and clean energy applications (Balaram, 2019). Although important, techniques for separating them from their ore are challenging, costly and often inefficient while their global demand is rapidly and constantly increasing. Moreover the current techniques for separating REEs are not environmentally friendly due to the production of large amounts of toxic and radioactive waste. For these reasons there is great interest to develop advanced clean and efficient separation methods. Common carbonate minerals like calcite or aragonite may be used for this purpose. Experimental work has demonstrated that REEs adsorb on the surface of Ca-Mg-Sr carbonates and are strongly partitioned into these minerals, substituting for Ca<sup>2+</sup> (Zhong & Mucci, 1995; Lakshtanov & Stipp, 2004), while poorly ordered precursors (amorphous Ca-Mg carbonate) and metastable phases (ikaite, monohydrocalcite and vaterite) are known to uptake foreign ions from solution (Rodriguez-Blanco et al., 2015). However, there is little information regarding the nucleation and growth of CaCO<sub>3</sub> polymorphs in the presence of REEs.

This study aims to understand the effects of REEs during the crystallisation of CaCO<sub>3</sub> polymorphs from solution. For this purpose, several experiments at low starting saturation conditions were carried out at ambient temperature, consisting of mixing 4 mM solutions of Na<sub>2</sub>CO<sub>3</sub> and CaCl<sub>2</sub> doped with small concentrations (0.05 – 0.3 mM) of different REEs (La, Nd, Dy), alone or in combination. Reactions were followed with UV-Vis spectrophotometry at time intervals of 1 sec. The nature of crystallising solids and their quantification was determined with powder X-ray diffraction (XRD) and the growth morphology of the solids was characterised with scanning electron microscopy with energy dispersive microscopy (SEM-EDS). Our results show that the interaction of REEs during the crystallisation of CaCO<sub>3</sub> was translated into a slowdown of the crystallisation kinetics compared to the pure CaCO<sub>3</sub> system. The delay in the induction time and rate of crystallisation were proportional to the number of REEs present in solution, their atomic number and concentration. The growth of vaterite and calcite polymorphs in the presence of REEs ions resulted into an increase of crystal imperfections and change of growth mechanism with increasing concentration and atomic number of REEs.

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## Deeply derived CO<sub>2</sub> transported by the main rivers of Tiber basin (Italy): quantifications of the CO<sub>2</sub> fluxes and implication for monitoring the seismic activity

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*Keywords:* Tiber river basin geochemistry, CO<sub>2</sub> degassing, seismic monitoring.

Central Italy is affected by an intense process of deep CO<sub>2</sub> degassing resulting in the presence of CO<sub>2</sub>-rich groundwater. The anomaly in the CO<sub>2</sub> degassing shows an evident correlation with the distribution of the seismicity in the region. Geochemical investigations have pointed out non-casual relationships between the two processes showing strong variations in the dissolved deep CO<sub>2</sub> associated with Apennine earthquakes. In this work we present a study of Tiber river basin geochemistry focused on the process of deep CO<sub>2</sub> degassing in central Italy. Tiber river basin is located in central Italy and receives water supplies from large springs discharging deep CO<sub>2</sub>-rich groundwaters, some of which have already been recognized as very sensitive to earthquakes. Major rivers of the Tiber basin were sampled in the proximity of CO<sub>2</sub>-rich springs and at the hydrometric stations, to couple geochemical data with water flow rate data. The sampled waters resemble the compositions and the variability of the groundwaters of the Apennine carbonate aquifers and show that the geochemical variations due to mixing between spring and river waters or between rivers with different compositions remain appreciable for many kilometres downstream to the mixing point. This is evident for the electrical conductivity, pH and for some mobile/conservative species. The dissolved inorganic carbon and its isotopic composition show that the carbon dissolved in rivers waters derives from both biological sources and deep CO<sub>2</sub>. In the upper part of the basin dissolved carbon derives solely from air-biogenic CO<sub>2</sub> and water-rock interaction while in the lower part, where the Nera-Velino and the Aniene rivers flow, is evident an enrichment in deeply derived CO<sub>2</sub> due to linear springs and tributaries inflows. The signal of deep CO<sub>2</sub> is well preserved for long distances. Considering the flow rates from the hydrometric stations, the dissolved flux of deep CO<sub>2</sub> was computed. By comparing these fluxes with those computed from the springs data, a reliable estimate of the deep CO<sub>2</sub> flux can be obtained by the rivers due to a minor carbon loss by the river for at least some tens of kilometres. This result points out that rivers could be very useful for obtaining information on deep CO<sub>2</sub> flux for large areas and quantifying its time variation, even at high frequency, coupling geochemical data and flow rate measurements. In particular we found that the electrical conductivity of the water, which is an easy-detectable parameter (EDP), is well correlated to the amount of dissolved deep CO<sub>2</sub>. Monitoring EDPs at rivers hydrometric stations could hence be the next frontier for a geochemical monitoring network for seismic activity. These preliminary results would need further studies, especially in different hydrological regimes of the rivers, to fully characterize the correlations between EDPs, dissolved deep CO<sub>2</sub> fluxes and seismic activity.

## **Preliminary hydrogeochemical characterization of the Agnana, Casignana and Bivongi thermal systems (South Calabria): application of a multidisciplinary geochemical approach for geothermal resource exploitation**

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*Keywords:* thermal waters, geothermometric model, Calabria region.

The Calabria Region represents a very interesting area from the low-enthalpy geothermal point of view, as testified by the presence of several thermal springs well distributed along the region (Apollaro et al., 2019; Vespasiano et al., 2021). Given its high spatial distribution, low-enthalpy geothermal energy may represent an important resource for the region, especially in response to the current energy transition phase (Moya et al., 2018). For sustainable resource management, the detailed geochemical characterizations of thermal fluids represent mandatory processes (Hou et al., 2018) to establish the origin of the fluids and define the geothermal conceptual model. In this context, the aim of the work is to define the geothermal conceptual model of the Agnana, Casignana and Bivongi thermal systems. The sites are located in the southeastern sector of the Calabria Region, in an area characterised by a complicated geological setting that is still poorly studied from a geothermal perspective.

Preliminary geochemical and isotopic characterization indicates that the deep thermal reservoirs of all three systems are mainly hosted within the crystalline-metamorphic basement of the Serre and Aspromonte Massifs. The thermal waters show low compositional variability from Na-Cl to Na-HCO<sub>3</sub> due to prolonged water-rock interaction with the crystalline units and ion exchange processes by interaction with the outcropping clayey successions (*Argille Variegate*). Geothermometric modelling allowed to infer that the thermal groundwaters in the deep reservoir are probably in equilibrium with several hydrothermal phases at temperatures of 54°C, 70 ± 5°C and 62°C for Casignana, Agnana and Bivongi, respectively. The δ<sup>18</sup>O and δ<sup>2</sup>H values of water suggest a meteoric origin for the thermal waters with average recharge elevations between 900 and 1100 m a.s.l. compatible with a recharge near the highest portions of the Serre and Aspromonte Massifs. Meteoric waters descend to a maximum depth between 1.2 and 1.7 km below the main emergence area, where NE-SW regional fault systems probably act as preferential pathways for the ascent of the thermal waters towards the surface. These waters discharge into the Agnana, Casignana and Bivongi areas, where Miocene-Holocene sedimentary successions, cropping out immediately downstream of the emergence, act as cap-rock and promote surface emergency. Further studies of trace elements, carbon isotopes and dissolved gases will provide a better understanding of the geothermal pattern that characterises the Ionian sector of southern Calabria. The resulting data will support the decision-making and management phases of the future geothermal exploitation projects of the geothermal aquifers, which have so far attracted little interest in the Calabria region.

*Acknowledgements:* The project Tech4You (ECS: 00000009; CUP: H23C22000370006) has supported the work in the frame of the PNRR 2023-2026.

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## **PHREESQL: a tool to process PHREEQC solubility-speciation computations as support to reaction and transport calculation on unstructured meshes**

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*Keywords:* PHREEQC, speciation, unstructured meshes, real-time.

Waters are ubiquitous in environment and represent the medium featured by a high reactivity respect to the abiotic and biotic natural spheres. Multivariable data collected to depict its quality is crucial and geochemical speciation simulations are usually performed by means of numerical modelling software, i.e. PHREEQC (Parkhurst & Appelo, 1999).

Simulation's output includes generally a huge number of new derived variables, and its size can grow up by order of magnitudes respect to input dataset. To be completely available to the user a so large amount of data requires to be handled appropriately during post-processing involving efficiency and flexibility.

PHREESQL, a toolkit able to store permanently output from PHREEQC computations has been conceived to help user to manage large dataset. The code includes both a C++ library, namely PHREESQLib, and a command-line interface, namely PHREESQLexe, to ease the usability of PHREESQLib by technical experts with low programming knowledge.

Thanks to its relational data structure based on an SQL database, PHREESQL allows to efficiently store, browse, and export a large amount of data deriving from speciation simulations. Results from standard SQL language scripts allow a reuse for further analyses and for a fast and efficient comparison of output dependent on thermodynamics. The parallel implementation and the background computation capability enable a fast and real-time execution perfectly transparent to the user.

The SQL database structure so defined by can be coupled with a hierarchically defined structure of unstructured tetrahedralized meshes discretizing the subsurface volume used in reaction-transport simulations. Groundwater exploitation, waste management, and geothermal systems can benefit of its implementation over a more complex investigation pipeline.

That integration of heterogenous information can then be used to embed speciation calculation of sampled water and results of fluid flow simulation over a geostatistically designed subsurface heterogeneity. A whole description of geochemistry and geology of a site concur thus to the understanding of the fate of contaminants in time and space managing different scenarios evaluating uncertainty and sensitivity of alternative models.

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**S8.**

**Multidisciplinary insights into rock-fluid interactions and  
fluid emissions: exploring tectonic settings, geochemistry and  
modelling approaches**

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## **New insights about the induced seismic sequence of the St. Gallen deep geothermal project (Switzerland)**

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*Keywords:* focal mechanism, stress field, pore fluid pressure.

In northeast Switzerland, close to the city of St. Gallen, a deep geothermal project was designed for power production, whose drilling operation started in 2013. The project made use of naturally circulating water in existing Molasse basin aquifers at a depth of over 4,000 meters. Between July and November 2013 close to St. Gallen more than 340 earthquakes were induced by reservoir stimulations, with a strongest event of  $M_L$  3.5, which was felt by population up to 10-15 km from epicenter. In this work, we analysed the 2013 St. Gallen seismic sequence computing fault plane solutions of micro-seismic events by inverting both polarities and low-frequency spectral level ratios, following the methodology proposed by De Matteis et al. (2016). We obtained well-constrained fault plane solutions despite the earthquakes mostly showing magnitudes below 1. For the spectral analysis, we used a new automatic algorithm, TESLA (Tool for automatic Earthquake low-frequency Spectral Level estimAtion for focal mechanism computation), designed to invert the P and S displacement spectra searching the optimal signal window to use. Moreover, we processed the fault plane solutions using the Bayesian Right Trihedra Method (D'Auria & Massa, 2015) in order to derive the stress field and its potential variation associated to the different well stimulation phases since July to October 2013. Then, we estimated the 3D excess pore fluid pressure field at earthquake depths from focal mechanisms (Terakawa et al., 2010).

Our preliminary results give new insights on: 1) the kinematics of the induced micro-seismicity, 2) the tectonic stress field acting in the area, and 3) the static image of pore fluid pressure at depth in the geothermal reservoir.

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Terakawa T., Zoporowski A., Galvan B. & Miller S.A. (2010) - High-pressure fluid at hypocentral depths in the L'Aquila region inferred from earthquake focal mechanisms. *Geology*, 38(11), 995-998.



## A MATLAB tool to assess the quality of focal mechanisms for different purposes

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Keywords: focal mechanism reliability, matlab tool, fault plane solution.

Knowledge of the reliability of focal mechanism solution is essential for seismological studies, especially for the analysis of low-energy earthquakes. Moreover, focal mechanisms are essential for constraining seismotectonic models, seismogenic fault geometries, and regional stress and strain fields. For this reason, we propose an updated version of the code introduced by Adinolfi et al. (2022), to estimate both the reliability of focal mechanisms and the capabilities of a seismic network in evaluating fault plane solutions with associated errors. The original code was mainly translated into MATLAB® language, and some functions expanded, such as the calculation of travel times and take-off angles. Moreover, new statistical analyses are provided to better define the quality and the reliability of a computed focal mechanism and its uncertainty. Given a seismic network configuration, this MATLAB tool can be used on the twofold purpose of evaluating the reliability of focal mechanisms of earthquakes, and classifying fault plane solutions derived by an existing seismic catalogue. Fault plane solutions and their quality are crucial also for calculating pore fluid pressure excesses at depth, and for analyzing the temporal evolution of pore pressure field, as described in recent published papers (Terakawa, 2014; De Matteis et al., 2021).

Adinolfi G.M., De Matteis R., de Nardis R. & Zollo A. (2022) - A functional tool to explore the reliability of micro-earthquake focal mechanism solutions for seismotectonic purposes. *Solid Earth*, 13, 65-83.

De Matteis R., Convertito V., Napolitano F., Amoroso O., Terakawa T. & Capuano P. (2021) - Pore fluid pressure imaging of the Mt. Pollino region (southern Italy) from earthquake focal mechanisms. *Geophys. Res. Lett.*, 48, e2021GL094552.

Terakawa T. (2014) - Evolution of pore fluid pressures in a stimulated geothermal reservoir inferred from earthquake focal mechanisms. *Geophys. Res. Lett.*, 41(21), 7468-7476.

## Fluid vents eruptions triggered by small-magnitude earthquakes in a pressurised CO<sub>2</sub> system, Caprese Michelangelo (Northern Apennines, central Italy)

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*Keywords:* fluid flow, structural geology, Northern Apennines.

Earthquakes produce significant changes in the stress field surrounding the causative ruptured fault. Such stress perturbations can be transferred through dynamic and static stresses. Passing seismic waves can trigger earthquakes and perturb volcanic and hydrogeological systems up to remote distances, occasionally driving these features into eruption.

In this study (Bonini et al., 2023), we describe an eruptive episode of mud volcano-like structures and cold gas seeps lying along steep, ~NE-trending faults, which are intimately connected to the deep CO<sub>2</sub>-(N<sub>2</sub>)-rich pressurised Caprese Reservoir (CR), which is located in the heart of the Northern Apennines (central Italy). The CR is structurally controlled by a subsurface fold anticline tied to a thrust in the upper crust (Bicocchi et al., 2013).

In August 2010, five vents erupted mud flows after a local, small-magnitude seismic sequence ( $M_{Lmax}$  3.2). Although the exact dates of such paroxysmal episodes are unknown, they occurred within 55 days after the main shocks. These eruptions are evidence of triggered responses of mud volcano-like vents induced by earthquakes with small magnitude ( $M_L$  3.0–3.2). Static stresses at the erupted vents are negligible, thereby dynamic strain is inferred to be the sole triggering mechanism. The main earthquakes produced a near-vent peak ground velocity (PGV) of  $\sim 0.5$  cm s<sup>-1</sup> ( $M_L$  3.2) and  $\sim 0.2$  cm s<sup>-1</sup> ( $M_L$  3.0). Although small, they are similar to other PGV values that triggered eruptive events in similar systems worldwide. A potential triggering mechanism can be searched in the enhanced permeability of fluid pathways produced by the passage of seismic waves. Fluid pressurization within the antiformal-shaped CR by seismic wave focusing can also have played a significant role. This implies that seismic waves carrying even small perturbing stresses have the ability to stimulate hydrogeological systems to produce eruptions.

Furthermore, our investigations allowed us to assess the relationship between distance and earthquake magnitude for an  $M \sim 3$  event, and corroborate the validity of some existing empirical triggering thresholds of mud volcano-like systems, even in the case of earthquakes with small magnitude.

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Bonini M., Bicocchi G., Montanari D., Ruggieri G., Tassi F., Capecchiacci F., Vaselli O., Sani F. & Maestrelli D. (2023) - Small-magnitude earthquakes triggering fluid vents in a pressurised CO<sub>2</sub> system, Caprese Michelangelo (Central Italy). *Tectonophysics*, 847, 229693.

## Understanding the Complex Interactions of Fluids and Rocks in the Earth's Crust using multidisciplinary approach: Insights from the Contursi Hydrothermal System (Italy)

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**Keywords:** geochemical interactions. hydrothermal system, carbon isotopic signature.

The geochemical properties of fluids that emerge at the Earth's surface are shaped by a complex interplay between gas, rock, and water in the deep and shallow crustal layers. This includes various processes such as mixing, outgassing of volatiles, and mineral precipitation. This study aimed to gain a deeper understanding of these interactions and how they impact the behavior and migration of fluids within the Earth's crust. Specifically, the investigation focused on fluid movement towards a hydrothermal system in the Contursi basin of Italy, exploring changes that may occur during the process of crustal fluid migration in both the shallow crustal layers and deeper regions. Conventional approaches based on fluid mixing and carbonate dissolution can be inadequate for identifying the origin of deep gas due to the complex processes involved. Therefore, this study examined the relationship between Total Dissolved Inorganic Carbon (TDIC) and  $\delta^{13}\text{C}_{\text{TDIC}}$  in groundwater from the Contursi hydrothermal system to investigate water-gas-rock interactions on a local scale, using detailed geological reconstructions at depth. The results indicate that both dissolved and free gas in the hydrothermal system likely come from a deep  $\text{CO}_2$  source with a  $\delta^{13}\text{C}_{\text{CO}_2}$  value ranging from +2.30‰ to +3.20‰ (PDB), which is dependent on the salinity in a local shallow (1-3 km) aquifers. It was observed that the deep  $\text{CO}_2$  lost its original carbon isotopic signature while being stored in the dolomite-composed reservoirs at depths of 7-12 km. This phenomenon makes it challenging to identify its deep origin, such as whether it is due to decarbonation or mantle/magmatic  $\text{CO}_2$ . Our calculations revealed that the output of  $\text{CO}_2$ , considering secondary processes such as degassing  $\text{CO}_2$  and calcite precipitation, as well as interactions with water at different salt concentrations, could be at least 40% higher than estimates obtained from the mixing-only approach. This output is comparable to that of several active and dormant volcanic systems worldwide. To interpret potential geochemical changes that may occur during future seismic events in earthquake-prone areas like Contursi, it is essential to develop models that can help understand the origin of fluids and the processes influencing their chemical and isotopic signature.

## Estimation of natural methane release originating from a structurally controlled system

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*Keywords:* methane, sedimentary basin, gas microseepage.

The Emilia-Romagna region (Italy) is characterized by an intricate tectonic regime, showing active compressive structures buried under an up to several thousand meters-thick Plio-Quaternary sedimentary sequence consisting of alluvial and marine organic matter-rich sediments. Hydrocarbon manifestations are widespread throughout the territory, and significant methane reservoirs at various depths are known for decades, leading to the extensive exploitation of this natural resource (Ricci et al., 2023). Such an active tectonic setting enhances fluid migration towards the surface, feeding diffuse and punctual emissions of CH<sub>4</sub>-rich gases whose overall amount has never been accurately evaluated. Significant CH<sub>4</sub> amounts migrating to the surface are sometimes accompanied by thermal anomalies in the soil and/or groundwater, likely related to secondary processes, such as massive microbial CH<sub>4</sub> oxidation in the presence of molecular oxygen from the air (Capaccioni et al., 2015). Since these manifestations often create discomfort or concern the local population, they are directly reported. Otherwise, micro-seepages in soils can be recognized in several areas marked by vegetation thinning in terrains or cultivated fields. The present study focuses on the evaluation of diffuse emissions of CH<sub>4</sub> and CO<sub>2</sub> fluxes ( $\phi\text{CH}_4$  and  $\phi\text{CO}_2$ ) from a barley field in the Bertinoro municipality, near Cesena (FC). The final aim is to conduct a comprehensive assessment of greenhouse gas emissions within the study area, with the possibility of expanding the survey to encompass the wider region for identifying the underlying structures and mechanisms that govern the seepage. According to the measurements of diffuse gas fluxes from the soil, up to 0.8 ton·d<sup>-1</sup> and 1.8 ton·d<sup>-1</sup> of CO<sub>2</sub> and CH<sub>4</sub> are discharged from the study area, with strong changes in different seasons and peak values where thermal anomalies occur. Drone surveys using thermal, lidar and visual sensors allow the mapping of thermal and vegetation growth anomalies with high spatial resolution. As emerges from the statistical processing of fluxes, microbial production is the process behind the positive correlation between the two carbon species, where the contribution by methanotrophic oxidation can be distinguished from the biological soil background. In addition to the diffuse gas release from the soil, gas emissions in the area also occur in a phreatic well near the investigated field which is permanently saturated with gas due to the bubbling of CH<sub>4</sub>. The occurrence and spatial distribution of gas seepage in the sedimentary basin indicate a significant influence of active tectonics, favoring the fluid upraise from different depths. Noteworthy, recent satellite data from the Tropospheric Monitoring Instrument (TROPOMI) on the Copernicus Sentinel-5 Precursor (ESA) has utilized absorption data to monitor CH<sub>4</sub> concentrations in the atmosphere, bolstering the theory of a shallow source horizon underlying the entire regional plain.

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## Decade-long monitoring of seismic velocity changes at the Irpinia fault system (southern Italy) reveals pore pressure pulsations

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*Keywords:* seismic velocity changes, pore-fluid pressure, rock-fluid interaction.

The contribution of pore fluid pressure changes to triggering earthquakes at different scales of rupture is recognized worldwide (1) and has been invoked in several Italian Apennine cases (2).

The Irpinia fault system (IFS), which is located in the southern part of the Apennine (Italy), generated the largest Italian event in the last 100 years: the 1980  $M_s$  6.9 Irpinia earthquake. Several studies have monitored crustal seismic velocity changes and attempted to relate them to the stress state and physical properties in volume embedding fault systems. The aim is to provide constraints on fault system dynamics and earthquake triggering mechanisms. Here, we reconstruct the spatiotemporal (4D) seismic velocity images of volume embedding the IFS. To unravel the complex dynamics of the fault, we tracked velocity changes between epochs and compared the temporal evolution of the  $V_p$ -to- $V_s$  ratio in two volumes of interest, located in the central part of the IFS and between depths of 1–5 km and 8–12 km, with hydrological and geodetic observables (3). By inverting data from more than ten years of continuous seismicity monitoring, we retrieved time-constant velocity anomalies, whose shapes correlate well with crustal lithology, while time-changing (up to 20%) velocity anomalies are mapped in the central region. This strong correlation is visible even for the deeper-volume, highly responsive to hydraulic head, where the 1980 Irpinia earthquake enucleated; thus, we interpreted it as fractured and saturated by over-pressurized fluids.

To explain the correlation between hydraulic forcing and seismic velocity variations in the crustal volume embedding the IFS, we propose an interpretative model that accounts for the rock volume rheology, pressure conditions, porosity, and fluid content type and saturation.

The SW-NE geological cross-section shows the shallower volume between the Apennines carbonates and the tectonic *mélange*. Intensely fractured and permeable Mesozoic limestones host shallow karst aquifers. The deeper volume is located beneath the *mélange* and between the two boundary faults where the 1980 Irpinia earthquake enucleated. In the two volumes in the IFS, the observed seismic velocity changes are caused by different mechanisms: one is related to meteoric water recharge processes in the shallower volume, and the other is related to pore pressure pulsations in the deeper volume.

The described mechanisms may represent an important part of the IFS dynamics that may play a key role in triggering intense current micro-seismic activity.

This correlation provides evidence for the existence of pulsating, pore pressure changes induced by groundwater recharge processes in a deep volume (8–12 km of depth), fractured and saturated with a predominant gas phase (likely  $\text{CO}_2$ ). We suggest that tomographic measurements of the  $V_p$ -to- $V_s$  spatiotemporal changes are a suitable proxy to track the pore pressure evolution at depth in highly sensitive regions of fault systems.

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## Multi-depth spatiotemporal evolution of the Sora seismic sequence ( $M_w$ 4.8, central Apennines) - enhanced catalog data and 3D cluster analysis for seismotectonic purposes

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**Keywords:** sora seismic sequence, 3D cluster analysis, Central-Southern Apennines.

The central-southern Apennines of Italy is a high seismic risk area undergoing Quaternary extensional tectonics at low rates in the SW–NE direction. The background seismicity is mainly located at upper crustal depths (<12-14 km), and the focal mechanisms of the major earthquakes show an SW–NE trending nearly horizontal T-axes consistent with the regional stress field. Seismic events occurring along the westward limit of the extensional domain are thought to be caused by the tectonic loading or overpressurized CO<sub>2</sub> reservoirs at upper crustal depth (Di Luccio et al., 2018).

This sector of the Apennines, near the Sora town, experienced four significant events during the last ~700 years: the 1349 ( $M_w$  6.8), 1654 ( $M_w$  6.3), 1915 ( $M_w$  7.1), and 1984 ( $M_w$  5.8) earthquakes. Notwithstanding, except for the 1984 seismic sequence, whose aftershocks helped to constrain the geometry of the Barrea active segment, up to 2009, before the L’Aquila seismic sequence, this area was not affected by other significant or minor seismic sequences that allowed to illuminate the active faults or the base of the seismogenic layer with confidence (e.g., Frepoli et al., 2017).

In this tectonic context, on the 16<sup>th</sup> of February 2013, a normal fault event of  $M_w$  4.8 occurred a few kilometers west of the Sora town at a depth of ~ 20 km. Enhancing the catalog (Vuan et al., 2018), we found that, the day before the main event, 25 foreshocks ( $-0.2 \leq ML \leq 1.6$ ) enucleated at the same depth. This seismic sequence shows a complex spatio-temporal evolution. It is composed of three clusters about 5 km apart, in map view, sequentially occurred. The first one developed at depths between 17-21 km, the second one at 11-16 km, and the third one at upper crustal depths 8-11 km. The first and second clusters shows a highly asymmetric time-magnitude distribution (seismic sequence behavior), while the same distributions for third cluster is characterized by many earthquakes of similar magnitude (swarm behavior). The  $V_p/V_s$  ratio, computed with the modified Wadati diagram, is 2.0 for the first cluster, 1.85 for the second one, and 1.75 for the last one. Our preliminary results show a complex evolution of this seismic sequence where the fluid could have played a significant role in triggering the main shock and controlling the up-dip migration of the foreshock.

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## Real-time monitoring of seismicity, groundwater and meteorological parameters: an approach for multidisciplinary studies

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*Keywords:* multiparametric network, hydrogeology, aquifer dynamics.

The interplay between earthquakes and aquifers mainly results in changes in water table levels and spring discharges as well as hydrogeochemical modifications. Several studies reported pre-, co- and/or post-seismic groundwater modifications either in chemical-physical parameters or in the chemistry of waters (e.g., Barberio et al., 2017; Wang & Manga, 2021). However, the aquifer response to seismic activity is site specific, and depends on lithological, tectonic and geomorphological features as well as distance from the epicentre and earthquake magnitude (e.g., Zhang et al., 2021). For these reasons, a regional study combined with a long-lasting multiparametric monitoring is needed to prepare to a seismic sequence.

Here we report on a new multiparametric network located around Lake Garda, in North Italy, that aims to contribute to the comprehension of the hydrogeological-tectonic system of the area and represent a model of approach to analogous study cases in other potentially seismic areas. The field infrastructure was set up starting from the end of 2021. The network comprises seven multiparametric stations placed on the major seismogenic structures and transmitting data in real-time to a database *ad hoc* developed. As to analyse various hydrogeological systems, selected aquifers show distinct degrees of confinement and lithologies. Groundwater parameters (water level, temperature and electrical conductivity) are monitored by means of CTD diver sensors installed in wells spanning a wide range of depths (35-200 m). Each site is also equipped of meteorological sensors (P, T, rain, humidity, wind speed and direction), and a seismic station providing accelerometric and velocimetric datasets.

The time-series acquired till now were modelled with a statistic approach to (i) recognize intra-annual and inter-annual trends, (ii) identify any influence and periodicity due to meteorological effects, (iii) evaluate the existence of a correlation in selected parameters among different sites. At first, the interpretation of these data will be targeted at shedding light on the dynamics (e.g., recharge capacity potential) of each aquifer. The knowledge of aquifers behaviour will be crucial for the subsequent investigations.

As groundwater represents a fundamental resource of freshwater for human settlements besides being exploited for agricultural and industrial purposes, ascertainment of its circulation and recharge appears essential for the community. The continuous monitoring of groundwater level coupled to meteorological parameters has the potential to assess the resources strengths, as well as the impact of environmental changes (e.g., land use and climate) on aquifer dynamics.

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## Mud flow dynamics and gas emissions at the mud volcanoes of Nirano, Italy

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*Keywords:* mud volcanism, aquifer, Nirano Salse.

Mud volcanoes are broadly distributed throughout the globe and their manifestation to the surface can happen via progressive and slow release of mud and gas, or in violent and explosive forms. Where tourist frequentation is high, site safety requires knowledge of the potential for sudden gas/mud eruption and the shallow structure of the pipe-conduits system in proximity to the mud volcanoes, as well the flow dynamics. In this work, we applied novel (for the context) integrated approach to define a comprehensive model of the mud volcano system of the Nirano Salse Nature Reserve (Modena, Northern Apennines). We performed continuous monitoring of mud levels within mud conduits and pools; characterized the fluid in terms of mud densities and grain size; quantified the gas-liquid ratio; and measured the carbon emissions (CH<sub>4</sub> and CO<sub>2</sub>) both from volcanoes and the surrounding soil by a portable gas fluxmeter. The results suggest that different mud levels are due to distinct gas-liquid ratios in the conduits and degassing mode, and support the presence of shallow aquifers at a depth of 5 to 30 m that act as temporary storage for the ascending gas. When fluid pressure in these aquifers exceeds the tensional strength of the sedimentary rock or the weight of the mud column in the conduit, leakage of fluids to the surface would occur. Finally, geophysical surveys confirm and highlight the main stratigraphic and structural discontinuities (faults), representing the preferential pathways for gas migration within the volcanos system. The outcomes have an important implication to evaluate the potential for dangerous abrupt mud eruptions, and the site safety in proximity to the mud volcanoes.

## Seismic harmonic tremor provides constraints on the hydrothermal outgassing at Pisciarelli area (Campi Flegrei Caldera, Italy)

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*Keywords:* hydrothermal degassing, tremor.

The vigorous and persistent hydrothermal degassing at active calderas is evidence of efficient fluid transfer from the underlying hydrothermal reservoir to the Earth's surface. The characterisation and monitoring of hydrothermal gases is used to obtain information about the ongoing dynamics of the magma feeding system. However, classical direct measurements of gas fluxes and compositions in active volcanic environments remain a challenge for the scientific community. The Pisciarelli fumarole field is a key area of the Campi Flegrei caldera (Italy) where continuous and intense degassing of hydrothermal fluids, partly of magmatic origin, takes place. Hydrothermal degassing is associated with a persistent shallow harmonic tremor recorded by the seismometers located near the fumarole, which has shown an increasing trend in magnitude over the last decade that correlates well with the other independent geochemical trends. All trends indicate an exponential increase in gas outflow rate from the Pisciarelli area. As part of the LOVE-CF and INGV-DPC B2 Projects, we characterised the seismic tremor in the Pisciarelli area with the aim of elucidating the possible source mechanism and the associated hydrothermal gas flow dynamics. We used data from a temporary 4-element very small aperture seismic array deployed only 70 m from the fumarolic hydrothermal field. Hydrothermal tremor at Pisciarelli is recorded as a (quasi-) persistent seismic signal associated with the presence of the boiling mud pool, whose amplitude is strongly controlled by water level changes within the hydrothermal conduits. Combining observations on the amplitude spatial distribution of the seismic waves and their back-azimuth and slowness angles with respect to the array, we located the tremor source at a shallow depth within the hydrothermal conduit. We modelled the tremor source as being due to the drastic volume reduction of the steam bubbles as they pass through the lower temperature shallow water layer. We showed that seismic-based gas monitoring can be an effective, rapid and innovative technique for monitoring fluid dynamics and outgassing in the Pisciarelli area, which may improve our ability to assess the volcanic-hydrothermal explosion hazard for the Campi Flegrei caldera.

## **Long-term geochemical monitoring in both cold and thermal aquifers in two seismically active sectors of southern Apennines: Irpinia and upper Sele Valley. Results from the INGV project “Myburp”**

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*Keywords:* geochemical monitoring, CO<sub>2</sub>-rich groundwater, Southern Apennines.

The study of geochemical transients in groundwater associated with seismicity needs long time series of observations for answering the main questions regarding the role of fluids in the earthquake-preparing phases. Generally, these studies are diffusely carried out in the co- and immediately post-seismic phase while, in the pre-seismic phase, a systematic acquisition of geochemical parameters is more sporadic. This could hamper a deep understanding of the chemical and physical processes occurring at depth, as well as define and model the groundwater-earthquake relationship. Accordingly, since May 2021, a multidisciplinary INGV project named “Myburp” is currently ongoing in the Irpinia area and in the upper Sele Valley (southern Italy). The sites selected for monthly samplings are: i) two large cold springs, Caposele and Cassano Irpino, and ii) two CO<sub>2</sub>-rich thermo-mineral aquifers (Capasso site, upper Sele Valley) and San Teodoro site, Irpinia. Cold and thermal waters are both Ca-HCO<sub>3</sub>-type, but physicochemical parameters, ionic abundance, minor and trace elements content, dissolved gas, and isotopic composition between the two groups show noticeable differences. Cold waters (T = 9 -11°C) have alkaline pH (7.7-8.2) and low salinity (290-380 μS/cm), while thermal waters, showing temperatures between 26 and 48°C, are slightly acidic pH (6.4-6.6) and with medium to high salt content (1.3-6.6 mS/cm). The observed water's features mainly reflect the differences in: i) lengths (i.e. residence time) and depths of the hydrological circuits, ii) type and degree of water-rock interaction (GWRI) processes and iii) CO<sub>2</sub> content. By combining Sr and S isotopes with geological data coming from deep oil wells drilled in the study area for hydrocarbons research, the source of some solutes (e.g., sulphate, as well as trace elements) particularly enriched in the thermo-mineral waters was recognised in the Messinian evaporitic deposits, found at different depths (up to 4 km). This finding has a noteworthy impact on the reconstruction of the different hydrological circuits from recharge areas to discharge sites.

The origin of the dissolved carbon was investigated by comparing the concentration of the C<sub>ext</sub> with its isotopic composition (d<sup>13</sup>C<sub>ext</sub>). Low C<sub>ext</sub> content and largely negative values of d<sup>13</sup>C<sub>ext</sub>, both falling in the expected range for the infiltrating waters dissolving the carbon from a biogenic source in the soils, characterizes cold waters. By contrast, thermal waters dissolve a heavier carbon component, having an isotopic signature similar to the typical values of the CO<sub>2</sub>-rich gas emissions located in the study area, where carbon derives from the thermo-metamorphism of crustal limestones. Geochemical time series acquired in a two-year aseismic period are presented and discussed in the frame of the geochemical, tectonic, and hydrological setting of the study area and allow, for these ground waters, the definition of the geochemical baseline.

## Multi-isotope tool (O, H, B, Sr) to distinguish salinity sources in a Mediterranean karstic aquifer (Murgia, Apulia, Southern Italy)

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*Keywords:* stable and radiogenic isotopes, coastal aquifers, salinization.

Scientific literature widely reports the presence of saline and brackish water in sedimentary formations along the Mediterranean coastal area (Gilli, 2015). In Italy, examples are the Apennine foreland basin and the Apulian carbonate platform (Boschetti et al., 2011; Fidelibus et al., 2011).

Marine water of Miocene or Plio-Pleistocene ages, trapped during regression/transgression events, underwent interactions with sediments and redox processes, during early- and late-state diagenesis, and mixed with the groundwater of meteoric origin to varying degrees.

In this study, 50 wells have been sampled from 2019 to 2021 (Frollini et al., 2022). A combined approach based on multi-isotopic (H, O, Sr, B) and chloride measures have been used to distinguish the sources of salinization in the Murgia coastal karst aquifer, located in Apulia, South-Eastern Italy.

Measures of  $d^{18}O$  and Cl and mixing calculations have been used to infer the saline contribution to the freshwater is of the order of 4-10%.

The good alignments of the samples along the meteoric line in the of  $dD$  vs.  $d^{18}O$  allowed us to distinguish two recharge areas.

The crossed evaluation of  $^{87}Sr/^{86}Sr$  and  $d^{11}B$ , supported by geomorphological, hydrogeological, and lithological knowledge, allowed us to infer some important characteristics of the study aquifer such as different underground pathways, water/rocks interactions, and groundwater salinity sources. First, several samples, all collected within the NW sector, characterized by  $^{87}Sr/^{86}Sr$  and  $d^{11}B$  values around 0.7076 and +20‰ respectively, indicate extensive water/rock interactions which cause water to acquire the above isotopic composition of the local Mesozoic carbonate rocks. On the contrary, all the remaining samples indicate seawater modified to different degrees of water/rock interaction, in agreement with the end members reported by Fidelibus et al. (2011).

The extensive multi-isotopic survey confirms that modern seawater is not the main source of salinity in the coastal Murgia aquifer, while a widespread presence of modified seawater characterizes the system. This work shows that a 4-5% proportion of modified seawater can be detected in fresh groundwater using isotopes and chloride and that B and Sr isotopes can support in assessing hydrological pathways and characterizing peculiar geochemistry of groundwater. Understanding salinization sources in coastal karstic aquifers is crucial for sustainable water resource management, given the increasing demand for good quality freshwater.

This research has been carried out within the frame of the VIOLA project developed by the IRSA-CNR. Isotopic analyses have been carried out at the lab Neptune Plus, Stable Isotopes, and Clean Room of the IGG-CNR, Pisa.

Boschetti T., Toscani L., Shouakar-Stash O., Iacumin P., Venturelli G., Mucchino C. & Frappe S.K. (2011) - Salt waters of the Northern Apennine Foredeep Basin (Italy): origin and evolution. *Aquat. Geochem.*, 17, 71-108. <https://doi.org/10.1007/s10498-010-9107-y>.

Fidelibus M.D., Calò G., Tinelli R. & Tulipano L. (2011) - Salt ground waters in the Salento karstic coastal aquifer (Apulia, Southern Italy). In: Lambrakis N., Stourmaras G. & Katsanou K. (eds.), *Advances in the Research of Aquatic Environment*. Environmental Earth Sciences. Springer, Berlin, Heidelberg, 407-415. [https://doi.org/10.1007/978-3-642-19902-8\\_48](https://doi.org/10.1007/978-3-642-19902-8_48).

Frollini E., Parrone D., Ghergo S., Masciale R., Passarella G., Pennisi M., Salvadori M. & Preziosi E. (2022) - An integrated approach for investigating the salinity evolution in a Mediterranean coastal karst aquifer. *Water*, 14(11), 1725. <https://doi.org/10.3390/w14111725>.

Gilli E. (2015) - Deep speleological salt contamination in Mediterranean karst aquifers: perspectives for water supply. *Environ. Earth Sci.*, 74, 101-113. <https://doi.org/10.1007/s12665-015-4042-2>.

## **Continuous CO<sub>2</sub> monitoring at Mefite d'Ansanto area (Irpinia, Southern Italy): preliminary test results in the frame of the FURTHER project**

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*Keywords:* CO<sub>2</sub> emission, soil gas survey, natural hazard.

Mefite d'Ansanto (Irpinia, Southern Italy) is considered the largest natural non-volcanic CO<sub>2</sub> emission ever measured in Italy and, probably, on Earth. This site is characterized by a small lake about 50m in diameter in which muddy gray water boils due to the violent release of gas. Compared to the other Italian degassing sites, Mefite d'Ansanto emits huge amounts of CO<sub>2</sub>: ~2000 tons/day are released over an area of 4000 m<sup>2</sup> (Chiodini et al., 2010). The main degassing area, where vegetation is absent, covers the flank of a steep-sloping hill, and the huge amount of gas flow heads west along a narrow valley, forming a dangerous and invisible gas river. The released gas is CO<sub>2</sub>-dominated (98 vol.%), with minor contents of N<sub>2</sub> (1.3 vol.%), H<sub>2</sub>S (0.33 vol.%) and CH<sub>4</sub> (0.23 vol.%). C and He isotopic signature ( $\delta^{13}\text{C} = 0.43\text{‰ VPDB}$ ; R/Ra = 2.83) indicate a deep origin, probably originated by a mixing of mantle (40%-50%) and crustal-derived fluids.

The site is considered very dangerous, because CO<sub>2</sub> is a colorless and odorless gas, undetectable by the human senses, and lethal concentration (> 30%) can be present up to 2–3 m above the ground surface; several fatal accidents involving humans and animals have occurred in the last decades.

Soil gas (CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>S, O<sub>2</sub> and H<sub>2</sub>) surveys and flux (CO<sub>2</sub> and CH<sub>4</sub>) measurements were performed in the Mefite d'Ansanto area. All these data were used to define the background soil concentrations and CO<sub>2</sub>(CH<sub>4</sub>) degassing in a timespan characterized by low seismicity. Other smaller CO<sub>2</sub> vents located about 4km from Mefite d'Ansanto, the Mefitinielle (little Mefite) and a series of little pools at 0.5-0.7 km north-east of Mefite gray lake were mapped and measured.

A multi-parametric continuous station monitoring meteorological and geochemical data was installed on December 2022 to jointly monitor air temperature, humidity, wind speed and direction, and CO<sub>2</sub> concentration.

Chiodini G., Granieri D., Avino R., Caliro S., Costa A., Minopoli C. & Vilardo G. (2010) - Non-volcanic CO<sub>2</sub> Earth degassing: Case of Mefite d'Ansanto (southern Apennines). *Geophys. Res. Lett.*, 37, L11303. <https://doi.org/10.1029/2010GL042858>.



## The role of fluids in the 1982-2016 seismicity of Aswan region (south Egypt)

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*Keywords:* reservoir induced seismicity, pore-pressure diffusion, earthquake location.

The Aswan High Dam is the largest water reservoir in Egypt and an intense continued reservoir induced seismicity has been recorded over the years: indeed, the combined effect of loading/unloading operations at Lake Nasser and the consequent variations of the fluid pore pressure in the crustal rocks may lead the faults to go beyond the critical stress for failure (Gahalaut & Hassoup, 2012; Telesca et al., 2017). To monitor the seismicity of the area and to supply with a safe management of the reservoir, a permanent seismic network was deployed since 1982 in the area after the occurrence of the November 1981 Ms 5.3 earthquake, thus contributing to the collection of a massive seismological dataset. Therefore, starting from an initial catalogue of 7833 natural and reservoir induced seismic events recorded in the Aswan region in the time period 1982-2016, we here aim at gaining insights on the structure and the triggering mechanisms of seismogenic faults of such a complex tectonic system. To this purpose, we first retrieved a new accurate 1-D velocity model of the area, inside which we determined both the absolute and the relative high-resolution earthquake locations for 2562 earthquakes. The latter allowed us: i) to better define the fault structure in the Aswan region; ii) to better follow the spatio-temporal evolution of seismicity. We were able to unearth numerous unmapped fault strands along the Kalabsha fault system and in the Wadi Kalabsha embayment area, which could not be identified from locations already reported in the original seismic catalogue. The spatio-temporal evolution of the seismicity highlighted an eastward migration of the seismicity, with a progressive shallowing of the hypocenters. We suggest that it could be due to the fluid migration process and the consequent increase of the pore-pressure in the Wadi Kalabsha embayment area. The combination of fluids pore-pressure diffusion and Coulomb stress variation due to the loading of the reservoir, may also explain the variable faulting style retrieved from focal mechanism computation of  $M_l \geq 2.5$  earthquakes located along a NW-SE striking alignment, east of the Seyal Fault. Earthquake projections onto an E-W cross-section of the investigated area highlights a seismic gap on the Kalabsha Fault: we hypothesize that it could be a locked fault patch of about 11 km length which, according to Wells and Coppersmith (1994), could be responsible for an up to  $M_w = 5.9$  earthquake in the eventuality of a unique rupture. We also carried out an earthquake clustering analysis which allowed us to distinguish: i) two clusters of earthquakes characterized by long-lasting swarm activity, for which pore pressure diffusion is supposed to be the driving mechanism; ii) four clusters characterized by seismic sequences and repeated earthquakes. Finally, we investigated the temporal evolution of the b-value and its correlation with the seismic activity of the area: its decrease corresponds with time periods characterized by higher seismic moment rates, whereas its increase up to 1.6 is temporally overlapped to a period in which earthquake swarms prevail.

Gahalaut K. & Hassoup A. (2012) - Role of fluids in the earthquake occurrence around Aswan reservoir, Egypt. *J. Geophys. Res.*, 117, B02303. <https://doi.org/10.1029/2011JB008796>.

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Wells D.L. & Coppersmith K.J. (1994) - New empirical relationships among magnitude, rupture length, rupture width, rupture area, and surface displacement. *B. Seismol. Soc. Am.*, 84(4), 974-1002.

## **An automatic monitoring platform as a tool to investigate the role of fluids in the natural/induced earthquake process**

Tarantino S.\*<sup>1</sup>, Adinolfi G.M.<sup>2</sup>, De Landro G.<sup>3</sup>, Picozzi M.<sup>3</sup>, Carotenuto F.<sup>3</sup>, Caruso A.<sup>4</sup>, Nazeri S.<sup>3</sup>, Colombelli S.<sup>3</sup>, Muzellec T.<sup>3</sup>, Emolo A.<sup>3</sup>, Zollo A.<sup>3</sup>, Orefice A.<sup>5</sup>, Ulivieri B.<sup>5</sup>, Calcagni D.<sup>6</sup> & Piantanida M.<sup>7</sup>

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*Keywords:* induced-seismicity, monitoring-platform.

The improvement of technology and the increase in the availability of highly performant seismic stations permit a better monitoring of the seismicity in areas characterized by a relevant seismic hazard, but as well it requires automated processing due to the huge increase of the amount of the continuously recorded data.

Here we present the recent published computational software platform, TREMOR (Adinolfi et al., 2023), for fast and reliable detection and characterization of seismicity recorded by a dense local seismic network. TREMOR integrates different open-source seismological algorithms for earthquake signal detection, location, and source characterizations in a fully automatic workflow and it is a valid tool to monitor the space-time-magnitude evolution of natural and/or induced seismicity recorded at a modern digital seismic network, with many stations optimally distributed on the earthquake causative seismic zone. A module for the near-real-time monitoring of the  $V_p/V_s$  ratio is also included in the computational platform. The latter quantity is directly correlated with the presence of fluids within the crust and the analysis of its spatio-temporal variations allows for the 4D imaging of large-scale medium properties.

The platform has been applied in playback mode to the continuous waveform data recorded during 1 month at the Japanese Hi-net seismic network in the Nagano region (Japan) and the resulting catalog has been compared with the Japan Meteorological Agency bulletin in terms of number of detections, location pattern and magnitudes. We found a high  $V_p/V_s$  anomalies along the Itoigawa–Shizuoka Tectonic Line fault and a mean VP/VS value of about 1.73 for the other areas, in accordance with the tomographic images of the area.

TREMOR is a valid tool 1) to study comprehensively the micro-seismicity, and 2) to have insights about the presence of fluids and pore fluid-pressure changes by defining a detailed spatio-temporal evolution of natural/induced seismicity.

Adinolfi G.M., De Landro G., Picozzi M., Carotenuto F., Caruso A., Nazeri S., Colombelli S., Tarantino S., Muzellec T., Emolo A., Zollo A., Orefice A., Ulivieri B., Calcagni D. & Piantanida M. (2023) - Comprehensive study of microseismicity by using an automatic monitoring platform. *Front. Earth Sci.*, 11, 1073684. <https://doi.org/10.3389/feart.2023.1073684>.

## Hydrological forcing of karst aquifers in the Southern Apennines, Italy

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Keywords: hydrological-forcing, coda-wave-interferometry.

The understanding of rock-fluid processes can enhance the monitoring of the active fault systems and provide a better characterization of the several phenomena which interest the seismogenic crust. It has been observed that the hydrological forcing deforms the upper crust inducing Coulomb stress perturbations up to ~10 kPa, which, although of apparently negligible amplitude, could modulate seismicity in seismic active zones (Hsu et al., 2021). Fluid content can furtherly modify the effective stress within the solid matrix of the rocks and the properties of the near-surface materials, changing the strength of the shallowest portions of the crust and consequently the seismic wave velocity (Mao et al., 2022).

Here we study the variations of seismic velocities in response to non-tectonic and anisotropic deformations associated to phases of groundwater recharge/discharge in large karstic aquifers in the Southern Apennines of Italy. Karst systems, common within the carbonate rocks of the Apennines, store large amount of groundwater which produces significant horizontal dilatational strains that modulate the secular, tectonic deformation (~3 mm/yr extension across the Apennines) and background seismicity (Silverii et al., 2019; D'Agostino et al., 2018) with seasonal and multi-seasonal signatures. We performed velocity variation measurements on seismic noise autocorrelation signals recorded at seismic stations for different coda waves time lapse and compared them with strain measured by the GPS network. We observe that seismic velocities decrease during dilatation episodes (high hydraulic head) and increase during contraction (low hydraulic head). Moreover, for the drought years, preceded by reduced rainfall and characterized by a flat hydrograph of the discharge, we observe a period of horizontal contraction and an increase of seismic velocity variation. We finally discuss the implications in terms of non-elastic behavior of the crust.

D'Agostino N., Silverii F., Amoroso O., Convertito V., Fiorillo F., Ventaffrida G. & Zollo A. (2018) - Crustal deformation and seismicity modulated by groundwater recharge of karst aquifers. *Geophys. Res. Lett.*, 45, 12, 253-262. <https://doi.org/10.1029/2018GL079794>.

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## Hot and cold degassing areas unravel deep regional fluids pathways in an extensional tectonic setting: insights from the Larderello geothermal system (Northern Apennines, Italy)

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**Keywords:** CO<sub>2</sub> degassing, geothermal exploration, transfer zones.

High-temperature geothermal areas are often characterized by widespread surficial manifestations, which location is strictly controlled by sets of faults of regional relevance. In this context, the geochemical and isotopic signature of the discharged fluids can reveal key information on the geothermal fluid pathways, shedding light on the sources and fluid-rock interaction within the geothermal reservoirs. In this work, geochemical and structural data collected at the Larderello geothermal area (Tuscany, Italy) and surroundings are presented and discussed. A total amount of 648 CO<sub>2</sub> flux measurements was carried out in nine different areas of the Larderello geothermal field and neighboring zones, following the accumulation chamber method. In specific degassing areas, interstitial gas samples (n.77) at 20 cm depth, for the determination of the δ<sup>13</sup>C-CO<sub>2</sub> (expressed as ‰ vs. V-PDB) values, were also collected and coupled with previously published data from the Monterotondo Marittimo area. The role of transfer and normal faults in controlling the geothermal circulation driven by a cooling magmatic intrusion underneath the Lago area (SW of Larderello) was constrained. The structural control on the fluids circulation is highlighted by both the location of the CO<sub>2</sub> emissions along the fault segments – where permeability is enhanced – and their degassing rates, which increase moving away from the core of the Larderello geothermal system. The main results unravel the presence of deep regional pathways along which endogenous fluids circulate before being discharged in the investigated areas. The peripheral zone emissions are affected by interaction with shallow aquifers and condensation processes whereas the CO<sub>2</sub> emitted from the central areas, located near the core of the geothermal system, are accompanied by high amounts of steam, and suffers intense shallow fractionation processes. The latter areas emit normalized CO<sub>2</sub>-degassing rates lower than 270 t d<sub>1</sub> km<sup>-2</sup>, which can be considered medium-to-low values when compared to the extremely high ones computed for the peripheral sectors (up to 1,300 t d<sup>-1</sup> km<sup>-2</sup>) of the Larderello geothermal systems. The high degassing rates, the geochemical characteristics of the fluids discharged at the periphery of the geothermal area, and the structural setting possibly suggest an incipient propagation of such a system, which might be wider than previously thought.

## **Continuous monitoring of seismic-electromagnetic signals: the case-study of the Gargano promontory**

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*Keywords:* seismic-electromagnetic, monitoring, electrokinetic.

The passage of seismic waves in the subsoil can be accompanied by electromagnetic signals of various types: the so-called pre-seismic, co-seismic or electromagnetic waves generated directly at the source. The phenomenon is closely linked to the presence of fluids in the subsoil and is attributable to the electrokinetic effect of grain-fluid contact in porous media.

The phenomenon is analyzed in the literature under various aspects, from the experimental one - especially with active seismic sources - to the numerical one.

Here we present the set-up and preliminary results of a passive experiment carried out in the Gargano Promontory, an area of southern Italy characterized by micro-seismicity and a huge karst system.

The primary purpose of the experiment is the systematic analysis of phenomenology related to natural earthquakes. To do this, a seismic station and a magnetotelluric station were placed on the same site.

Finally, we combined geoelectric and geotechnical data to confirm the hypotheses arising from the observations made so far.

## Geochemical monitoring of Tramutola thermal water (High Agri Valley, Southern Italy): relationships to seismic activity and hydro-meteorological parameters

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*Keywords:* geochemical monitoring, seismogenic processes, Tramutola well.

The relationships between fluids and crustal stress linked to seismogenic processes have been investigated in different areas of the world. In seismically active areas, when fluids show a deep isotopic signature, the study of gases and thermal waters coupled with continuous geochemical monitoring can represent an important tool in the comprehension of local crustal deformation processes. In this framework, the High Agri Valley (southern Italy) can be considered a natural laboratory to better define the relationships between geochemical, geophysical and hydro-meteorological signals by means of continuous monitoring activity. The valley is a NW-SE trending quaternary basin located in the axial zone of the Southern Apennines, characterized by a complex geological setting, large historical natural earthquakes (e.g., the 1857 M7 event) and anthropogenic micro-seismicity, the presence of the largest onshore oil field in west Europe, the Pertusillo artificial lake and thermal water in the Tramutola artesian well, an old borehole of 400 meters deep. The Na-HCO<sub>3</sub> Tramutola waters have a constant temperature (~ 28°C), flow with a rate of about 500L/min and CH<sub>4</sub>-dominant bubbling gases with an estimated total flux amount of about 160 tons/year (Panebianco, 2022). Noble isotopes indicate a main radiogenic component of fluids, with a significant contribution from a deeper source.

The main goals of this work are the analysis of the background fluctuations of the geochemical signals, the correlations between geochemical and hydro-meteorological parameters and an investigation of possible relationships between geochemical anomalies and local seismic activity. Since October 2021, the Tramutola well was equipped with multiparametric probes (OTT ecoLog800) for continuous data acquisition (sampling frequency of five minutes) and remote data transmission of the groundwater level, temperature (T), and electrical conductivity (EC). Preliminary results indicate that the daily water T fluctuations are about 0.03°C whereas the seasonal trend is of 0.3°C. The EC values are extremely constant while groundwater level values vary mainly with the bubbling activity. However, some anomalies can be found. The observed values were correlated with hydro-meteorological parameters (rainfall and air temperature) showing no significant correlation. A preliminary catalogue of seismicity with accurate absolute locations of earthquakes in a 3D Vp and Vs velocity model of the study area (Serlenga & Stabile, 2019) is still running from continuous data streams acquired by the local HAVO seismic network managed by the CNR-IMAA and the Italian National Seismic Network by INGV. Our preliminary results would be a key tool for future investigation on the possible role of geochemical parameters for seismic hazard and monitoring purposes. Indeed, we expect to gain new insights into the correlation between the monitored parameters and seismicity after a longer period of data collection.

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**S9.**

**Geochemistry of fluids from hydrothermal and volcanic environments: classical, innovative, and prospective approaches to investigate the behavior of natural systems**

*CONVENERS AND CHAIRPERSONS*

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## Geochemical survey on fumarolic discharges from Peteroa volcano (Argentina-Chile): insights into the 2018-2019 eruptive phase

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*Keywords:* volcano monitoring, fluid geochemistry, volcano fumaroles.

Peteroa, one of the most active volcanoes of the Southern Volcanic Zone (SVZ) of the Andes, is part of the Planchón-Peteroa Volcanic Complex (PPVC), including Azufre, Planchón and Peteroa volcanoes. From 1660 to 1998, Peteroa volcano experienced at least 18 phreatic and phreatomagmatic eruptions. The last eruptive phase, in 2018-2019, was preceded by three periods of unrest started in 2016. After this period, Peteroa volcano has shown a continuous fumarolic emission from different areas of the volcano summit, marked by sporadic emission peaks producing gas columns up to 800 m high.

The geochemical dataset presented and discussed in this study includes unpublished geochemical data, i.e. chemical and isotopic compositions of fumarolic gases collected from 2016 to 2021, and published ones covering the 2010-2015 period. Based on these analytical results, a conceptual model describing the evolution of the magmatic-hydrothermal system feeding the fumaroles during such a long period of observations was constructed, aiming at investigating (i) the mechanisms triggering the eruptive phase in 2018-2019 and (ii) geochemical precursors to be used for monitoring purposes.

Fumarolic gases showed substantial compositional differences: During quiescent periods, the  $\text{SO}_2/\text{H}_2\text{S}$ ,  $\text{HF}/\text{CO}_2$  and  $\text{HCl}/\text{CO}_2$  ratios were  $< 0.1$ , whereas in 2018-2019 (pre- and syn-eruptive) those ratios were up to 2 orders of magnitude higher. The increment of magmatic-related acidic gases, coupled with the evolution of the seismic activity, suggests the occurrence of conspicuous hot fluids inputs from magmatic degassing, able to affect the overlain hydrothermal system significantly and, consequently, causing the 2018-2019 eruptions. Accordingly, the hyper-acidic gases of the fumarolic discharges can be considered as the most promising precursory parameters for eruptive (phreatic and phreatomagmatic) events of this volcano.

## Development and machine-learning-based calibration of a low-cost multiparametric station for the measurement of CO<sub>2</sub>, CH<sub>4</sub>, (or H<sub>2</sub>S and SO<sub>2</sub>) in the air: an innovative approach for investigating the impact on air quality of natural and anthropogenic contaminant sources

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*Keywords:* low-cost sensors, air quality, machine-learning-based calibration.

Atmospheric pollutants have a harmful impact on human health, ecosystems, and public infrastructures. Most anthropogenic and natural environments, e.g., urban areas and hydrothermal manifestations, emit toxic mixtures of greenhouse gases (GHGs) and sulfur volatile species into the air. Among GHGs, CO<sub>2</sub> and CH<sub>4</sub> are climate forcers of major concern, while sulfur species (e.g., H<sub>2</sub>S and SO<sub>2</sub>) are toxic gases that may contribute to acid rain. Therefore, moving towards reliable, affordable and high-density air pollution measurements is a key issue. However, the high costs of air quality stations set-up and maintenance make applying the traditional instruments at multiple sites unfeasible, resulting in scarce-density resolution of data both in time and space.

This study presents the development of a low-cost station prototype that houses (i) a non-dispersive infrared sensor for CO<sub>2</sub> concentration, (ii) a solid-state metal oxide sensor for CH<sub>4</sub> concentrations, or alternatively electrochemical sensors for H<sub>2</sub>S and SO<sub>2</sub>, and (iii) sensors for temperature and relative humidity of the air. The main issue of this low-cost approach regards the in-field accuracy of the sensors, which significantly depends on (i) cross-sensitivities to other atmospheric pollutants, (ii) environmental parameters, and (iii) detector stability over time. An in-field machine learning-based calibration method has been developed for CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>S, and SO<sub>2</sub> sensors, applying the Linear Random Forest (LRF) regression. The calibration model was built based on measurements carried out using, in parallel, the low-cost sensors and two reference instruments (i.e., a Cavity Ring-Down Spectroscopy analyzer for CO<sub>2</sub> and CH<sub>4</sub>, and a Pulsed Fluorescence analyzer for H<sub>2</sub>S and SO<sub>2</sub>). The raw concentrations (raw\_conc) of these compounds recorded by the sensors, together with measured air temperature (T), and relative humidity (RH), were assigned as features of the models:  $y = f(\text{raw\_conc}, T, RH)$ .

The dataset consisted of measurements performed in different environments and seasons, to collect a wide variety of concentrations and ambient conditions used to train the calibration model, according to the following strategy: 70% of the measurements were dedicated to training the model, 15% for validating it, and 15% for testing the accuracy of predictions.

The LRF regression model showed excellent performance in predicting CO<sub>2</sub> and CH<sub>4</sub> concentrations, with R<sup>2</sup> values on test data of 0.9978 and 0.9260, and mean absolute errors of 1.34 and 0.014, respectively. H<sub>2</sub>S and SO<sub>2</sub> predictions displayed some criticalities, possibly related to the scarce sensitivity of the sensors at low concentrations. To overcome this issue, further investigations may be focused on a calibration model that includes the CO<sub>2</sub>/H<sub>2</sub>S and CO<sub>2</sub>/SO<sub>2</sub> ratios. The encouraging results gained for the carbon species lay the basis for integrating the station of sensors for monitoring other contaminants (e.g., PM, NO<sub>x</sub>, CO, etc.) to be calibrated with the same procedure.

## Soil CO<sub>2</sub> emission and stable isotopes (δ<sup>13</sup>C, δ<sup>18</sup>O) of CO<sub>2</sub> and calcites reveal the fluid origin and thermal energy in the supercritical geothermal system of Krafla, Iceland

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*Keywords:* soil CO<sub>2</sub> emission, C isotopes, supercritical fluids.

The Krafla geothermal system extends over a fissure swarm that periodically emit basaltic lavas, and has recently attracted an economic interest due to supercritical fluids forming nearby a shallow magma intrusion (~ 2 km depth). Here, we discuss new soil CO<sub>2</sub> flux and stable isotope data of the CO<sub>2</sub> efflux (d<sup>13</sup>C) and hydrothermal calcites (d<sup>13</sup>C, d<sup>18</sup>O) of drill cuttings, to estimate both the current magmatic outgassing from soils and the thermal flows in the geothermal system. Soil CO<sub>2</sub> emission is controlled by the tectonic, following the NNE-SSW fissure swarm direction and a WSW-ENE trend, and accounts for ~ 62.5 t d<sup>-1</sup>. While the d<sup>18</sup>O of the H<sub>2</sub>O in equilibrium with deep calcites is predominantly meteoric, both the d<sup>13</sup>C of the soil CO<sub>2</sub> efflux and of the fluids from which calcite precipitated have a clear magmatic origin, overlapping the d<sup>13</sup>C estimated for the Icelandic mantle (-2.5 ± 1.1‰). Estimates based on the soil CO<sub>2</sub> emission from the southern part of the system show that these fluxes might be sustained by the ascent and depressurization of supercritical fluids with a thermal energy of ~800 MW. Such significant amount of energy might reach 1.5 GW, if supercritical conditions extended below the whole investigated area. Finally, we report an increase in the soil CO<sub>2</sub> emission of about 3 times with respect to 14 years ago, likely due to recent changes in the fluid extracted for power production or magmatic activity. Pairing the soil CO<sub>2</sub> emission with stable isotopes of the efflux and calcite samples has important implications for both volcano monitoring and geothermal exploration, since can help us to track magmatic fluid upflows and the associated thermal energy.

## Lanthanoids chemistry in Etna's rainwater during the paroxysmal sequence of 2021

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*Keywords:* rainwater, lanthanoid, volcanic emissions.

Despite only a few studies on the concentration of the lanthanoid elements (from La to Lu) in rainwater are available in the literature, their significant environmental impact has been recognised. The lanthanoids are commonly divided into three groups: light lanthanoids (LLs) from La to Nd, middle lanthanoids (MLs) from Sm to Dy, and heavy lanthanoids (HLs) from Ho to Lu. Chondrite-normalised lanthanoid patterns are used to determine the source of lanthanoids in rainwater, and the behaviour of these elements in volcanic aerosol/precipitation systems. Their incompatible behaviour during mineral formation in magmatic bodies makes them useful in evaluating the magma source. Lanthanoid concentrations were measured in 21 rainwater samples collected, from March 2021 to November 2021, at 4 sites, located at different distances from the main vents of Mt. Etna. Rainwater samples were collected using traditional bulk collectors and underwent a pre-concentration procedure, according to Arslan et al. (2018) before analytical determination by ICP-MS (Agilent 7800ce). The total dissolved lanthanoids (TDLs =  $\Sigma$  of lanthanoids) concentrations in the collected rainwater samples were inversely correlated with the pH values ( $r = 0.56$ ,  $p\text{-value} = 0.0011$ ), and with the distance from the main active craters. No correlation was observed, however, between lanthanoid concentrations and rain amounts. Higher median TDLs concentration was measured at the Citelli site ( $171.4 \text{ ng L}^{-1}$ ), followed by Cratere 2001 ( $73.6 \text{ ng L}^{-1}$ ), Zafferana Etnea ( $60.1 \text{ ng L}^{-1}$ ), and finally Mt. Intraleo ( $55.6 \text{ ng L}^{-1}$ ). The Citelli site was located downwind of the dominant propagation direction of the volcanic plume (from West to East). During the monitoring period, Mt. Etna was characterised by intense paroxysmal activity with the release of large quantities of gas, lapilli, and ash whose fallout frequently affected the Citelli area. This could explain the high concentrations measured at this site. The Mt. Intraleo site, on the contrary, was located upwind of the plume and ash dispersion direction, thereby providing a local background site. Lanthanum concentrations were elevated in all the sampling sites, reaching median La/Ce ratios up to 3.80 at Zafferana Etnea. The chondrite-normalised REE patterns of precipitation samples perfectly mirror that of the typical Etna's basalt. This extraordinary consistency represents a fingerprint that highlights that lanthanoids in acid rainwater interacting with the Etna volcanic plume, derive from the dissolution of silicate particles. The scientific evidence produced by our research forms the basis for future detailed studies concerning the possible relationship between magma composition and the lanthanoids chemistry of rainwater interacting with volcanic products, especially during periods of intense activity.

Arslan Z., Oymak T. & White J. (2018) - Triethylamine-assisted  $\text{Mg}(\text{OH})_2$  coprecipitation/preconcentration for determination of trace metals and rare earth elements in seawater by inductively coupled plasma mass spectrometry (ICP-MS). *Anal. Chim. Acta*, 1008, 18-28. <https://doi.org/10.1016/j.aca.2018.01.017>.

## Geochemical survey of the main low temperature fluid discharges in Southwestern Tuscany (Italy): review and implementation of previous data

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*Keywords:* Tuscany, hydrothermal manifestations, geothermometry.

Tuscany (central Italy) is a region characterized by intense hydrothermal activity, consisting of high temperature, currently exploited, geothermal reservoirs, related to quiescent volcanism (Mt. Amiata) and cooling batholith (Larderello). Additionally, a large number of low-to-medium temperature systems occurs in areas characterized by anomalous geothermal gradients due to local tectonics. In Southwestern Tuscany, thermal fluid discharges are recognized, some of which have been known since ancient times for health therapies. Geochemical data sources on these fluids are not homogeneous and scarce are some important parameters (e.g. isotopes of He and C-bearing compounds) to define their origin and circulation paths. The present study is aimed to fill this gap, based on specific surveys to characterize waters and free- and dissolved gases from natural hot and cold springs delimited by the Tyrrhenian coast to the west, the Municipality of San Vincenzo to the north, Orbetello to the south, and the Larderello and Mt. Amiata geothermal fields to the east. So far, more than 25 waters, with temperatures from 18 to 45°C and electrical conductivity from 285 to 12,000  $\mu\text{S}/\text{cm}$ , were sampled in order to analyze major dissolved species, trace elements, water stable isotopes,  $\delta^{13}\text{C}$ -TDIC, as well as the composition of dissolved gases and the  $^{13}\text{C}$ - $\text{CO}_2$  and  $-\text{CH}_4$  values. Three different water facies were recognized, as follows: (i) shallow groundwaters, characterized by low salinity ( $< 855 \mu\text{S}/\text{cm}$ ) and temperature ( $< 25^\circ\text{C}$ ) with a  $\text{Ca-HCO}_3$  composition; (ii) high salinity (from 7,870 to 11,960  $\mu\text{S}/\text{cm}$ ), low temperature ( $< 26^\circ\text{C}$ ) waters with a  $\text{Na-Cl}$  composition; (iii) medium-high salinity (from 1,585 to 5,410  $\mu\text{S}/\text{cm}$ ) and temperature (from 26 to 45°C) waters with a  $\text{Ca-SO}_4$  composition. The  $\text{CO}_2$  concentrations in the dissolved gases range from 0.04 to 0.75 mmol/mol, with  $\delta^{13}\text{C}$  values between -21.5 and -8‰ V-PDB. The concentrations of methane were found to be extremely low as, in most cases, the isotopic signature was not possible to be detected. The free gas sample from S. Martino sul Fiora shows a composition dominated by  $\text{CO}_2$  (99%) with  $\delta^{13}\text{C}$  of 0.14‰ V-PDB. Group (i) is representative of local recharge waters, while waters belonging to group (ii) reflect the mixing between a shallow and a marine component, as also suggested by the Br content and the Br/Cl molar ratio, a slightly thermally anomalous. Eventually, group (iii) is referred to those waters affected by deep circulation and interacting with the Triassic carbonate–evaporite (mainly gypsum) formations. According to the  $\text{HCO}_3$ - $\text{SO}_4$ -F geothermometer, the waters from group (iii) allowed to estimated equilibrium temperatures of the deep reservoirs up to 70°C and a low  $\text{pCO}_2$  ( $\sim 1$  bar).



## The 2021-2022 unrest of Vulcano Island volcanic system (Aeolian islands): geochemical evidences from fumarolic gas discharges and well waters

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Keywords: volcanic unrest, fluid geochemistry, Vulcano Island.

Since September 2021, a gradual unrest at Vulcano (Aeolian Islands) has been recorded by monitoring systems. It was marked by a progressive variation of different geochemical, geophysical and ground deformation parameters. The fumaroles located on the crater rim and along the northern outer flank of the La Fossa crater were characterized by a general increase in temperature (up to 350°C) as well as CO<sub>2</sub> and SO<sub>2</sub> fluxes. New fractures and fumaroles and a fumarolic plume, up to >100 m high, also formed. Furthermore, an increasing number of VLP events was recorded by the seismic network, combined with an uplift of about 1 cm/month. In this work, we present the analytical results obtained during several sampling campaigns were carried out by DST-UNIFI from November 2021 to February 2023 in agreement with INGV-Palermo, to verify how the volcanic system was evolving. Nine fumaroles from the summit crater and five from the Baia di Levante area, together with 9 hot and cold wells located in Vulcano Porto, were sampled. The geochemical dataset revealed that the crater fumaroles had a significant increase in both the concentrations of acidic gases of marked magmatic origin (SO<sub>2</sub>, HCl and HF) and the gas/vapor and SO<sub>2</sub>/H<sub>2</sub>S ratios in November 2021, associated with significant chemical-physical variations of the waters and dissolved gases from the wells located at the foothill of the volcanic cone. On the contrary, the gas discharges at Baia di Levante did not show significant compositional variations when compared with the previous data. From February 2022, the SO<sub>2</sub>/H<sub>2</sub>S ratios as well as the concentrations of magmatic gases, H<sub>2</sub>, and CO from crater gas emissions decreased, concurrently with a general decrease of the fumarolic flux. Since June 2022, the Baia di Levante manifestations were characterized by a dramatic increase in the H<sub>2</sub>S, H<sub>2</sub>, and CO concentrations whereas those of CH<sub>4</sub> decreased. Such compositional changes were marked by the occurrence by seawater whitening events caused by enhanced emission of sulfur-rich fluids. In this period, the temperature, as well as the SO<sub>4</sub>/Cl ratios and the concentrations of dissolved CO<sub>2</sub> in the thermal wells of the Vulcano Village, also increased. The chemical-physical evolution of the crater fumaroles, culminated in February 2022, was likely related to a strong pulse of magmatic fluids occurred in summer 2021. The fluid reservoir feeding the discharges at the periphery of the magmatic fluid plumbing system, the latter being directly connected to the crater fumaroles, seems to have buffered the pulse until May 2022, when the heat and magmatic fluids fed by the deep source partially bypassed the hydrothermal aquifer. Further observations related to the continuation of the geochemical and geophysical monitoring of the Vulcano hydrothermal-magmatic system in the next months could provide fundamental insights to confirm the decline of the volcanic crisis as suggested by the recent evolution of the crater gas chemistry.

## Geochemical characterization of cold and thermal waters from the Pontina Plain (Latium region, Italy)

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*Keywords:* fluid geochemistry, thermal and cold waters, gas emissions.

The Pontina Plain (central-western Italy) is a large NW-SE-oriented flat area covering a surface of about 1,300 km<sup>2</sup> between the Lepini and Ausoni carbonatic mountain ranges, the southernmost deposits of the Colli Albani Volcanic District and the Tyrrhenian Sea.

A classical investigation on the chemical and isotopic features of thermal and cold springs was carried out to evaluate the geochemical processes controlling fluids from the shallow-to deep-aquifers and the geothermal potential of the area. The geochemical survey is still underway. Up to date, 88 water samples and 6 gas emissions from bubbling pools were sampled and analyzed.

Preliminary results indicate a meteoric origin of the collected waters. The chemical composition reflects various fluid sources and water-(gas)-rock interaction processes. Basal springs emerging from the carbonate outcrops have temperatures from 13.3 to 24.2°C and show a variable composition from low-TDS Ca-HCO<sub>3</sub> type, which is typically observed in fluids interacting with carbonate rocks, to unexpectedly high-TDS (up to 3,000 mg/L) Na-Cl type, where the Na/Cl ratio is approaching that of sea water. Waters from the degassing areas of Solforata di Pomezia and Tor Caldara, showing temperatures from 18.9 to 27.4°C, have the typical acid-SO<sub>4</sub> composition (pH values down to 1.5) produced by the interaction of shallow meteoric aquifers with CO<sub>2</sub>- and H<sub>2</sub>S-rich gases. Waters from the peripheral volcanic deposits of the Colli Albani, with temperatures from 13.2 to 30.5°C, generally display low TDS and a Na(K)-HCO<sub>3</sub> composition likely derived from the interaction of the alkaline volcanic rocks of this area, while those from the sedimentary deposits of the plain are characterized by variable TDS values (from 250 to 2,000 mg/L), temperatures (from 9.1 to 21.2°C) and compositions, likely related to the particularly high heterogeneity of the local lithological types.

Gas composition is dominated by CO<sub>2</sub> (from 812 to 977 mmol/mol). As commonly observed in the Tyrrhenian sector of central-southern Italy, CO<sub>2</sub> is mainly produced by thermo-metamorphic decarbonation occurring within carbonate-evaporite reservoirs, with minor contribution from mantle degassing. A dominant crustal source is also indicated by the relatively low helium isotopic values (0.19-0.91 Ra). Methane and light hydrocarbons in bubbling gases are mostly thermogenic, while a significant fraction of biogenic dissolved CH<sub>4</sub> was detected in most of the waters discharging from the sedimentary domain of the plain.

Deep temperature estimations using geothermometers both in the liquid and gas phases are strongly influenced by near surface secondary processes. Reliable estimations are only provided by the Na-K-Mg system, suggesting equilibrium temperatures from 50 to 70°C for partially equilibrated Na-Cl waters, which are consistent with the maximum temperature measured in two 1000 m-deep wells (about 50°C) drilled in the plain in the 1970s for geothermal purposes.

## Physico-chemical characterization of fluids discharged by natural manifestations in Le Biancane area (Larderello geothermal field, Italy)

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*Keywords:* fluid geochemistry, gas analysis, Larderello geothermal field.

The Larderello geothermal field is characterized by a vapor-dominated reservoir producing superheated steam, which began to be used for electricity production more than one century ago. In this field there are different areas where permeable reservoir rocks outcrop and meteoric water can infiltrate. Among these, there is the Le Biancane area, where the carbonate formations of the Tuscan Nappe outcrop, which is characterized by the presence of thermal manifestations, such as fumaroles, steaming ground and diffuse degassing.

Very poor chemical and isotopic data are available for fluids discharged by these natural manifestations (in particular for fumaroles), making difficult to provide a detailed physical-chemical characterization of the local hydrothermal/geothermal system, especially considering its evolution during the last decades of production and reinjection processes. This work tackles this issue, trying to provide information regarding the origin of fluids, the thermal equilibrium conditions reached by the fluids at depth and the occurrence of secondary processes, such as phase separation and/or condensation at shallow level.

Starting from gas samples taken from fumaroles located in the Le Biancane area and in the nearby zones, chemical and isotopic analyses have been carried out. These samples have been analysed for major and trace components. Among them, particular attention is addressed to the determination of new trace sulphur-bearing compounds, such as COS, CH<sub>3</sub>HS and CS<sub>2</sub>, which can contribute to define new T and P geo-indicators. They are determined using the GC-ICP-MS (gas chromatography-inductively coupled plasma-mass spectrometry), one of the most useful hyphenated method (Michalski et al., 2006; Easter et al., 2010), combining the high separation capacity of the GC with the high sensitivity and specificity of the ICP-MS. Chemical compounds containing C, S and O are abundant in volcanic/geothermal gases and they can be detected at low levels via GC-ICP-MS technique. First applications of this technique in volcanic-geothermal gases are recently described by Lelli et al. (2023).

In this work we present the results of gas sample analyses, providing new insight on Le Biancane area in terms of origin of fluids and equilibrium conditions reached at depth by the fluids in this part of the geothermal field.

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## Preliminary estimation of the CO<sub>2</sub> output at Solinari (Florina Basin, Greece)

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*Keywords:* geogenic degassing, carbon dioxide, stable isotopes.

The Florina basin is one of the major degassing areas of mainland Greece (Daskalopoulou et al., 2019a). In the area, many cold CO<sub>2</sub>-rich gas emissions are present as a bubbling free-phase in groundwater (both springs and wells) and soil gases. Quaternary volcanism along with the geological and geodynamic regime of the basin, created the ideal conditions for CO<sub>2</sub> accumulation in vertically stacked reservoirs. One of these, industrially exploited by the company Air Liquide Greece, produces 30,000 t/a of CO<sub>2</sub> (Daskalopoulou et al., 2019a). Diffuse degassing areas are also known in this basin. The results of a soil CO<sub>2</sub> flux prospection in one of these areas are presented here. The area is known as Solinari and is located at the southern border of the Florina basin, about 2.5 km NW of the village of Xino Nero. In this area many strongly degassing spots are present. These can be recognised during wet periods by vigorous bubbling in pools accumulating rainwater or during vegetative periods by absent or stunted vegetation. Gases are mainly composed of CO<sub>2</sub> (up to 99%) with a C isotope composition around -1.5 ‰ (vs. VPDB). Helium isotopes indicate a crustal origin with a small mantle contribution (0.2 R/R<sub>A</sub>). In April 2023 about 150 flux measurements were made covering a surface of about 11,000 m<sup>2</sup>. The highest fluxes are in the order of 10<sup>6</sup> g/m<sup>2</sup>/d. The total estimated CO<sub>2</sub> output of this area is in the order of 500 t/a, comparable with the output estimated in the area of Giatsovo close to the town of Florina (Daskalopoulou et al., 2019b).

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## Soil diffuse CO<sub>2</sub> flux emission from Nea Kameni (Santorini), 2015-2022

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*Keywords:* Nea Kameni (Santorini), soil diffuse CO<sub>2</sub> flux, volcanic risk.

Geochemical variations in the activity of quiescent volcanoes are viewed with considerable interest in terms of any early recognition of precursors and are, therefore, of interest for the mitigation of the volcanic risk. Diffuse soil CO<sub>2</sub> flux measurements are an important tool in monitoring programs to be undertaken during volcanic surveillance. Important clues in understanding the evolution of volcanic activity can indeed be provided by CO<sub>2</sub> flux pre-, during and post-unrest phases. Santorini is an active volcanic system of the South Aegean Active Volcanic Arc (Greece), which extends from Methana peninsula to the west to Nisyros Island to the east. Santorini consists of a small archipelago of five islands: Thera, Thirasia, and Aspronisi, which constitute a ring structure delimitating the Santorini caldera, and Palea Kameni and Nea Kameni which emerge inside the caldera centre. Between January 2011 and April 2012, Santorini was affected by a volcanic unrest recognized by the onset of detectable seismicity, caldera-wide uplift and chemical changes in the fumarolic gas discharges. Most earthquakes occurred along the NE–SW-oriented Kameni tectonic line, corresponding to the preferential vent location of the historical eruptions at Nea Kameni. The unrest also showed an increase in the CO<sub>2</sub> diffuse fluxes from the soil, which decreased once the unrest was over. In this work, we report the results of the temporal evolution of soil diffuse degassing CO<sub>2</sub> at Nea Kameni that have been carried out on an annual basis, during the dry season, in 2015 and 2018, 2019, 2021 and 2022 (in 2020, due to the sanitary emergence, no measurements were performed). The CO<sub>2</sub> flux measurements were carried out in 87, 79, 108, 104 and 90 sites to cover about 34,000, 24,000, 40,000, 58,000 and 27,500 m<sup>2</sup>, respectively. In the five campaigns, the soil CO<sub>2</sub> fluxes varied from 0.09 to 2,621 g m<sup>-2</sup> day<sup>-1</sup> (mean value: 247 g m<sup>-2</sup> day<sup>-1</sup>), from 8.98 to 27,672 g m<sup>-2</sup> day<sup>-1</sup> (mean value: 1,555 g m<sup>-2</sup> day<sup>-1</sup>), from 0.09 to 1,994 g m<sup>-2</sup> day<sup>-1</sup> (mean value: 167 g m<sup>-2</sup> day<sup>-1</sup>), from 0.13 to 5,253 g m<sup>-2</sup> day<sup>-1</sup> (mean value: 170 g m<sup>-2</sup> day<sup>-1</sup>), and from 0.04 to 3,953 g m<sup>-2</sup> day<sup>-1</sup> (mean value: 268 g m<sup>-2</sup> day<sup>-1</sup>), in May 2015, October 2018, July 2019, October 2021 and September 2022, respectively. These measurements were then used to estimate the total CO<sub>2</sub> output, which resulted to be varying between 5.9 and 11 ton/day although in 2018 an anomalous output was recorded, i.e. 32 ton/day. By comparing the CO<sub>2</sub> outputs computed in this study with those carried out during the unrest, those obtained in 2018 were in the same range whereas the others were an order of magnitude lower. It is to mention that in 2018, no significant changes in gas chemistry and seismicity were recorded. Although more data are to be acquired, we may speculate that the variability of the soil diffuse CO<sub>2</sub> at Santorini can be related to a waving and waning process after the 2011-2012 unrest.

## Geochemical characterisation of hydrothermal waters from Mila Province (north-eastern Algeria)

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*Keywords:* Algeria, hydrothermal system, water.

North-eastern Algeria is characterised by the occurrence of several hydrothermal surface manifestations, including thermo-mineral springs, gas vents and hydrothermal altered soils. Despite this area is nowadays considered in Algeria as the most suitable one for geothermal purposes, extensive and detailed hydrogeochemical surveys have not actually been carried out so far. Reported here is a systematic and detailed study focussed on the geochemical features of thermal and cold springs from Mila Province. The study area (about 6,000 km<sup>2</sup>) lies on the Kebir Rhumel basin, which is characterised by a complex geological setting, consisting of alternate sequences of limestone, clayey and marly formations and evaporites, affected by a complex tectonic due to the conjugation of folds and faults of various age and style. A total of 50 samples were collected from cold and thermal springs, wells and boreholes, for chemical and isotopic analysis of water and dissolved gases. The chemical compositions of water samples range over six hydrochemical facies: Ca<sup>2+</sup>-HCO<sub>3</sub><sup>-</sup> (25 water samples); Na<sup>+</sup>-HCO<sub>3</sub><sup>-</sup> (2); Ca<sup>2+</sup>-SO<sub>4</sub><sup>2-</sup> (9); Na<sup>+</sup>-SO<sub>4</sub><sup>2-</sup> (4); Ca<sup>2+</sup>-Cl<sup>-</sup> (2); Na<sup>+</sup>-Cl<sup>-</sup> (8). Water temperatures range from 12 to 52°C, whilst pH values are mostly from 5.5 to 7.9. Overall, the total dissolved solid (TDS) content increases from HCO<sub>3</sub><sup>-</sup> (ranging from 385 to 1,400 mg/L) to SO<sub>4</sub><sup>2-</sup> (260 to 5,000 mg/L) to Cl<sup>-</sup>-dominated waters, the latter exhibiting values up to 37,000 mg/L. The Cl<sup>-</sup>/Br<sup>-</sup> ratios are relatively high (mostly from 700 to 13,000) and display a good correlation with the TDS contents, suggesting interaction with evaporite deposits. Relatively high concentrations of Li, B, Al, Mn, Fe, Zn, As, Sr, Ce and Ba seem to support this hypothesis. At increasing TDS, the chemical composition of dissolved gas switches from N<sub>2</sub>-dominated to CO<sub>2</sub>-dominated, the latter being strongly enriched in He (i.e., He/Ne ratios up to 5) presumably due to the addition of crustal <sup>4</sup>He that may reflect a deep hydrological circulation. The δD-H<sub>2</sub>O and δ<sup>18</sup>O-H<sub>2</sub>O values suggest a common meteoric origin for both cold and thermal waters. Slight positive <sup>18</sup>O-shifts exhibited by some samples with intermediate TDS are likely due to evaporation, although a <sup>18</sup>O enrichment due to water-rock interaction cannot be excluded. As also observed in other hydrothermal systems belonging to Apennine–Maghrebide fold-and-thrust belt, the different chemical facies of the waters from Mila Province are related to the involvement of different lithologies along the fluid hydrological circulation, although evaporite formations seem to play a major role.



## Peculiar bulk stable isotope composition of methane in high-temperature volcanic gases from Vulcano Island (Italy)

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Keywords: volcanic gases, methane, stable isotopes.

Active volcanoes often discharge hot ( $T \gg 100^\circ\text{C}$ ) magmatic gases whose original composition has been modified through partial interaction with an externally fed hydrothermal system. Seminal works suggested that methane ( $\text{CH}_4$ ) in these volcanic discharges may provide useful information on the interplay between deep magmatic gases and shallow circulation of hydrothermal fluids assuming that the methane in these discharges predominantly derives from the shallow hydrothermal system. However, the origin of  $\text{CH}_4$  in high-temperature volcanic gases and the factors exerting control on its abundance and stable isotope composition are still largely unknown. Here, we present the abundances and stable isotopic composition of  $\text{CH}_4$  in hot ( $99\text{--}387^\circ\text{C}$ ) volcanic gases from the La Fossa volcanic crater of Vulcano Island (Southern Italy).

Our investigation reveals low ( $<1.5 \mu\text{mol/mol}$ )  $\text{CH}_4$  concentrations and an extraordinarily large variability in  $\text{CH}_4$  stable isotopic composition, with  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$  values being positively correlated and varying from  $-35$  to  $-9.2\text{‰}$  and  $-670$  to  $-102\text{‰}$ , respectively. Notably,  $\text{CH}_4$  isotopes measured at Vulcano almost encompasses the global-scale variability observed in natural fluids, with  $\delta^2\text{H}$  values  $\leq -500\text{‰}$  being the first ever reported in nature. Gases showing extremely negative  $\delta^{13}\text{C}\text{-CH}_4$  and  $\delta^2\text{H}\text{-CH}_4$  values systematically display higher  $\text{CH}_4$  abundances.

We propose two possible scenarios in order to explain the observed huge variation in  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$ : (1) mixing of isotopically light  $\text{CH}_4$  of possible magmatic origin with  $^{13}\text{C}$ - and  $^2\text{H}$ -enriched  $\text{CH}_4$  of thermogenic origin provided by the seawater-sourced hydrothermal envelope surrounding the La Fossa cone; (2) post-genetic removal and isotopic alteration of isotopically light, magmatic  $\text{CH}_4$  occurring during the ascent of volcanic gases. Comparing our dataset with available isotopic data from naturally occurring and artificially produced  $\text{CH}_4$ , a thermogenic origin for the magmatic  $\text{CH}_4$  seems unlikely. We postulate that the magmatic  $\text{CH}_4$  end-member may have formed via kinetically-controlled abiotic synthesis through  $\text{CO}$  (or  $\text{CO}_2$ ) hydrogenation reactions in the hot ascending gas phase, possibly at close-to-magmatic temperatures. Further investigations of methane in high-temperature volcanic gases are necessary to test this hypothesis.

## **Modeling the priming mechanism of phreatic eruptions: numerical integration of 1D- and 2D-systems**

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*Keywords:* phreatic eruptions, numerical modeling.

Phreatic eruptions are non-magmatic eruptions in which hydrothermal fluids hosted within the upper crust are heated and over-pressurized by interacting with the heat and gases released from a deeper magmatic emplacement but without the direct contact between magma and reservoir fluids.

As these eruptions are impulsive events and show no (to the present date) clear precursory signals, the risk associated with such events greatly increases, possibly leading to fatalities (e.g. the 2016 Ontake and 2019 Whakaari/White Island eruptions). To the present date, no forecast of phreatic eruption has been successful. Understanding the physics of such systems will eventually help the community to develop monitoring strategies to mitigate the associated risk.

In this work we propose a physical model for the priming mechanism of phreatic eruptions. We employ the multiphase multicomponent transport theory treating the hydrothermal fluids as a non-isothermal multicomponent and multiphase system flowing in a porous medium. The fluid velocity is described using Darcy's law for multiphase fluids. The equilibrium between phases is modeled minimizing the Gibb's free energy of the system.

We present the results of the numerical integration of a few simplified applications in 1D and 2D axisymmetric geometries of this model obtained using the finite element numerical method to cases, relevant for natural systems. The results and the development of this will give us insights on the physics of the phenomenon and likely can help to develop strategies for risk mitigations.

## Geochemical features of fumarolic discharges from Alitar volcano (Chile): Insights into fluid source(s) and implications for volcanic surveillance

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*Keywords:* fluid geochemistry, geochemical monitoring, fumarolic gas.

Alítar (23.1377°S; 67.6414°W; 5,337 m a.s.l.) is a 5,300 m high composite stratovolcano, whose volcanic products mostly consist of Pliocene-Pleistocene lavas of andesitic to dacitic composition, placed on the Upper Miocene rhyolitic La Pacana and the Pliocene dacitic Atana ignimbrites. No historical eruptions have been reported for this volcano, which is currently characterized by persistent fumarolic activity from the northern sector of a parasite 500 m wide maar occurring on the SW flank of the volcano, where sulfur deposits were exploited in the 1950's. Several thermal pools with bubbling gases occur along a small, NS-oriented creek 200 m west of the maar. In this study, the chemical and isotopic (noble gases and <sup>13</sup>C/<sup>12</sup>C ratios in CO<sub>2</sub> and CH<sub>4</sub>) compositions of gases from the Alitar fumaroles and bubbling pools sampled in 2018, 2019 and 2023, are presented and discussed. The main aim is to construct a theoretical geochemical model of fluid source(s) and plumbing system. The 2018-2023 data were also compared to published analytical results of gases collected from the same areas in 2007, to obtain information on the recent evolution of the degassing activity of this volcano. The vapor-dominated fumarolic fluids are characterized by significant concentrations of hyperacid gases from magma degassing (SO<sub>2</sub>, HCl, HF), which contrast with the relatively low temperature (up to 85°C) of these emissions, and comparable amounts of reduced gas species (H<sub>2</sub>S, H<sub>2</sub>, CO, CH<sub>4</sub>, C<sub>2</sub>-C<sub>3</sub> hydrocarbons) typical of a hydrothermal environment. Differently, the bubbling gases are dominated by CO<sub>2</sub>, followed by N<sub>2</sub>, H<sub>2</sub>S, CH<sub>4</sub>, and H<sub>2</sub>, with no detectable magmatic-related gases. The d<sup>13</sup>C-CO<sub>2</sub> values of the fumaroles are slightly lower than those of mantle CO<sub>2</sub>, whereas the d<sup>13</sup>C-CH<sub>4</sub> values are consistent with those of thermogenic gases, confirming a mixed magmatic-hydrothermal fluid source. Accordingly, the R/Rc values indicate the occurrence of a significant fraction of mantle component, only partially affected by a crustal source. The analytical dataset depicts an intriguing temporal evolution, although the observations are quite discontinuous, and, consequently, a detailed reconstruction of the events that affected this volcano in the last 16 years is quite difficult. However, it is a matter of fact that the strong increases (up to one order of magnitude) shown by both gases from magmatic degassing (SO<sub>2</sub>, HCl, HF) and those favored by temperature (H<sub>2</sub>, CO, and light alkenes), accompanied by a decrease of CH<sub>4</sub>, univocally suggest some disturbance, possibly occurred between 2010 and 2018, on the balance between the deep magma source and the overlain hydrothermal reservoir. The poor information on the eruptive style and the age of the most recent products of this volcano, and more in general, the lack of dedicated installations for the detection of the geophysical signals, currently prevents any reliable hypothesis on the current status of the activity of Alitar volcano. Notwithstanding, the promising results from these geochemical surveys encourage the development of a systematic survey strategy, possibly adopting a multidisciplinary approach, to shed light on the mechanisms regulating the evolution of the fumarolic fluid chemistry and to evaluate possible implications for volcanic hazard.

## **Preliminary results on atmospheric deposition monitoring during the recent volcanic unrest at Vulcano Island (Italy)**

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*Keywords:* trace elements, rainwater, Vulcano Island.

Volcanoes are an important source of gas and particles into the atmosphere, during the eruptive periods or even during passive degassing activity. The study of volcanic gases is a robust geochemical tool to understand, monitor and predict the behaviour of volcano activity, but it is also important to evaluate the effects of volcanic emission on a local and regional scale. The study of the chemistry of atmospheric deposition can provide important information in this regard. Vulcano Island is a stratovolcano located in the southernmost sector of the Aeolian archipelago (Sicily). Since the last eruption occurred in 1888-1890, volcanic emissions are characterized by intense fumarolic activity localized on the northeastern rim of La Fossa crater. Several episodes of volcanic unrest have occurred over the past 130 years, and the most recent period of crisis was between 2021 and 2022. It was characterised by the increasing fumarole temperatures and gas fluxes, shallow long-period seismicity and diffuse soil degassing around the main crater. This study reports on the chemical composition of rainwater samples collected from November 2021 to January 2023, during the last unrest period of Vulcano island. Fifteen rainwater samples were collected through a network of three bulk collectors; two of them were placed inside the fumarolic field, and the last one was located near Vulcano Porto. Rainwater samples were analysed for major and trace elements contents, and physicochemical parameters were also measured. The pH of rainwater collected near the summit area reaches very low pH values (min 1.63), with a mean value of 2.29, which is significantly lower respect to the mean value at Vulcano Porto (5.7). The concentrations of dissolved solutes in rainfall (expressed as Total Dissolved Solids) are inversely proportional to pH and reach extremely high values in the most acidic samples (up to 1133 mg/L). The most influenced samples by the volcanic emissions are strongly enriched in sulfate, chlorine and fluorine as a direct result of the dissolution of acid gases in rainwater. In addition to the major species, high concentrations of potentially toxic trace elements (Al, As, B, Cd, Fe, Pb, Sb, Te, Ti, Tl, and REE) were found. At the most distal site (Vulcano Porto) the impact of volcanic emissions on rainfall is much less pronounced and the dominant source is mainly related to marine aerosol. These preliminary results on trace element concentrations in rainfall at Vulcano highlight the importance of these studies to fully evaluate the potential impact of volcanic emissions on rainwater and consequently on other environmental matrices (e.g. soils and plants), especially during a period of intense outgassing.

## Geochemical features of Volatile Organic Compounds (VOCs) in punctual and diffuse hydrothermal manifestations across the Sabatini Volcanic District (Latium, Italy)

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**Keywords:** volatile organic compounds, hydrothermal systems, fluid geochemistry.

Volatile Organic Compounds (VOCs) ubiquitously occur in hydrothermal gases emitted from both punctual vents and diffuse soil degassing. Their origin is mainly ascribed to the presence of organic matter embedded in the geological materials. The physicochemical features of hydrothermal reservoirs (e.g. T, redox, sulfur fugacity) shape the speciation of organic gaseous compounds. Once at shallow depth, deep-sourced VOCs encounter sharply different physicochemical conditions and microbial communities able to exploit VOCs as carbon substrates. Hence, in such areas, the composition of the released VOCs can be regarded as a chemical cocktail resulting from the co-occurrence of multiple physical, chemical and biological processes acting from the deep hydrothermal reservoirs up to the soil-atmosphere interface.

The Sabatini Volcanic District (SVD; Latium, Italy) offers an ideal large-scale natural laboratory to investigate the response of VOCs speciation from punctual and diffuse emissions to variable conditions controlling the feeding hydrothermal reservoir. In the whole SVD, a regional hydrothermal system supplies the fluid discharges occurring from the Apennines to the coastline. Nevertheless, a geochemical gradient in the composition of both thermal waters and gas emissions was evidenced by Cinti et al. (2017) moving from the eastern to the western SVD sectors.

In this study, we present the results from sampling campaigns of gas vents and soil gases from Caldara di Manziana (MZ) and Solforata di Nepi (NP), sited in the western and eastern SVD sectors, respectively. The study aimed to investigate and compare the VOCs speciation in fluids emitted at MZ and NP to highlight similarities and dissimilarities between the two areas, exploring the capability of soil gases to mimic the compositional features of the feeding hydrothermal system.

Sharp differences in both the abundance and distribution of VOCs observed in punctual gas vents from the two sites were also reflected in the composition of soil gases. The MZ gas vent was enriched in CH<sub>4</sub> and H<sub>2</sub>S, accompanied by high abundances of S-bearing compounds and alkenes, testifying reducing conditions and high temperature of the hydrothermal reservoir. Conversely, the NP gas vent showed an overall abundance of VOCs, mainly represented by alkanes (both short and long chains) and an enrichment in O-bearing compounds with respect to the MZ gas, pointing to the involvement of a larger fraction of fresh organic material and oxygen availability, in line with the hypothesis of a feeding system affected by larger mixing with recharging meteoric waters (Cinti et al., 2017). Despite the occurrence of shallow secondary processes that partially altered their composition with respect to punctual gas vents, soil gases collected at 40 cm depth were able to keep track of the peculiar compositional features of the feeding hydrothermal fluids in the two SVD sectors.

Cinti D., Tassi F., Procesi M., Brusca L., Cabassi J., Capecchiacci F., Delgado Huertas A., Galli G., Grassa F., Vaselli O. & Voltattorni N. (2017) - Geochemistry of hydrothermal fluids from the eastern sector of the Sabatini Volcanic District (central Italy). *Appl. Geochem.*, 84, 187-201. <https://doi.org/10.1016/j.apgeochem.2017.06.014>.

## **EMOTION-Project for creating a geochemical web portal useful to accelerate the geothermal exploitation in central-northern Italy**

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*Keywords:* geothermal prospection, geochemical database, low-medium-high temperature resources.

An ever-increasing demand of energy coupled with environmental issues, that are two of the main global concerns nowadays, give a strong pulse to new energy strategies involving the use of renewable and sustainable sources, including geothermal ones. The geothermal resource in Italy is significant in the European context, although only the high enthalpy systems in Tuscany are currently fully exploited. In the past decades, several prospections were carried out by different private companies and scientific institutions, mainly through drilling activities, seismic and geochemical surveys. These prospections provided a draft of the geothermal potential of the Italian territory, especially for the central-southern Tyrrhenian margin, where the main hydrothermal areas, volcanoes and impressive geothermal manifestations are located. In this context, the three years EMOTION project (GeochemICAL characterization of fluid manifestations in central-northern Italy for geOTHERmal assessment and development of the geothermal fluid natIONAL web portal), led by INGV and funded by MUR (Ministero dell'Università e della Ricerca), aims to provide a detailed geochemical characterization of the manifestations of geothermal interest (thermal springs, mineral waters and gas emissions) in central-northern Italy (from Tuscany and Umbria northward) including published data and new acquisitions. In detail, the different hydrothermal systems occurring in the large study area of the EMOTION project will be investigated to gather information on: (I) the minimum temperature of the fluid reservoirs; (II) the chemical features of the thermal fluids; (III) the chemical physical processes controlling the chemistry of fluids circulating within the hydrothermal plumbing systems. In light of this, the ambition of EMOTION is to support the geothermal exploration for low, medium and high temperature (enthalpy) resources, especially in the early stages of the potential assessment. As a final goal, an open-access, geochemical web portal of all Italian geothermal manifestations will be made available, also including the previously investigated geothermal manifestations of central-southern Italy.

In this framework, we will show the project work-flow and the preliminary geochemical critical review for Tuscany and Friuli Venezia Giulia, highlighting the missing information and the planned new sampling. The objectives of EMOTION, from the implementation of the geothermal information in the central-northern part of Italy to the easy access to the geochemical data, will facilitate the geothermal exploration, especially in the early stages, and will hopefully contribute to the enhancement of the exploitation of geothermal resources and other strategic materials throughout the national territory.



## **S10.**

### **Geochemistry of sediments and sedimentary ores: addressing paleogeographic restoration and georesources exploration**

#### *CONVENERS AND CHAIRPERSONS*

*Roberto Buccione (Università della Basilicata)*

*Rabah Kechiched (Ouargla University, Algeria)*

*Giovanni Mongelli (Università della Basilicata)*

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## Detrital quartz from NE Adriatic flysch basins: an FTIR and trace elements provenance study

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Keywords: quartz, provenance, flysch.

The flysch basins of the North-eastern part of the Adria Plate are represented by several elongated turbiditic sedimentary units, which are filled by carbonatic and siliciclastic material. In this study we focus on the Julian, Brkini, and Kvarner Islands basins (Italy, Slovenia, and Croatia). The carbonatic part is thought to derive by the disassembly of the nearby carbonate platforms, while the provenance of the siliciclastic material is still a matter of debate. To fill this gap in knowledge and identify the possible source of the siliciclastic portion of the filling sediments, this work presents a new quartz analyses dataset. Quartz can incorporate chemical impurities as defects in the crystal lattice (Al, Li, B, 4H), which are coupled to OH groups and form specific IR absorption bands. These so called OH-defects are correlated to petrogenetic conditions during crystal growth, and they may be used as a provenance tool. The amount of Al-related defects can be used to discriminate between a igneous (> 5 ppm) and a non-igneous source (< 5 ppm) (Stalder, 2014). In this study, FTIR spectroscopy of quartz has been used to investigate the sample set, with interest to its OH defect speciation and content. Julian Basin's quartz show differences in the supply source within the succession: the oldest ones (JB5 and JB1) show an almost 1:1 ratio between igneous and non-igneous origin; samples JB10 and JB17 show a change with a predominantly igneous source; the youngest samples (JB23 and JB26) have a neat predominance of a non-igneous source (Bernardi et al., 2022). Brkini samples show again a difference in the source with the older BK41 having a more igneous source than the younger BKNV. Samples from the Kvarner Islands Basin indicate a predominantly non-igneous source (DOB) while in RAB1 the non-igneous source seems to be clearly prevalent, even if only few clear spectra were obtained.

Trace elements such as Al, Li, B, Ge, Ti, and others have been analysed and quantified by LA-ICP-MS on the same grains. Regarding the Al trace content, it is important to notice that it follows the Al-related OH defects' trend, demonstrating the possible existence of a correlation between the two analytical methods. Other classifications based on trace elements demonstrate different behaviour within the quartz set, confirming the trend displayed by the OH-defects method.

Bernardi F., Skogby H. & Lenaz D. (2022) - OH-defects in detrital quartz grains from the Julian Basin (NE Italy and Slovenia): a Fourier Transform Infrared study. *Geosci.*, 12, 90. <https://doi.org/10.3390/geosciences12020090>.

Stalder R. (2014) - OH-defects content in detrital quartz grains as an archive for crystallisation conditions. *Sediment. Geol.*, 307, 1-6. <https://doi.org/10.1016/j.sedgeo.2014.04.002>.

## **Geochemical features of southern Apennines shales (Italy): constraints on paleoweathering and provenance**

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*Keywords:* geochemistry, Apennine shales, paleoweathering and provenance.

The southern Apennines (Italy) chain is a fold-and-thrust belt mainly derived from the deformation of the African-Apulian passive margin where shallow-water, basinal and shelf-margin facies successions including fine-grained sediments, occur. Here we provide a review of the geochemistry of Meso-Cenozoic shales from the Lagonegro Basin to elucidate provenance and paleoweathering. The different suites of these shales are dominated by 2:1 clay minerals and are Fe-shales and shales. R-mode factor analysis suggests Ti, Al, and LREE (F1) and K<sub>2</sub>O-MgO (F2) covariance, both likely related to the illite ® smectite ® kaolinite evolution during weathering. HREE and Y are distributed by phosphate minerals suggesting LREE/HREE fractionation. The CIA paleoweathering proxy rules out non-steady state weathering conditions and indicates source area was affected by moderate to intense weathering. The paleoprecipitation values derived by the CIA-K and CALMAG indices show median values in the 1214-1610 mm/y range. The Eu/Eu\*, Sm/Nd, and Ti/Al provenance ratios point toward an UCC-like source excluding any mafic supply and suggesting the Lagonegro Basin was connected, through a southern entry point, with the African cratonic area. However, the Eu/Eu\* median value of the southern Apennine shales is shifted toward the value of the Archean shales, possibly indicating a less differentiated component. This is consistent, in many samples, with the value of the (Gd/Yb)<sub>ch</sub> ratio, suggesting the shales likely incorporated ancient sediments derived from African Archean terranes through a cannibalistic process.

## Image analysis on ore deposits: The case of southern Italy Cretaceous karst bauxites

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Keywords: karst bauxites, image analysis, fractal dimension.

Recently, it has been stated that image analysis and its integration with other analytical techniques could represent an innovative and useful tool for karst bauxite exploration. This study presents the results of image analysis performed on several karst bauxite deposits from Southern Italy. The growth of sub-spherical concretions in bauxite can be modeled using a molecular diffusion pattern (Buccione et al., 2016; Mongelli et al., 2016). The aggregation of small particles to form larger structures is important in a wide range of natural processes, including mineral formation, and the aggregates can be described in terms of fractal geometry (Meakin, 1991). The growth of ooids within a bauxite matrix can be regarded as the growth of fractal aggregates. In southern Italy, karst bauxites mainly occur in Apulia and Campania regions. The D values for the Apulia bauxite deposits are close to values associated with experimental diffusion-limited aggregation (DLA) models ( $D = 1.62 \pm 0.4$ ), where particles are added to a growing aggregate via random trajectories originating from outside the space containing the growing cluster. The Campania bauxite deposits, instead, have fractal dimension higher than those of the Apulia bauxites and close to the fractal dimension associated with the diffusion-limited cluster aggregation processes ( $1.75 \leq D \leq 1.80$ ), where particles join together to form small clusters that continue to move and join other clusters to form larger and larger clusters. It is generally assumed that the Campania bauxites ( $D$  median = 1.85) formed during longer emersion events with respect to the Apulia bauxite deposits ( $D$  median = 1.63). The karst bauxite from Matese Mts. formed during the Albian-Lower Coniacian, whereas the Caserta district bauxite formed from Albian to Cenomanian. Recent studies confirmed that these deposits are the pristine bauxite from which formed the para-autochthonous deposits of Vitulano. The formation of the Murge and Gargano deposits is related to the Cenomanian-Late Turonian exposure of the Apulian carbonate platform, while the primary Salento-type bauxite deposit likely formed during an upper Campanian exposure event. This suggests that during long-lasting sub-aerial events, promoting concretions formation in bauxite, the diffusion-limited cluster aggregation processes can prevail over the simpler diffusion-limited, which is instead responsible for ooids formation during time-limited exposure events. Furthermore, the correlation between image analysis and compositional features can provide information on the genesis and conditions during bauxite formation.

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Mongelli G., Buccione R., Gueguen E., Langone A. & Sinisi R. (2016) - Geochemistry of the Apulian allochthonous karst bauxite, Southern Italy: distribution of critical elements and constraints on Late Cretaceous Peri-Tethyan paleogeography. *Ore Geol. Rev.*, 77, 246-259.

## Data-centric approach for predicting critical metals distribution: heavy rare earth elements in cretaceous Mediterranean-type karst bauxite deposits, southern Italy

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*Keywords:* machine learning, critical metals, bauxite.

In recent years a striking challenge regarding natural resource is to guarantee supplies of Critical Metals (CMs) that perform essential functions in modern engineered materials but are subject to supply risks or concerns about long-term availability.

In the last decade, several efforts have been devoted to the geochemical factors affecting the distribution of CMs in karst bauxites residual deposits hosted in exhumed carbonate rocks, forming in humid tropical to sub-tropical climates. Karst bauxites, due to high concentrations of Al-bearing mineral phases and their potential as a source of metals critical to industry may have significant economic value. Among the CMs, the REEs are largely employed in new technologies and emerging electronics.

The distribution of trace elements, as well as the mineralogy and the texture, of Mediterranean-type karst bauxites in southern Italy, have been extensively studied in the last two decades and, although these karst bauxite deposits do not have a particular economic relevance, they are considered analogous of valuable economic bauxite deposits occurring in other parts of the world (Mongelli et al., 2017).

Recently, there is an increasing interest in exploring the usefulness of machine learning applications devoted to geochemically based datasets (e.g. He et al., 2022; Nathwani et al., 2022) although, as for the Authors' knowledge, no international literature exists yet facing with geochemical exploration for CMs in bauxite ores. With this in mind, we present here, for the first time, a machine learning arrangement aiming to find the proper input, limited to major elements, for predicting the HREEs' distribution in southern Italy karst bauxite deposits. This approach can facilitate to assessment of different concentration clusters of REEs from historical measured data and can provide a valuable tool for exploration in similar deposits elsewhere worldwide.

The dataset compiled for this study was derived from previously published data and includes 111 samples collected in 6 different deposits throughout southern Italy and having chemical composition mostly made by  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{SiO}_2$ , and  $\text{TiO}_2$ . Geochemical data was utilized to develop two "tree-based" Machine Learning (ML) algorithms, Random Forest (RF) and Extreme Gradient Boosting (XGBoost), that varied their inputs to create a model using a data-centric AI approach. The dataset is divided into 80% of data records making up a training subset and 20% of data records making up a test subset unseen by the ML models during their training. Their results were compared with a suite of statistical prediction accuracy performance metrics. It can be seen that the exclusion of the " $\text{TiO}_2$ " variable, thus a predictive model based on just  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{SiO}_2$ , is the one conducting the worst performance accuracy impact in both RF and XGBoost suggesting that  $\text{TiO}_2$  is a relevant input for predicting the HREE concentrations in karst bauxite deposits in the southern Italy districts.

He Y., Zhou Y., Wen T., Zhang S., Huang F., Zuo X., Ma X. & Zhu Y. (2022) - A review of machine learning in geochemistry and cosmochemistry: Method improvements and applications. *Appl. Geochem.*, 140, 105273.

Mongelli G., Boni M., Oggiano G., Mameli P., Sinisi R., Buccione R. & Mondillo N. (2017) - Critical metals distribution in Tethyan karst bauxite: the Cretaceous Italian ores. *Ore Geol. Rev.*, 86, 526-536.

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## Geochemistry and mineralogy of bauxite residues (red muds) from Porto Vesme (Sardinia): from disposal material to new resource

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**Keywords:** bauxite residues, Bayer process, critical metals.

In last decades, there is a growing and relevant interest for bauxites since they represent the main source of aluminum and concentrate several minor critical metals (Mongelli et al., 2017; 2021). The aluminum production is based on the Bayer process which generate high amount of residual material and great interest is now being focused on "red muds" the bauxite processed waste material. Until now, the production of red muds involved a major problem related to recovery and disposal as they also contain elements that are potentially harmful to the environment. However, it has widely reported that red muds can concentrate large amounts of valuable critical metals which can be used for several industrial, electronic and nano-technological purposes (Liu & Naidu, 2014; Borra et al., 2016). The compositional features of red muds stored in Porto Vesme (southern Sardinia) disposal sites have been performed. The aim of this work is to highlight and further detail the processes promoting the concentration of critical metals in red muds. The analytical characterization was performed in order to assess geochemical and mineralogical composition by using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and X-ray powder diffraction (XRPD) while micromorphological and micro-chemical features were provided using a Scanning Electron Microscope (SEM-EDS) at the Department of Sciences of University of Basilicata.

XRPD revealed that the main mineral phases in red muds are hematite,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>; gibbsite, Al(OH)<sub>3</sub>; boehmite, AlO(OH); anatase, TiO<sub>2</sub>; cancrinite, (Na,Ca)<sub>8</sub>(Al<sub>6</sub>Si<sub>6</sub>)O<sub>24</sub>(CO<sub>3</sub>,SO<sub>4</sub>)<sub>2</sub>\*2H<sub>2</sub>O; sodalite, Na<sub>4</sub>(Si<sub>3</sub>Al<sub>3</sub>)O<sub>12</sub>Cl and quartz, SiO<sub>2</sub>. Geochemical analysis with ICP-MS showed that major oxide composition (wt.%) is dominated by SiO<sub>2</sub> (11.9 ÷ 22.6), Al<sub>2</sub>O<sub>3</sub> (17.4 ÷ 24.9), Fe<sub>2</sub>O<sub>3</sub> (22.2 ÷ 30.3) with less abundances of MgO (0.7 ÷ 4.7), CaO (2.6 ÷ 5.9), Na<sub>2</sub>O (3.5 ÷ 11.5) and K<sub>2</sub>O (0.2 ÷ 0.7). Regarding trace elements (ppm) high concentrations of Zr, Cr, Ce, V, Sr, Ni, Zn, Ga and Y were detected. It has been observed that, among rare earth elements, Ce is the most abundant element showing abundances in the 93 to 258 ppm range. Since red muds contain high concentrations of critical metals, their reuse can be an important achievement for the valorization of these materials as opposed to their disposal.

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## Clayey sediments characterization as a useful tool to assessing the geodynamic evolution of fold-and-thrust belts: a case study of the Southern Apennines (Italy)

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Keywords: sediments provenance, paleowethering, upper Messinian.

This study aims to contributing to the reconstruction of the geodynamic evolution of the Southern Apennines fold-and-thrust belts (SA-ftb). The upper Messinian terrigenous deposits of the Monte Alpi key area were investigated using a multi-tool approaches such as X-ray diffraction, X-ray fluorescence, and both optical and scanning electron microscopies (Cavalcante et al., 2023). The data indicate that the Upper Messinian samples plotted in the V–Ni–La\*4 ternary plot, derive from felsic rocks, with a mafic-ultramafic supply. This is in accordance with the Ni, Cr and Mg amounts, as well as the higher amounts of C/S + Chl phases estimated by XRPD. The microscope observation of the coarse fraction shows grains derived from medium- to fine-grained siltstones, with an evident lamination due to presence of dark laminae of clay, organic matter and/or opaque minerals, and quartz. SEM/EDX analysis performed on siltstone fragments indicates the presence of mafic grains such as amphiboles and/or clinopyroxenes. Sandstone fragments are also present. These fragments include predominantly quartz, and minor amounts of altered feldspar and clayey matrix. Such availability of mafic fraction could be also related to the ophiolite-bearing Liguride Units in the source area, as documented by the presence of mafic minerals in the coarser fraction of the upper Messinian sediments. Several chemical indices such as CIA and CIA' was used to evaluate the compositional maturity of sediments based on the ratio between alumina and the other major cations (Perri, 2018 and reference therein). The results indicate that the degree of palaeowethering of the source areas is moderate-to-intense in accordance with the mineralogical composition of the studied samples characterized by appreciable amounts of kaolinite (ca. 15-20%) and the absence or very scarce presence of feldspars and micas (< 2%). Accordingly, the CIA values of the studied samples were used to calculate the mean annual paleotemperature (MAT) of ca. 21°C for the Upper Messinian Fm. Furthermore the mean annual precipitation (MAP; mm) of ca. 1,306 was also calculated following the method proposed by Sheldon et al. (2002). These MAT and MAP values are in accordance with the results of previous palynological studies (Fauquette et al., 2006). In addition, the minero-petrographical and geochemical data indicate that these sediments were deposited in areas adjacent the growing Messinian accretionary wedge of the southern Apennines in agreements with the presence of polygenic conglomerates (Cavalcante et al., 2023 and reference therein), at the bottom of the upper Messinian siliciclastic succession. The depositional realm could be represented by a foredeep or by a thrust top basin of the Monte Alpi Unit.

Cavalcante F., Perri F., Belviso C., Lettino A., Prosser G., La Bruna V. & Agosta F. (2023) - Clayey sediments analysis as a useful tool to assessing the geodynamic evolution of fold-and-thrust belts: The case study of the Monte Alpi area (southern Apennines, Italy). *Mar. Petrol. Geol.*, 151, 106204. <https://doi.org/10.1016/j.marpetgeo.2023.106204>.

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## Provenance and tectonic evolution of bauxite deposits in Tethys: perspective from random forest and logistic regression analyses

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*Keywords:* machine learning, major element, titanium.

Developments in Earth system research have led to widespread interest in the control of bauxite formation by multi-sphere processes. Although karst bauxite ores are abundant in the Tethyan Metallogenic Domain, understanding of evolution and controls on their genesis and distribution remain ambiguous and dispersive. Here, we use the Random Forest model to analyze the geochemical datasets of three bauxite provinces in Tethys (i.e., the Mediterranean, Central Asian, and Chinese provinces) to identify the most important variables influencing the formation of these bauxite deposits, evaluating such factors as provenance, paleolatitude and tectonic setting. Then the Logistic Regression model is used to verify the role of various factors. Our research shows that when Random Forest model achieves the best classifier performance,  $\text{TiO}_2$  is the variable that has the greatest impact on the model, of which the content is the highest in Central Asian Bauxite Province. The high  $\text{TiO}_2$  content in bauxite is due to the magmatic rock provenance, which come from Subduction Provenance Zone (SPZ). And the  $\text{TiO}_2$  content similar to the average value of continental basement is derived from siliciclastic sedimentary rocks and carbonate rocks, mainly from Orogenic Provenance Zone (OPZ). We also find that  $\text{TiO}_2$  in bauxite of TMD is sensitive to the changes of provenance and tectonic background. This study illustrates a new link between geochemical composition ( $\text{TiO}_2$  content) and provenance characteristics and even regional tectonic setting. The difference of provenance generated under different tectonic backgrounds in Tethys may eventually be reflected in the  $\text{TiO}_2$  content of bauxite deposits.

## Mineralogical and REE-geochemical characteristics of fine-grained fraction of phosphorites from the Tébessa region (NE Algeria): Glauconitization and REE distribution

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Keywords: phosphorites, glauconites, REE.

Algerian phosphorites, mainly found in the Tébessa region in the northeast of the country, were deposited during the Paleocene-Eocene age, resulting from a large period of phosphogenesis. The phosphorites resources can exceed 2 billion metric tons and are now attracting growing interest for their enrichment in rare earth elements plus yttrium (REY), as reported in the main phosphate layer of the current phosphate mine ( $\sum\text{REY} = 777 - 1211$  ppm, Kechiched et al., 2020). The amounts of REY vary significantly among deposits, phosphate facies and particles, with glauconite particles yielding the highest REY contents (up to 1000 ppm, Kechiched et al., 2018).

Previous studies have focused on whole-rock and separate particles, but the matrix phase of phosphorites has not been investigated in detail. This study proposes a mineralogical and geochemical characterization of the fine-grained fraction ( $< 45 \mu\text{m}$ ) with the aim of extracting its geochemical fingerprint to unravel the paleoenvironmental conditions promoting the REY enrichment.

Twenty-two samples of the fine-grained fraction were separated from whole-rock samples using humid grain-size classification, representing four sampled profiles from the northern (Djebel El Kouif and Djebel Dyr) and southern (Kef Essenoun) basins. Mineralogical, major, and trace (including REY) analyses were conducted on these samples using X-Ray Powder Diffraction and Fusion Mass Spectrometry.

The results show that the fine-grained fraction is mostly composed of calcite, dolomite, carbonate fluorapatite, glauconite, quartz, chlorite, and gypsum, reflecting the matrix component of phosphorites. Chemically, the samples yield an average  $\text{P}_2\text{O}_5$  of 12.48 wt%, while REY contents range from 55 to 863 ppm. The REY contents appear to have a positive relationship with the amount of glauconites in most samples, accordingly to what observed in previous studies. REE-geochemistry has shown a seawater like of REY-uptake, with a variation in redox conditions on both a horizontal and vertical scale. However, REY- and glauconite- rich samples display relatively high  $(\text{La}/\text{Yb})_{\text{N}}$  ratios, resulting from adsorption during early-diagenesis. The glauconitization of phosphorite occurred under sub-reduced conditions and was enhanced at the Paleocene-Eocene boundary, known as the Paleocene-Eocene Thermal Maximum, with a marked effect in the southern basin due to the restricted basin during this period.

On the other hand, the matrix fraction of phosphorites, usually considered wastes, could represent an economic target due to their REY contents.

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## Geochemistry of Paleozoic-Mesozoic Iranian karst bauxite deposits, Irano-Himalayan belt: paleogeographic constraints

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Keywords: geochemistry, Iranian karst bauxite, paleo-restoration.

Widespread bauxite deposits are reported from Iran. The Iranian bauxite deposits are a part of Irano-Himalayan karst bauxite belt and are genetically similar to the Mediterranean-type bauxites. They are deposited in karstified carbonate bedrocks of late Paleozoic-Mesozoic as irregular lenses and pockets with variable thicknesses and trends. These deposits spatially occur in the northwestern Iran, Alborz Mountain Chain, Central Iranian Plateau, and Zagros Simply Folded Belt and formed during warm periods of the middle-late Permian, Permo-Triassic, middle-late Triassic, late Triassic-early Jurassic, and late Cretaceous. The bauxite deposits of late Cretaceous are entirely reported from the Zagros Simply Folded Belt. The Iranian bauxite deposits are dominated by remarkable geological, mineralogical, and geochemical characteristics (Abedini et al., 2022 and references therein; Ahmadnejad et al., 2017; Khosravi et al., 2017; 2021), indicating that they derived from distinct parent rocks under different physico-chemical conditions. Intermediate-mafic igneous rocks and argillaceous carbonate bedrock are suggested as protoliths of the Iranian karst bauxite deposits. Due to the association of bauxite deposits and palaeoclimate, palaeoenvironment, and tectonic events, the Iranian bauxite deposits provide insights into the reconstructions of the geodynamic evolution of Pangea. Based on palaeogeographic maps using the PANALEISIS model, the Iranian bauxite deposits are located in intertropical zones. From the palaeogeographic point of view, the middle Permian-late Triassic bauxite deposits are related to the rift and drift of Cimmerian blocks. The detachment of the continental ribbon is associated with an uplift, which led to the karstification of former rocks and filled up with bauxite, followed by a flooding associated with thermal subsidence. The Triassic-Jurassic bauxite deposits are most likely linked to the collision of Cimmerian and Eurasia. These deposits formed at quite high latitudes (ca. 40°–50°), suggesting warm climate conditions. Finally, the late Cretaceous bauxite deposits are related to the arc-continent collision and obduction of the Semail plate with the Arabian margin, in which they formed at low latitudes (ca. 0°–10°).

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## Chemosynthetic precipitation of Mn-phases: the coated pebbles of the Scala Erre conglomerate (NW Sardinia, Italy)

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Keywords: Mn-phases, bacteria, coated pebbles.

The work focuses on a conglomerate, deriving from the dismantle of the Variscan basement of NW Sardinia, made up with quartz and minor metarenite clasts. The conglomerate was referred to an alluvial braided system and overlays a clayey Messinian palaeosol. Noticeably the rounded pebbles are cemented by Mn oxides and even the loose, single, clasts are coated by a black patina that was submitted to mineralogical XRD and SEM- EDS and INAA chemical analyses. The coatings, similar to that of varnished rocks, have thickness variable from 20 up to 400  $\mu\text{m}$ . Lithiophorite, birnessite and hollandite with traces of micas are the main mineral phases. The chemical analyses revealed a  $\Sigma\text{REE}$  in the range of 3000-5000 ppm and a strong LREE fractionation with  $(\text{La}/\text{Yb})_{\text{ch}}$  in the range of 7-20. In respect to the UCC composition (McLennan et al., 2006), Ni, Co and Zn are the trace elements that show higher enrichments, close to 100X, whereas Pb, Ba and Cu are less enriched, though their enrichment never drops below 10X. The SEM-EDS observations evidenced the foliated structure of phyllophanates, such as birnessite and lithiophorite, and cocci colonies consisting of grape-like aggregates of spheroids diameter around 0.5  $\mu\text{m}$  that testify for chemosynthetic microbial activity. According with Lovley (1995) several bacteria act as catalyst able to control redox reactions involving metals oxides and organic matter. Among these Mn oxides and oxyhydroxides are the most common and reactive. The precipitation of insoluble Mn(IV) from the soluble Mn(II) occurs thanks to some enzymes and is very effective even in pH conditions not favourable to Mn oxidation (Tebo et al., 2005; Huelin et al., 2006). Presently in the study area such concretions neither affect pebbles in streams flowing from the Variscan basement nor coat pebbles in the shore of pods where this water accumulates. Mn contents of the pods water varies seasonally from 20 to 13000 ppb mostly controlled by pH, Eh and temperature conditions. The palaeoclimatic condition, perhaps of the savannah type, characterized by relatively humid seasons alternating with periodic droughts, favored the bacterial activity which explains both the manganese coating of the individual pebbles and the cementation of the finer-grained conglomerate by coalescence of the coating from one pebble to another.

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## Polygenetic origin for terra rossa: petrographic and geochemical inferences from the Apulian karst

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Keywords: terra rossa, REEs, polygenetic origin.

Terra rossa is a reddish clay soil which is often present on the surface of limestone in Mediterranean-type climate regions. Its genesis is a controversial subject in terms of the origin of the parent material, from the residuum of underlying (carbonate/dolomite) bedrock in the absence/presence of an external silicate contribution (Durn, 2003; Muhs et al., 2010). With the main goal of understanding the geochemical processes leading to the formation of the terra rossa we report the results of a multi-method analysis on a residual deposit occupying the bottom of a Quaternary karst depression on Mesozoic limestones exposed in the Murge area (Apulia Foreland, southern Italy). Geological, petrographic, textural, and chemical data were collected on karst products (reddish calcite incrustations and nodules, and fine-grained portion of terra rossa) by a detailed field mapping, optical microscopy, XRF and fusion ICP/MS analyses and by scanning electron microscope (SEM). New collected data show how starting from the calcareous bedrock, a regular increase of SiO<sub>2</sub>, TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> and some trace elements (Rb, Y, Zr, Nb, V, Cr, Pb, Th, U, REE) in the red incrustations and calcite nodules can be observed. The mineralogical composition of reddish incrustations and nodules is comparable, consisting of fibrous and impure calcite, detrital fragments of quartz, K-feldspar, zircon and authigenic minerals as (Mn, Ba, Ca) phases, (Al, Si, Mn, Fe, Mg, Ba, Ca) minerals, Fe-kaolinite and anatase. The prevailing minerals, instead, in the fine-grained portion of terra rossa are hematite, kaolinite, and goethite. Based on the chemical composition, and especially on REE patterns, a progressive interaction of silicate aqueous solutions (with Al, Si, Fe), containing pelite material, with the calcareous bedrock, as a source of carbonic acid, was the process driving the formation of terra rossa. Based on changing Ce anomaly from negative in red incrustation and nodules to no anomaly in fine-grained terra rossa, different paleoenvironmental conditions can be envisaged: an oxygenated environment persists during the accumulation of allochthonous siliciclastic input; anoxic conditions prevail in the underlying levels of the incremental limestone karst, due to percolation of acidic and silicate solutions, producing more or less thick red incrustations, calcite nodules, and clayey terra rossa. These preliminary data indicate that the karst alteration process on limestone was promoted and accelerated by allochthonous siliciclastic supply and silicate solution circulation between the carbonate bedrock and the overhead pelite materials (Micheletti et al., 2023). Obtained results add new elements to the definition of the long-lasting question about the genetic processes responsible for the formation of terra rossa, corroborating their polygenetic origin, as result of limestone alteration in conjunction with the chemical interaction in presence of allochthonous siliciclastic material.

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## The degree of continental weathering during the Toarcian OAE in Yorkshire, UK

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Keywords: chemical weathering, clay minerals, W value.

The Toarcian Oceanic Anoxic Event (T-OAE) was associated with active volcanism, increased atmospheric pCO<sub>2</sub>, and global warming. It is stratigraphically marked by the global deposition of organic-rich black shales and a negative carbon isotope excursion (CIE). One of the many models advocated to explain the cause of OAEs is the “weathering hypothesis” (Weissert et al., 1998). In this hypothesis, the enhancement of continental weathering is considered as an initial trigger of OAEs. However, as for the T-OAE, the link between increased weathering and oceanic anoxia has not been well investigated.

The present contribution aims to reconstruct the degree of continental weathering during the T-OAE in the European epicontinental seaway. In this study, mudstone samples from the T-OAE section located in Yorkshire, UK were collected, and the geochemical and mineralogical compositions were measured by XRF and XRD, respectively.

The influence of grain-size on the geochemical and mineralogical composition of the mudstones was first examined by TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and quartz/phyllsilicates proxies. The obtained TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> values range from 0.050 to 0.075 and quartz/phyllsilicates values range from 0.1 to 0.9 except for one sample. Both proxies demonstrate a continuous decreasing trend in grain-size through the negative CIE in Yorkshire. This decrease in grain-size corresponds to a transgressive system tract denoted in previous studies (e.g., Hesselbo, 2008). Therefore, we interpret that grain-size fluctuations were primarily regulated by sea-level changes.

Kaolinite/illite ratios range from 0.25 to 1.89 and show relatively high values during the interval from the onset to the termination of the negative CIE. This finding suggests a warmer and more humid paleoclimate during the T-OAE. The hinterland chemical weathering indices (W value; Ohta & Arai, 2007) (K<sub>2</sub>O/Na<sub>2</sub>O) increase synchronously at the onset of the negative CIE. W values during the T-OAE range from 50 to 90. These values are comparable to the W values obtained from modern soils developed under temperate or tropical rainforest climates. This again supports temperate and humid conditions during the T-OAE. However, the highest chemical weathering index values occur above the T-OAE interval. This is probably due to changes in grain-size, as finer sediments generally have higher weathering index values. In Yorkshire, the facies become finer above the T-OAE due to transgression.

In conclusion, we infer an enhancement of continental paleoweathering during the T-OAE in the European epicontinental seaway. However, the present contribution also reveals that grain-size effects related to sea-level change can mask hinterland weathering signals. Therefore, geochemical variation related to grain-size (sea-level change) should be assessed to determine changes in hinterland paleoweathering more robustly.

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## Application of multivariate statistics and artificial intelligence to sediment geochemistry

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Keywords: geochemistry, statistics, AI.

As a basic premise, statistical analysis, multivariate analysis, and Artificial Intelligence (AI) cannot be performed to geochemical data of sediments. This is because geochemical data are compositional data, which are not real numbers, and the sample space is not real space. Therefore, four arithmetic operations, digit “zero”, distance function are undefined in compositional data. Furthermore, compositional data does not meet the prerequisites for statistical analysis, multivariate analysis, and AI because of the constant-sum constraint inherent in compositional data.

Fortunately, with the development of logratio analysis and simplex analysis, multivariate analysis and AI can now be applied to the geochemical composition of sediments. In this presentation, the impact of multivariate analysis and AI to sediment geochemistry will be discussed with specific examples.

As an example of multivariate analysis, the weathering index W value will be introduced, which was extracted from the geochemical composition of soils. First, geochemical data of pristine igneous rocks and their weathered products were collected globally. Principal component analysis was performed on this database through the simplex analysis. As a result, “chemical variation by source rock type” and “chemical variation due to weathering (W value)” were mathematically isolated. Because these two types of chemical variations are inherited in geochemical data, the conventional weathering indices could not accurately quantify the degree of weathering. On the other hand, the W value is an index that can quantify only the weathering effects. Furthermore, when the W value was applied to modern soils around the world, it was found that the climate in which the soils were formed could be estimated. Therefore, the W index can be used to predict the climate.

In the next example, application of AI to discriminate the tectonic setting from the geochemical composition of sediments will be demonstrated. In this study, sediment geochemical data from island arc (58), continental arc (89), craton (99) and collision zone (59) were collected globally and conducted the random forest, a type of machine learning technique. The correct response rate of the tectonic setting was 47-67% for the conventional discrimination diagrams. In contrast, the result of random forest using logratio analysis showed a 93.4% correct response rate. This scheme can predict the tectonic setting from the composition of sediments.

In the future, the application of multivariate analysis and AI to sediment geochemistry will be potentially promising method for solving various sedimentological problems.

## Mg-Fe ratio in dravite-schorl series analysed by Raman spectroscopy for provenance studies

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Keywords: tourmaline, Raman spectroscopy, composition.

Dravite and schorl belong to the Alkali subgroup-1 (Henry et al., 2011) of Tourmaline mineral supergroup and are the most diffused tourmaline species. Their complex chemical formula  $(XY_3Z_6(T_6O_{18})(BO_3)_3V_3W)$  and their high chemical and mechanical stability make tourmalines remarkable sources of geological information regarding their genesis and provenance (Mange & Morton, 2007). As tourmalines are widespread in all type of detrital sediments, their composition can be used as a source rock indicator in provenance studies. For this reason, obtaining information on tourmalines composition with quick analysis is of great importance.

Raman spectroscopy is an optimal technique for this aim as it allows rapid, effective and easy measurements without any sample degradation. With a high spatial resolution, down to  $\sim 1 \mu\text{m}$ , single tourmaline grains in sediments can be analyzed. Moreover, Raman measurements can be performed with portable spectrometers for in situ investigations.

We focused on dravite-schorl series to study the correlations between variations in Raman spectra parameters and changes in the Y-site occupation, i.e. the Mg-Fe ratio, in different samples with different provenance. Nevertheless, a complete sample composition analysis is needed for a fine calibrated Raman model of the Mg-Fe ratio behavior in Y-site, as also other sites-occupation seems to slightly change. For this reason, together with SEM-EDS (Scanning Electron Microscope coupled with Energy Dispersive Spectroscopy), we used LIBS (Laser Induced Breakdown Spectroscopy) to obtain information also on light element concentration in tourmalines.

We analyzed different spectral ranges in the Raman spectra, according to previous studies (Watenphul et al., 2016a; 2016b). In particular, we studied the variations mainly in the  $200 - 315 \text{ cm}^{-1}$  region, where  $YO_6$  octahedra vibrational modes are located, and in the  $3400 - 3770 \text{ cm}^{-1}$  range, corresponding to the OH stretching region. Additionally, other regions such as  $360 - 375 \text{ cm}^{-1}$  and  $600 - 750 \text{ cm}^{-1}$  have been studied, as all of these modes can be influenced by the occupation of Y-site. Finally, we correlated these variations with changes in composition in order to have a quick and reliable distinction between dravite and schorl. Thanks to this approach we can reconstruct sediments provenance by comparing tourmalines spectra of different analysed samples.

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## **Mineralogical and geochemical constraints from the mudrocks of the Calcare di Base Formation (Calabria basin, Southern Italy)**

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*Keywords:* calcare di base, messinian salinity crisis, geochemistry and mineralogy of mudrocks.

The Mediterranean area recorded the Messinian Salinity Crisis (MSC) during the late Miocene (5.97-5.33 Ma), where the combination of paleoclimate conditions and geodynamic processes produced huge evaporate deposits such as the “Calcare di Base” (CdB) that is a lithostratigraphic unit composed of carbonate, marls and locally gypsum. The bulk mineralogy and geochemistry of mudrocks from the CdB Formation collected in the Catanzaro Basin (Calabria, Southern Italy) are contributing valuable information about the paleoweathering and paleoclimate evolution during the onset of the MSC (5.97-5.60 Ma). The mineralogical composition mainly consists of phyllosilicates, calcite, quartz and minor/trace amounts of feldspars, hematite and gypsum. Among the major elements, SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO and MgO are the most abundant oxides on average. The chemical weathering indices such as the CIA (Chemical index of Alteration), indicates weak-moderate source area(s) weathering conditions under a mainly dry/arid paleoclimate environment alternating with relatively wet (humid) conditions in non-steady-state conditions. Furthermore, the studied mudrocks recorded recycling effects as illustrated in the Al-Zr-Ti plot and their mineralogical composition shows low kaolinite amounts; this confirms a low-moderate degree of weathering processes. The provenance proxies based on Cr/V vs. Y/Ni and V-Ni-La\*10 plots suggest that the studied samples are mainly related to felsic sources such as the rocks composing the Sila Massif.

Moreover, the analogies between the argillaceous marls from the Calcare di Base formation of the Rossano Basin (Perri et al., 2015) and the mudrocks of the Catanzaro Basin investigated in this work indicate that they formed in the same paleoclimatic conditions characterized by non-steady-state weathering processes. This research intends to give new information for the understanding of many unresolved issues regarding the Messinian Salinity Crisis.

Perri F., Dominici R. & Critelli S. (2015) - Stratigraphy, composition and provenance of argillaceous marls from the Calcare di Base Formation, Rossano Basin (northeastern Calabria). *Geol. Mag.*, 152(2), 193-209. <https://doi.org/10.1017/S0016756814000089>.

## Phosphate rocks as potential source for critical rare earth elements

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*Keywords:* REE, phosphorite, Tunisia.

Rare earth elements (REEs) are essential components in many modern technologies. Their importance is only expected to grow in the future as new technologies emerge. However, there are concerns about the long-term availability and sustainability of these elements. Despite these challenges, the use of sedimentary phosphate deposits as a secondary resource of REEs is a promising solution to the REEs global crisis (Emsbo, 2015). For this purpose, six phosphate layers from two different phosphorite deposits from central Tunisia were geochemically investigated. Mineralogical characterizations of these samples were undertaken by X-Ray diffraction, revealed that the main mineral is the carbonate-fluorapatite (francolite), with dolomite, gypsum, and quartz as accessory minerals. The chemical analysis of the studied samples by ICP-MS demonstrates that they are significantly enriched in REEs with an average of 1464 ppm. Our data suggest that phosphorites currently mined in Tunisia, has a significant proportion that can be extracted to support the increasing demand for these elements in high technological applications.

Emsbo P., McLaughlin P.I., Breit G.N., du Bray E.A. & Koenig A.E. (2015) - Rare earth elements in sedimentary phosphate deposits: Solution to the global REE crisis? *Gondwana Res.*, 27(2), 776-785. <https://doi.org/10.1016/j.gr.2014.10.008>.

## **S11.**

# **Mercury as a global contaminant: from geogenic and anthropogenic sources to environmental impact and potential remediation strategies**

*CONVENERS AND CHAIRPERSONS*

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## Identification of mercury species via thermodesorption in environmental samples from a tetrahedrite historical Cu-Sb(-Ag) mining site (Mt. Avanza, Friuli Venezia Giulia, Italy)

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*Keywords:* mercury, thermodesorption, speciation.

Fahlore minerals of the tetrahedrite-tennantite series are common constituents of a variety of mineral deposits. The chemical formula of tetrahedrite (TTR) is  $\text{Cu}_6[\text{Cu}_4(\text{Fe,Zn})_2]\text{Sb}_4\text{S}_{13}$  and can host high quantities of several trace elements such as Ag, As, Bi, Cd, Cu, Fe, Hg, Mn, Se, Te, Zn. The mineral deposit of the Mt. Avanza (Carnic Alps, Friuli Venezia Giulia, Italy) is an ancient fahlore mine near Forni Avoltri village, where tetrahedrite was the main ore mineral extracted for the recovery of Cu and Ag (Barago et al., 2023). In the (Zn-Hg-rich) tetrahedrite (TTR) minerals, mercury (Hg) is present in the 1.48 – 8.66% wt. range (Casari, 1996), thus posing potential environmental risks due to the dispersion of Hg due to weathering and transport processes.

In this work, thermodesorption technique coupled with continuous determination by atomic absorption spectrometry (AAS) was used for the determination of Hg species in different matrices (ore minerals, waste rocks, soils and stream sediments). This technique is based on the gradual heating of a sample, from ambient temperature up to 700°C, which releases Hg at different temperature intervals depending on its chemical form. Thus, a single Hg species that desorbs at a specific temperature may be identified via a thermogram of the sample. In addition, X-Ray Powder Diffraction (XRD) was used to identify the main mineral phases in the same samples. The aim of this study was to identify the desorption temperature of Hg corresponding to TTR mineral and to recognise additional chemical forms of Hg associated to different environmental samples nearby the fahlore mine site.

Once TTR minerals were manually separated from samples of the main waste rock piles and identified via XRD, they were desorbed to identify the desorption temperature of Hg, which is occurred at  $437 \pm 11.5^\circ\text{C}$ . However, by applying the thermodesorption technique to soils, sediments, and waste rocks enriched of TTR minerals, usually with total Hg concentrations < 1000 mg/kg, a second release peak was evidenced at lower temperature, varying between 200 - 250°C. Two hypotheses were considered to explain this second peak: the first could be related to lithogenic sources, being Hg associated with Devonian to Permian rock-forming minerals, the second to Hg-bearing secondary minerals as alteration products of tetrahedrite primary sulfosalt minerals.

Barago N., Mastroianni C., Pavoni E., Floreani F., Parisi F., Lenaz D. & Covelli S. (2023) - Environmental impact of potentially toxic elements on soils, sediments, waters, and air nearby an abandoned Hg-rich fahlore mine (Mt. Avanza, Carnic Alps, NE Italy). *Environ. Sci. Pollut. R.*, 30, 63754-63775. <https://doi.org/10.1007/s11356-023-26629-7>.  
Casari L. (1996) - Tetrahedrite–tennantite series in the Carnic Chain (Eastern Alps, Italy). *N. J. Miner. Mh.*, 5, 193-200.

## Duplicate measurements of airborne gaseous mercury in contaminated environments using Lumex RA 915 analyzers: results, problems and optimization of operating procedures

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*Keywords:* Lumex, gaseous mercury, cinnabar.

The Lumex RA 915 analyzer is widely used for real-time measurement of airborne concentrations of gaseous mercury in remote, man-made or known contaminated areas. In the case of the former cinnabar mine of Abbadia San Salvatore (Mt. Amiata, southern Tuscany), in order to validate the monitoring results during the remediation works, duplicate measurements were carried out, using a pair of analyzers equally set and with 4' averaging time for each measure. Three monitoring campaigns were carried out in different seasons, for a total of #93 duplicate measurements in the mining area, both in confined and open environments. For each monitoring campaign the results show an excellent linear correlation between the answers provided by the two instruments ( $0.98 < R^2 < 0.99$ ), however the measures of instrument #1 were systematically higher by about 20% compared to the instrument #2 ( $1.167 < m < 1.225$ ) over the entire investigated range.

Both instruments have highlighted a common criticality, due to the possible contamination of the components of the sampling and measurement line, especially in presence of high levels of contamination, which the analyzer is able to quantify thanks to the wide measurement range ( $2 \div 50,000 \text{ ng/m}^3$ ). The observation of the values read by the two instruments at the end of the measurements in a contaminated environment resulted in very long cleaning times, in particular for instrument #1, which is more frequently used and therefore more exposed to high concentrations of  $\text{Hg}^0$ . This suggests the possibility of residual internal contamination, as confirmed by subsequent periodic maintenance. Further confirmations were acquired by verifying the deviations between measurements carried out in an  $\text{Hg}^0$ -free environment with or without the use of a dust filter and piping at the instrument inlet, already used in field measurements. This suggests limiting the use of filtering devices or even simple sections of pipe at the head of the sampling line, as they constitute a factor of alteration of the measurements in case of prolonged use at high concentrations. The tests conducted with a rotameter and digital flowmeter have also highlighted how the insertion of filtering devices in the head can generate pressure drops such as to significantly decrease the flow rate of the analyzer suction pump.

To solve the criticality detected, a procedure was developed, to be performed at the beginning of the measurements: the zero check is preceded by the instrument flushing for an adequate time with  $\text{Hg}$ -free air, obtained by inserting a specially prepared cartridge containing Activated carbon. The appearance of negative values during flushing indicates that the chamber is being decontaminated. In any case, even when using the cartridge with activated carbon, it is to be avoided to perform zero checks in contaminated environment, in order to prevent subsequent measurements from being altered by residual contamination of  $\text{Hg}^0$  in the measuring cell.

## **Mercury pollution in artisanal small-scale gold mining: new approach to estimate emissions and impact of releases**

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*Keywords:* mercury, pollution, asgm.

Artisanal small-scale gold mines represent a danger for ecosystem and human because of the mercury dispersed in the environment, both for the fraction directly released into the water and soil matrices, and for the part that goes into the atmosphere (Crespo-Lopez et al., 2021). In the water, the mercury can be transformed into the methylated form and can enter in the food chain up to humans, eventually causing important neurological damages. Since these mining are still illegal, it is still not clear what contribution it makes to the global mercury cycle, fundamental under the Minamata Convention to understand the role of the various countries on mercury pollution. In this light, here a method has been applied to describe the atmosphere emissions scenarios for a set of tropical and subtropical countries with ASGM. A Monte Carlo method was used to combine the data and generate emission values. These data were processed with a non-parametric resampling (bootstrap) method to obtain reliable and robust emissions and their relative 95% confidence intervals, both for the current state and for six emission scenarios designed in this study. Estimates of small-scale mercury emissions agree with those reported in the Global Mercury Assessment (Unep, 2019). However, the overall uncertainty is reduced by about 100% (Bruno et al., 2022). Subsequently, we spatialized the emission quantities only to the rural areas of the countries, considering land use and population density, since these places are with great probability the sites of ASGM. Comparison of spatial distributions and quantities to the GMA was made. Finally, to evaluate the impacts of the mercury releases so calculated, a Vulnerability Indicator was also designed, showing the potential impact of each release point on the downward hydrological basin.

Bruno D.E., De Simone F., Cinnirella S., Hedgecock I.M., D'Amore F. & Pirrone N. (2022) - Reducing Mercury Emission Uncertainty from Artisanal and Small-Scale Gold Mining Using Bootstrap Confidence Intervals: An Assessment of Emission Reduction Scenarios. *Atmosphere*, 14(1), 62. <https://doi.org/10.3390/atmos14010062>.

Crespo-Lopez M.E., Augusto-Oliveira M., Lopes-Araújo A., Santos-Sacramento L., Takeda P.Y., de Matos Macchi B., do Nascimento J.L.M., Maia C.S., Lima R.R. & Arrifano G.P. (2021) - Mercury: What can we learn from the Amazon? *Environ. Int.*, 146, 106223. <https://doi.org/10.1016/j.envint.2020.106223>.

UNEP (2019) - Global Mercury Assessment. UN Environment Programme, Chemicals and Health Branch, Geneva, Switzerland.

## Mercury distribution in environmental matrices (water, air, sediment) at former mining sites: the case study of the “Argento Vivo” mine (Levigliani, Apuan Alps)

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*Keywords:* mercury distribution, water air sediment, former mining sites.

The toxicity of mercury in its various forms is a widespread issue in a framework of steadily increasing anthropization and global change. Although its pervasiveness in the environmental matrices (air, water, sediment) is a cause of great concern, a comprehensive understanding of mechanisms and processes that regulate its spread and diffusion is still a challenge. In this regard, abandoned or disused mining sites are certainly of interest, as the release of Hg into the environment may continue even decades after the end of excavation, processing, and production works.

In Tuscany, besides the well-known and most productive areas of Monte Amiata, other mining sites have been exploited in the Apuan Alps since the Middle Ages, where Hg-rich ore deposits belonging to the Apuan Metamorphic Complex occur (Dini et al., 2001). One of the oldest mining excavations is the native mercury and cinnabar “Argento Vivo” mine of Levigliani, consisting of (i) a series of tunnels and descending galleries of various sizes and lengths, which are partially included in tourist tours, and (ii) an external area dedicated to the processing of the extracted material. The present study focuses on the characterization and quantification of mercury dispersed in air, water, and sediments in and around the mining area, with the aim to evaluate the environmental impact. Two surveys (March and June 2021) were carried out to highlight possible variability associated with the different seasonal conditions.

The GEM (Gaseous Elemental Mercury) measurements, performed using a Lumex RA-915M portable analyzer, highlighted that the highest concentrations (up to 16,500 ng/m<sup>3</sup>) were recorded, as expected, at the furnace located in the external processing area, while the galleries showed values ranging from a few dozen up to 3,651 ng/m<sup>3</sup>. The noticeable variations of GEM concentrations (even an order of magnitude) inside the galleries between the two measurement periods were probably due to the higher humidity and ventilation in June than in March. Up to 22 water samples (each survey), from the downstream water courses up to the Versilia River, were analyzed for dissolved Hg concentration using a Lumex RA-915M equipped with a RP-92 attachment. 17 sediment samples (collected in March) from the mine and surrounding areas, were dried, grinded, and homogenized, and let interacting with CO<sub>2</sub>-saturated water. The leachate was analyzed by ICP-MS after centrifugation, whilst the sediment by AAS. The results showed that the contamination mainly affects the water and the leachates pertaining to the mining area (up to 3.6 and 31.3 µg/L, respectively), while downstream the mine the Hg concentrations were even <10 ng/L and <0.1 µg/L, respectively, i.e., well below the Italian law limit (1 µg/L). The more polluted sediments (up to 1,100 mg/kg) were those collected into the galleries, although only 5 more distal samples were characterized by Hg contents below the limit for residential use (1 mg/kg).

Dini A., Benvenuti M., Costagliola P. & Lattanzi P. (2001) - Mercury deposits in metamorphic settings: the example of Levigliani and Ripa mines, Apuan Alps (Tuscany, Italy). *Ore Geol. Rev.*, 18(3-4), 149-167. [https://doi.org/10.1016/S0169-1368\(01\)00026-9](https://doi.org/10.1016/S0169-1368(01)00026-9).

## Limit values for gaseous mercury: an overview

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Keywords: mercury, limit values.

Mercury (Hg) is a toxic and persistent element, easily bio-accumulable in the food chain with highly dangerous effects on people's health. Among Hg airborne species, gaseous elemental mercury (GEM) is dominant (>95%), the more persistent in atmosphere (0.6 months-1 year of residence time), and highly absorbable by humans (~80% at the pulmonary level). The topic of atmospheric Hg pollution is largely discussed by several environmental agencies: the debate gives rise to a remarkable number of different threshold values to avoid a dangerous exposure to Hg in its different species.

The present work aims to depict an exhaustive framework of the threshold limit values (TLVs) suggested/recommended by the federal or executive agencies regarding the exposition to gaseous Hg. For this purpose, the scientific literature on this topic released by the most important environmental (i.e., ACGIH, ATSDR, EPA) and executive agencies (i.e., OSHA and NIOSH) was reviewed.

The literature revision identifies more than twenty TLVs: among these, only three are legally transposed to environmental laws (OSHA, 1989; European Commission, 2009), while the great part is just recommended. The remarkable number of different TLVs often employ an unclear terminology. This is the case of the exposure duration. TLVs are roughly divided based on the exposition time between chronic and time-weighted average (TWA), i.e. occupational exposure. Despite this, based on the definitions found in literature, it is not easy to find substantial differences or understand if a chronic exposure cannot be compared to a working lifetime exposure. Moreover, the criteria to derive the TLVs are different between the environmental or federal agencies. For example, the uncertainty factors (UFs), i.e., the mathematical adjustments employed to calculate TLVs to account for people's variability, are not uniform. This is the case of ATSDR, that for the calculation of the minimum risk level (MRL) for chronic exposition to Hg<sup>0</sup> employs an UF = 10, compared to the CalEPA that, for the same chronic exposition, employs an UF of 30 (CalEPA, 2014; ATSDR, 2022).

Moreover, it could be interesting to observe that a substantial lowering of the Hg TLVs, both for chronic and occupational exposure, was proposed by the different agencies over the years. This evidence reflects a revision trend towards a more protective approach for people's health.

The revision of the literature for gaseous Hg TLVs showed a high variability among their values, probably resulting from the uncertainty between Hg exposure levels and the related effects on human health. This issue brings to a considerable degree of freedom between agencies that suggest or enforce Hg limit values.

ATSDR (2022) - Toxicological Profile for Mercury (Draft for Public Comment). Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service.

CalEPA (2014) - Technical Support Document For the Derivation of Noncancer Reference Exposure Levels. Office of Environmental Health Hazard Assessment, California Environmental Protection Agency.

European Commission (2009) - Commission Directive 2009/161/EU of 17 December 2009 establishing a third list of indicative occupational exposure limit values in implementation of Council Directive 98/24/EC and amending Commission Directive 2000/39/EC (Text with EEA relevance).

OSHA (1989) - Occupational safety and health standards, toxic and hazardous substances. All contaminants, final rule. Code of Federal Regulations, 29 CFR 1910.1000.

## Mercury pollution of the University of Florence herbaria wooden cabinets: assessment of gaseous emissions and wood characterization

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*Keywords:* mercury, herbaria, museum.

Herbaria, i.e. the botanical sections of natural history museums, are key-places for plant biodiversity conservation. Most of the herbaria in the world are strongly affected by mercury (Hg) pollution, due to the past use of corrosive sublimate (HgCl<sub>2</sub>) to prevent plants infestation.

The Central Italian Herbarium (Natural History Museum of the University of Florence, hereafter CIH) is one of the most important herbaria of the world, hosting about five million samples and collections dating back to the 16<sup>th</sup> century. Previous research showed the presence of high mercury concentrations, both as gaseous elemental mercury (GEM) and as particulate Hg, in all the CIH rooms (Cabassi et al., 2020; Ciani et al., 2021). In this study, GEM emissions (ng m<sup>-3</sup>) from the wooden cabinets containing herbaria samples were measured in different conditions (instantaneously upon opening the cabinet doors, after a “recharge” time, emptied of plant samples) by using a Lumex RA-915M analyzer. To determine the GEM degassing rate of wooden substrata, GEM fluxes (ng m<sup>-2</sup> h<sup>-1</sup>) from a wooden tablet used as a support for herbarium plants samples were evaluated by setting up a steady-state flux chamber. Moreover, cabinets were drilled and the resulting cores were analyzed at regularly intervals (every 1 cm) by a DMA-80 evo to determine the total Hg concentration (THg, µg kg<sup>-1</sup>) and by SEM-EDS.

The GEM emissions from the wooden cabinets displayed a mean (±SD) of 1938±754 ng m<sup>-3</sup>, with the highest concentrations (mean 2663±432 ng m<sup>-3</sup>) reached after the first two minutes since the cabinets opening. The cabinets displayed the same GEM emissions after one hour, while the empty cabinets reached similar concentrations (mean 1473±888 ng m<sup>-3</sup>) to those recorded from full cabinets. The GEM fluxes from the wooden tablet showed a mean value of 17±4 ng m<sup>-2</sup> h<sup>-1</sup>, with a maximum value of 21 ng m<sup>-2</sup> h<sup>-1</sup>, and a minimum of 12 ng m<sup>-2</sup> h<sup>-1</sup>. The THg of the wooden drill cores reached a mean concentration of 3918±1254 µg kg<sup>-1</sup>: these values decreased mostly linearly going from the surface (in contact with the contaminated samples closed in the cabinets) towards the inner parts. SEM-EDS analysis of the surface of the wooden sections showed the presence of particles of both Hg sulfide and metallic Hg.

The results here presented clearly demonstrate that wooden cabinets of the CIH are contaminated by Hg as a result of the storage of the Hg-rich herbaria sheets; they then act as a secondary source of pollution, contributing to the observed GEM concentrations of CIH. Since it is unrealistic to plan any cleaning treatment of all the herbarium samples due to their high number, this study indicates that a decontamination treatment of the wooden cabinets may help in minimizing the Hg pollution of the museum.

Cabassi J., Rimondi V., Yeqing Z., Vacca A., Vaselli O., Buccianti A. & Costagliola P. (2020) - 100 years of high GEM concentration in the Central Italian Herbarium and Tropical Herbarium Studies Centre (Florence Italy). *J. Environ. Sci.*, 87, 377-388. <https://doi.org/10.1016/j.jes.2019.07.007>.

Ciani F., Chiarantini L., Costagliola P. & Rimondi V. (2021) - Particle-Bound Mercury Characterization in the Central Italian Herbarium of the Natural History Museum of the University of Florence (Italy). *Toxics*, 9(6), 141. <https://doi.org/10.3390/toxics9060141>.



## Gaseous mercury emissions from forest and urban soils heavily impacted by past mining in the Idrija mining district (Slovenia)

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*Keywords:* legacy soil contamination, ore roasting, GEM fluxes.

The historical mining and ore roasting activities lasted for about 500 years at Idrija (Slovenia), the second largest mercury (Hg) mine worldwide, have caused a widespread contamination of the surrounding environments through direct losses and discharges of residues and atmospheric depositions (Gosar & Teršič, 2012). Substrate enriched in Hg can release notable amounts of gaseous elemental mercury (GEM) into the atmosphere (Agnan et al., 2016), potentially contributing to widen the spatial distribution of this metal and to increase the exposure to Hg of inhabitants through inhalation.

This study is focused on the evaluation of GEM fluxes at the soil-air interface within both the urban area of Idrija and its surroundings. Site selection was aimed at comparing emissions from substrates subject to different Hg supplies. The selected urban soils were characterised by different degree of Hg enrichment due to its natural occurrence in underlying bedrock or variable atmospheric depositions related to ore roasting in modern furnaces. In addition, GEM fluxes were measured at an ancient roasting site in the forests surrounding Idrija subject to considerable Hg supplies during ore processing in XVI-XVII centuries. Measurements were performed during the summer season, the most favourable for GEM evasion (Floreani et al., 2023).

A non-steady state flux chamber coupled with a real-time GEM analyser was used to evaluate fluxes from soils with the natural vegetation cover performing replicate measurements at each site. Topsoil Hg content and speciation were also assessed through thermo-desorption technique.

Overall, GEM fluxes observed from undisturbed soils ranged between 70.7 and 702 ng m<sup>-2</sup> h<sup>-1</sup> with the highest average value obtained for the natural enriched site at Idrija. The spatial variability of fluxes was mainly related to total Hg content in soils. However, a more developed herbaceous vegetation may limit GEM releases at the atmospherically influenced site near the most recent furnace despite the greater availability of Hg bound to organic matter, which is potentially more available for reduction to GEM and evasion. This is especially evident considering the low fluxes observed at the forested ancient roasting site despite the extremely high Hg concentrations in soils (up to 10,400 mg kg<sup>-1</sup>).

Results from this study highlight that shading by vegetation can significantly limit GEM re-emission to the atmosphere even in extremely contaminated areas. However, a significantly high flux (2466 ng m<sup>-2</sup> h<sup>-1</sup>) was recorded at the ancient roasting site on a bare soil surface under an uprooted tree, suggesting that care should be taken in forest management practices to avoid potential strong re-emission of GEM related to direct exposure of these heavily contaminated soils to solar radiation.

Agnan Y., Le Dantec T., Moore C.W., Edwards G.C. & Obrist D. (2016) - New constrains on terrestrial surface-atmosphere fluxes of gaseous elemental mercury using a global database. *Environ. Sci. Technol.*, 50, 507-524. <https://doi.org/10.1021/acs.est.5b04013>.

Floreani F., Zappella V., Faganelli J. & Covelli S. (2023) - Gaseous mercury evasion from bare and grass-covered soils contaminated by mining and ore roasting (Isonzo River alluvial plain, Northeastern Italy). *Environ. Pollut.*, 318, 120921. <https://doi.org/10.1016/j.envpol.2022.120921>.

Gosar M. & Teršič T. (2012) - Environmental geochemistry studies in the area of Idrija mercury mine, Slovenia. *Environ. Geochem. Health*, 34, 27-41. <https://doi.org/10.1007/s10653-011-9410-6>.

## The origin of mercury in the area affected by artisanal mining in the Ponce Enriquez Gold District (Southern Ecuador): a preliminary investigation

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*Keywords:* artisanal mining, amalgamation, geochemical baseline.

The Ponce Enriquez mining district (south of Ecuador) is one of the most important gold mining areas in Ecuador, active since 1980's. The gold mineralization is hosted within Cretaceous mafic rocks (mainly basaltic lavas, with porphyritic or aphanitic texture) of the Pallatanga Unit.

The mining activity is a recognized economic activity that can be presented as large-scale mining, medium-scale to small-scale mining, artisanal mining and illegal mining. Gold is recovered by leaching with cyanide and flotation in artisanal activity and by a combination of amalgamation with mercury in the illegal mining activity. In all cases, the lack of efficiency is a common point along with the environmental damage. As a matter of fact, the high level of potentially toxic elements (PTEs) concentration (As, Cu, Cd, Zn, Hg, and Pb) in stream sediments and other environmental matrixes (surface water, soil, and biological) has been discussed in several studies (e.g., Jiménez-Oyola et al., 2021). However, in same case, the presence of PTEs in the mining district has been considered as due to the superposition of geogenic sources and mining activity. To determine whether the environmental matrixes are actually contaminated by anthropic activity or not with mercury, it is necessary to know the natural pre-anthropogenic content or the natural background of these elements.

In this framework, we conducted a preliminary investigation to determine the content of Hg into the bedrock, to create a preliminary database to assess the geochemical baselines of the area.

We collected twenty bedrock samples, considering the different textures of the rocks and abundance of mineralization, to have a good representative number of this variability.

Total Hg concentrations in bedrocks were quantified with a Milestone tri-cell Direct Mercury Analyzer (DMA-80) in the Earth Sciences Department of university of Pisa. Stream sediment geochemical data were obtained from the work of PRODEMİNCA (1998) and Jiménez-Oyola et al. (2021).

Mercury concentrations in bedrock nearly the mined area is low and are taken to represent background concentrations, ranging from 0.002 to 0.148 ppm. Bulk mercury values in stream sediments are elevated to several times these background concentrations. Indeed, stream sediments have Hg content ranging between 0.15 and 33.84 ppm in the investigated area. These results may suggest an anthropic contribution of mercury concentration in specific areas.

These conclusions are considered preliminary because the number of sample sites is relatively small. We plan to expand the number of samples and process this data with statistical methods to obtain the geochemical baseline values.

Jiménez-Oyola S., Chavez E., García-Martínez M.J., Ortega M.F., Bolonio D., Guzmán-Martínez F., García-Garizabal I. & Romero P. (2021) - Probabilistic multi-pathway human health risk assessment due to heavy metal(loid)s in a traditional gold mining area in Ecuador. *Ecotox. Environ. Safe.*, 224. <https://doi.org/10.1016/j.ecoenv.2021.112629>.  
PRODEMİNCA (1998) - Monitoreo Ambiental de las áreas mineras en el sur del Ecuador. Ministerio de Energía y Minas.

**Determination of Hg<sup>0</sup> in solid matrices: a new approach with Lumex-Pyro thermal desorption.  
The case study in the former mine of Abbadia San Salvatore  
(Mt. Amiata, Southern Tuscany, Italy)**

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*Keywords:* cinnabar, pyrolyzer, Lumex.

The variability of chemical-physical, toxicological, and bioavailability characteristics diversifying Hg species (volatile metallic, insoluble sulfide, soluble salts, organic forms) is a factor that conditions the study of contamination of environmental matrices and related environmental and health risks. Consequently, it influences the design of interventions for the reclamation of contaminated sites and the evaluation of the outcomes of such interventions. For these reasons, within the monitoring activities carried out at the former mining site of Abbadia San Salvatore (Mt. Amiata, Southern Tuscany), where a remediation project is underway, an analytical method aimed at discriminating the content of Hg<sup>0</sup> from HgS (cinnabar), which was the mineral cultivated and processed in the mining plants, has been developed for solid matrices. The method uses the Lumex RA-915M instrument as a detector through atomic absorption spectrophotometry (AAS) and a pyrolyzer (Lumex Pyro-315+). The combined use of this instrumentation allows the quantification of the various Hg species in previously ground and homogenized solid samples, differentiating them by applying a temperature ramp set taking into account the different volatilization temperatures of the species themselves. The pyrolyzer consists of two separate cells: the first heats the sample, causing the release of Hg vapours, while the second is heated to approximately 800°C to prevent contamination. The desorption temperature in the sample holder is measured with a thermocouple that monitors the effects of the voltage applied to the pyrolyzer. The air is continuously drawn by the instrument pump, filtered with activated carbons, and introduced into the measurement cell which is exposed to UV radiation emitted by a Hg lamp. The temperature ramp consists of five steps, differentiated by increasing voltage values set independently to the three cells, with a sample processing duration of approximately 15'. The pump flow rate can be placed in the range of 1÷3 L/min, depending on the presumed concentration of Hg in the sample. A straight line on three points was built for the calibration, using increasing amounts of a certified reference material (Montana soils 2711a). The method was tested on samples of cinnabar, calcines, sediments, and soils collected at the Abbadia S. Salvatore mine. To observe the effect of different matrices on thermal desorption, cinnabar was mixed with calcite and synthetic silica. The method allows Hg speciation, avoiding complex sample preparation procedures. However, in order to optimize working conditions, a preliminary mineralogical characterization is desirable. Further benefits could be achieved by implementing temperature control in the cells, avoiding the use of an external thermocouple.

## Novel determination of elemental mercury in silicate rock by thermal desorption

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*Keywords:* mercury determination, Hg(0) speciation analysis.

Mercury is highly toxic for humans (Beckers & Rinklebe, 2017) and may occur in the environment in a variety of species derived from geogenic and anthropogenic sources. Both elemental and oxidized mercury forms volatilize from contaminated terrestrial ecosystems into the air, even if gaseous elemental mercury (Hg(0)) represents most of the total airborne mercury (> 95%). The inhalation of mercury gas may produce harmful effects to the person exposed. Improvements in the experimental approaches for measuring Hg(0) in environmental matrices are particularly important for risk assessment. At present, a validated analytical method for the quantitation of Hg(0) in solid matrices does not exist. In this study, an experimental approach based on thermo-desorption has been developed in order to quantify the Hg(0) fraction in a mercury-bearing mineralized rock from the Levigliani mine site in the Apuan Alps (Tuscany Region, Italy) considered representative of mine tailings. Mercury release has been measured at variable temperature using a thermo-desorption method combined with a mercury vapor analyzer. The results allowed the peak temperature for the emission of free and matrix-bound Hg(0) components to be identified, suggesting that 100°C represents a suitable temperature for Hg(0) isothermal release. Subsequent experiments with the sample exposed to a specific sorbent (Carulite), keeping the temperature at 100°C, demonstrated that free Hg(0) was recovered after 6 h, while 60 h were required for the free and matrix bound Hg(0) release. This approach allowed to determine elemental mercury in contaminated mine tailings and it is well-suited for samples with low Hg(0) content (up to 1.3 ng). It may also be applied to contaminated soil, even if the time necessary to release Hg(0) cannot be generalized due to the complexity of the natural samples. In fact, the kinetics of thermal desorption are limited by diffusion, which is dependent upon temperature as well as the shape and distribution of Hg in the solid sample.

Beckers F. & Rinklebe J. (2017) - Cycling of mercury in the environment: sources, fate, and human health implications: a review. *Crit. Rev. Environ. Sci. Technol.*, 47(9), 693-794. <https://doi.org/10.1080/10643389.2017.1326277>.

## Mercury distribution in plants and soils from the former mining area of Abbadia San Salvatore (Tuscany, central Italy)

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Keywords: monte Amiata, mercury, bioaccumulation factor.

The scientific importance of studying the distribution of heavy metals in plants growing in active and abandoned mining areas lies in understanding their ability to survive in hostile environments and providing valuable information for phytoremediation efforts. This study focused on analyzing twenty-one top soils (0-15 cm) from the former Hg-mining area of Abbadia San Salvatore (Tuscany, Central Italy) for total, leached, organic, and inorganic mercury content, as well as dehydrogenase enzyme activity (DHA) to assess soil quality. Additionally, the concentration of mercury in eight different plant species (*Castanea sativa*, *Sambucus nigra*, *Verbascum thapsus*, *Populus* spp., *Salix* spp., *Acer pseudoplatanus*, *Robinia pseudoacacia*, *Cytisus scoparius*) growing on these soils was examined. The plant samples were divided into bark, internal and external roots bark and internal trunks, medulla part (when the trunk or root presented it), and foliage. Total mercury content in plants and soils, and the mercury speciation in soils were carried out with Lumex 915M coupled with Pyro 915+. Results showed that the soils contained up to 1068 mg kg<sup>-1</sup> of mercury, with inorganic mercury, presumably associated with cinnabar, dominating in most samples (up to 92%). The areas with the highest mercury concentrations were found near the Nesa and Gould furnaces buildings, which were used to process minerals during the active mining period. DHA concentrations were below 151 µg TPF g<sup>-1</sup> day<sup>-1</sup>, indicating that the presence of mercury did not significantly affect soil enzymatic activity, but it highlights an area highly contaminated by PTEs. Bioaccumulation factors were less than 1 in all plants, suggesting that mercury uptake was minimal. Leaves were found to be the main pathway for mercury uptake, as observed in other mining areas, such as Almaden (Spain). This suggests that particulate mercury and Hg<sup>0</sup> are the main forms entering the plant system, with the latter derived from GEM emissions from both the roasting furnaces and soils.

## Heavy metal enrichment and potential ecological risks from solid mine waste: The case study of the Lame Hg mining dump (Abbadia San Salvatore, Mt. Amiata, Southern Tuscany)

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*Keywords:* mercury, mining dump, enrichment factor.

Mining activity has generated substantial amounts of solid byproducts, despite its notable role in advancing the socio-economic progress worldwide. Mining leftovers, such as excess earth and debris, as well as waste materials from mineral processing operations, often contain hazardous substances such as heavy metals (HMs) that can have severe consequences for both human well-being and the environment. Solid mine wastes consist of multiple elements including sulfides, Fe-Mn oxides, carbonates, silicates, and HMs. Each of these elements possesses distinctive chemical, biological, and ecotoxicological properties. As a result, the effective management of mine wastes requires the use of diverse analytical techniques to accurately assess the elemental constituents, their concentrations, and their individual and combined effects. Researchers frequently apply various indexes such as enrichment factor (EF), contamination factor/degree, and ecological risk (ER) to evaluate the quality of the surrounding environment or to determine the potential ecological hazards associated with distinct solid wastes. Located on the eastern side of Mt. Amiata, a few km north of the Abbadia San Salvatore (ASS) mine, the Le Lame mining dump covers an area of roughly 120,000 m<sup>2</sup>. The transportation of calcines, which are post-processed products, to the mining dump commenced during the 1930s. This was done in order to increase the production of liquid Hg, and new automated conveyor belt systems were established to transfer the Hg-rich material from the extraction shafts to the highly efficient Gould Furnaces. One of the objectives of the remediation of the former Hg mine in ASS is to secure and morphologically reshape the mining dump at Le Lame. In 2022, a new soil sampling was carried out at two depths (0.8-1.2 m and 1.2-2.5 m) to obtain detailed information on the distribution of HMs (e.g. Hg, Sb, As, Be, Cr, Co, Cd, V, Zn, Cu, Fe, Mn, Ni, Pb, Tl) and the respective EF and ER index in the Lame soil. Only Hg, Sb and As were found to have concentrations higher than the D.Lgs 152/06, which regulate the threshold concentrations of contamination, being characterized by the following ranges 6.6-890 mg/kg, 1-1980 mg/kg and 5-88 mg/kg, respectively. In order to understand the relationship between metals, in top and sub-soil, a Compositional Data Analysis (CoDA) approach was adopted on the two datasets. The EF of Co, Cr, Ni, V, Zn and Cu in the top soils is found to be minimal to significantly enriched. Arsenic appears to have an EF up to very high enrichment, while Sb up to extremely high enrichment. Mercury is the only element to have a consistently very high enrichment in the top- and sub-soils. In the sub-soil Co, Ni and Zn are found to have minimal to moderate enrichment, while Cu has significant enrichment. Arsenic, Sb and Hg in the sub-soil reflect the same result as in the top soils. The ER, calculated only on Hg and Sb in both top- and sub-soils, appears to be low to severe.



## Suspended load and mercury pollution: towards a simple method to measure Hg flux from the Monte Amiata Mining District (Southern Tuscany, Italy)

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*Keywords:* mercury, suspended load, stream discharge.

Mining activities produce huge amounts of waste material heavily polluted by toxic elements. Over time, these wastes can pollute fluvial ecosystems due to runoff. Moreover, mining can significantly alter river morphology by modifying sediments supply, erosion, transport, and (re-) deposition. The interplay between geomorphic processes (e.g., flooding events) and anthropic activities plays an important role in the contaminants redistribution across the environment, even at long range. Mercury (Hg) is listed as a critical contaminant due to its high toxicity, mobility, and persistence in the environment. Its use is progressively banned, and Hg mining is limited to a few countries. However, legacy mine wastes are still releasing Hg into the environment, particularly to fluvial ecosystems. The Monte Amiata Mining District (MAMD, Southern Tuscany) was the 3<sup>rd</sup> largest Hg producer worldwide. The Paglia River (PR) drains the SE sector of the MAMD and its catchment covers an area of 1320 km<sup>2</sup>. The widespread Hg pollution of this river basin and its low resilience to contamination was demonstrated in previous studies. Disastrous flooding events remobilized and redistributed massive amounts of polluted sediments across the catchment (Colica et al., 2019). The Hg flux discharged by PR to the Tiber River, and ultimately to the Mediterranean Sea, was estimated around 11kg/y (Rimondi et al., 2019; Fornasaro et al., 2022a; Fornasaro et al., 2022b). However, this estimate is based on spot samplings throughout the year. In this study, the relationship between Hg transported by particulate (Hg<sub>p</sub>) and total suspended solids (TSS) for PR was investigated to set up a method for the calculation of Hg fluxes from TSS monitoring. Water samples were collected during low and high river discharge. Samples were taken along the PR, upstream and downstream of the Elvella creek confluence (ECC), a tributary that is not polluted by Hg, in order to evaluate its effects on the Hg budget. The samples were filtered and the TSS collected on the filters were analyzed for Hg. TSS ranged between 1.3 and 621.4 mg/L, whereas Hg varied between 0.8 and 321.8 ng/L. The highest Hg and TSS values were measured during the recession phase of flooding events, whereas the lowest ones were found during low flow conditions. A linear relationship was found between Hg and TSS. Hg was higher in the upstream samples than in those collected downstream the ECC, confirming that Hg source is the heavily polluted PR basin. The relationship between the two parameters could be applied to the indirect, continuous measurement of Hg fluxes discharged by PR with an automated TSS/turbidity sensor. Such monitoring would allow assessing the variability of Hg pollution across the PR basin in real time especially in case of flooding, that are expected to become more frequent due to climate change, leading to an increase of Hg delivery to the Tiber River and ultimately to the Mediterranean Sea.

Colica A., Benvenuti M., Chiarantini L., Costagliola P., Lattanzi P., Rimondi V. & Rinaldi M. (2019) - From point source to diffuse source of contaminants: The example of mercury dispersion in the Paglia River (Central Italy). *Catena*, 172, 488-500.

Fornasaro S., Morelli G., Costagliola P., Rimondi V., Lattanzi P. & Fagotti C. (2022a) - Total Mercury Mass Load from the Paglia–Tiber River System: The Contribution to Mediterranean Sea Hg Budget. *Toxics*, 10(7), 395.

Fornasaro S., Morelli G., Rimondi V., Fagotti C., Friani R., Lattanzi P. & Costagliola P. (2022b) - The extensive mercury contamination in soil and legacy sediments of the Paglia River basin (Tuscany, Italy): interplay between Hg-mining waste discharge along rivers, 1960s economic boom, and ongoing climate change. *J. Soils Sediments*, 22(2), 656-671.

Rimondi V., Costagliola P., Lattanzi P., Morelli G., Cara G., Cencetti C., Fagotti C., Fredduzzi A., Marchetti G., Sconocchia A. & Torricelli S. (2019) - A 200 km-long mercury contamination of the Paglia and Tiber floodplain: Monitoring results and implications for environmental management. *Environ. Pollut.*, 255, 113191.

## Mercury transport in stream sediments from a former mining area to the sea: the case of the Fiora River basin, Southern Tuscany, Italy

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Keywords: monte Amiata, Fiora catchment, Hg pollution.

Mercury (Hg) is a top-priority contaminant at a global scale due to its high toxicity, mobility, and persistence in the environment. It was observed that remobilization of Hg polluted soils and sediments represents the main source of Hg release in mining areas. The Monte Amiata Mining District (MAMD, Southern Tuscany) represented the 3<sup>rd</sup> largest Hg producer worldwide (Nannoni et al., 2022). Previous works studied Hg dispersion into fluvial ecosystem from the MAMD through the Paglia River catchment (SE sector of the MAMD) and to the Mediterranean Sea, proving that this mining area is a persistent source of pollution and that the Paglia River has a low resilience to Hg pollution (Rimondi et al., 2019; Fornasaro et al., 2022a, Fornasaro et al., 2022b). The contribution of the Fiora River basin (S sector of the MAMD) to the dispersion of Hg-polluted sediments and its temporal variability is presented here. The Fiora River originates on the S flank of Mount Amiata and flows for 80 km towards the Mediterranean Sea. Fifty-one stream sediment samples were collected in 2022: a) 15 samples were taken along the main course of the Fiora River, b) 27 on the secondary creeks draining abandoned mining areas, and c) 9 samples along the Fiora River tributaries that do not drain the mining areas. The total Hg content (Hg<sub>t</sub>) of the samples were compared with the data obtained in 1985 by the RIMIN company (E.N.I. Group) in the Tuscan section of the river catchment. The 2022 sampling also included the downstream part of the Fiora River down to the outlet in the Latium region. Hg<sub>t</sub> varied between 0.4 and 3300 mg/kg, with mean and median values of 111.1 and 3.7 mg/kg, respectively. The RIMIN data in the same sites showed a wider range of Hg<sub>t</sub> (0.5-6450 mg/kg), a higher mean value (592 mg/kg) and a median (3.8 mg/kg) similar to that of the 2022 sampling campaign. Both samplings showed that Hg<sub>t</sub> frequently exceeded the Italian law limit for residential, public green and agricultural soil (1 mg/kg) and the highest Hg<sub>t</sub> values were found in the NE part of the catchment, i.e., along the tributaries that drain the Abetina-Solforate (AS) mining site (up to 3300 mg/kg in 2022). Between 1985 and 2022, Hg<sub>t</sub> decreased in the AS area and along the secondary tributaries that drain the other former mines. The samples collected in the non-mining areas showed Hg<sub>t</sub> ranging from 0.4 to 3.5 mg/kg. Sediments along the main course of the Fiora River showed Hg<sub>t</sub> above 1 mg/kg, with most of the highest values (30-39 mg/kg) in the downstream segment, close to the outflow in the Mediterranean Sea.

This study demonstrates that a) the Fiora River gives a significant contribution to the transport of Hg towards the sea, and b) this river catchment has a low resilience to Hg pollution, similarly to the Paglia River, since the contamination did not decrease significantly in the last 40 years.

Fornasaro S., Morelli G., Rimondi V., Fagotti C., Friani R., Lattanzi P. & Costagliola P. (2022a) - Mercury distribution around the Siele Hg mine (Mt. Amiata district, Italy) twenty years after reclamation: Spatial and temporal variability in soil, stream sediments, and air. *J. Geochem. Explor.*, 232, 106886.

Fornasaro S., Morelli G., Rimondi V., Fagotti C., Friani R., Lattanzi P. & Costagliola P. (2022b) - The extensive mercury contamination in soil and legacy sediments of the Paglia River basin (Tuscany, Italy): interplay between Hg-mining waste discharge along rivers, 1960s economic boom, and ongoing climate change. *J. Soils Sediments*, 22(2), 656-671.

Nannoni A., Meloni F., Benvenuti M., Cabassi J., Ciani F., Costagliola P., Fornasaro S., Lattanzi P., Lazzaroni M., Nisi B., Morelli G., Rimondi V. & Vaselli O. (2022) - Environmental impact of past Hg mining activities in the Monte Amiata district, Italy: A summary of recent studies. *AIMS Geosci.*, 8(4), 525-551.

Rimondi V., Costagliola P., Lattanzi P., Morelli G., Cara G., Cencetti C., Fagotti C., Fredduzzi A., Marchetti G., Sconocchia A. & Torricelli S. (2019) - A 200 km-long mercury contamination of the Paglia and Tiber floodplain: Monitoring results and implications for environmental management. *Environ. Pollut.*, 255, 113191.

## **Gaseous elemental mercury and total and leached mercury from the Rezzaio treatment plant (NW Tuscany, central Italy)**

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*Keywords:* Apuan alps, elemental mercury, total and leachable mercury.

Anthropic activities are the main source of Hg released to the environment, although it also has natural sources (e.g., weathering of rocks, mineral deposits, volcanic emissions and volatilization from the ocean). In the Apuan Alps range (NW Tuscany, central Italy), numerous ore deposits have discontinuously been cultivated for many centuries. In terms of extracted mass ores and activity duration, the most important mining works were those distributed along a 10 km-long NE-SW band in the southern portion of the Apuan Alps. In this context, the Rezzaio treatment plant (Valdicastello Carducci, Pietrasanta), dismissed since 1991, was the site where pyrite ± baryte ± iron oxide ore bodies hosted within the metamorphic rocks of the Apuane Unit, mainly from Monte Arsiccio, Pollone and Buca della Vena mines, were transported and processed to exploit BaSO<sub>4</sub>. Extractive activities, even those currently discontinued, exert a significant impact on the ecosystem of a territory. This study is aimed at evaluating the degree of mercury contamination released by treatment plant and dump of Rezzaio from past-mining activity. The main goals are, as follows: (a) measuring gaseous elemental mercury (GEM, Hg<sup>0</sup>gas) in air and interstitial soil inside and outside the plant, including the working areas and the edifices where the workers were operating (e.g., offices, laboratory, library rock storage) by a portable Lumex RA-915M; (b) determining the total amount of Hg in the top- and sub-soils, mostly developed on a small mining dump; (c) quantifying the release of Hg from leaching tests carried out with CO<sub>2</sub>-saturated Milli-Q water. Real-time GEM air measurement surveys were carried out in 3 different ways: (1) express surveys, performed in the edifices and structures of the Rezzaio plant with GPS control for each measured position; (2) network surveys, with cumulative measurement based on an average of measured values at each 33 selected points inside the buildings; (3) one fixed point survey in the NE portion of the study area for ca. 15 hours. For (1) and (3), the average measured values corresponded to 33 and 22 ng/m<sup>3</sup>, whilst the maximum values to 226 and 34 ng/m<sup>3</sup>, respectively. A total of ~ 30 selected sites were sampled in August 2021 inside and outside the Rezzaio plant by means of a stainless-steel tube (inner diameter 0.4 cm) inserted at 20 to 40 cm depth to collect interstitial soil gases. Moreover, 30 top- and sub-soils (0-30 and 30-50 cm, respectively) samples were collected to analyse the total and leachable Hg on the <2 mm fraction. The mercury distribution showed a heterogeneous distribution in the Rezzaio area. However, the highest concentrations (up to 5.2 mg/kg) were detected near the former plant. In the leachates, Hg showed exceedances >1 µg/L (up to 5 µg/L) on 7 samples. The low content of leachable Hg suggests that mercury is likely trapped within crystalline structures resistant to alteration processes.

## Occurrence and speciation of mercury in the recent sediments of the western coastal area of the Gulf of Trieste (northern Adriatic Sea): is the legacy of historical mining still present?

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*Keywords:* mercury, sediment, grain size.

Mercury (Hg) contamination in the northern Adriatic Sea (Italy) is still an issue of environmental concern due to historical mining at Idrija (Slovenia) which was the second largest Hg mine worldwide (Covelli et al., 2001). The Isonzo/Soča River inputs continue to convey mercury-enriched particles into the coastal area where the element was accumulated in the sediment compartment and transported longshore towards the nearby Marano and Grado Lagoon (Covelli et al., 2007).

This study is focused on the surface sediments from the coastal area in front of the eastern sector of the Marano and Grado Lagoon, where a nearshore depositional system made up of relict and active migrating sandbanks extends up to 2 km seawards from the beachfront (Bezzi et al., 2021). The primary aim of this research is to evaluate the occurrence and distribution of Hg in the surface sediments, their grain size composition and potential relationships between Hg concentrations and the prevalence of distinct grain size fractions. Since sediments may also act as a secondary source of contamination due to biogeochemical processes at the sediment-water interface and resuspension events induced by both natural and anthropogenic factors, Hg speciation through thermal desorption technique (Petranich et al., 2022) was also performed to identify the main Hg compounds.

A total amount of 122 surface sediment samples was collected and analysed for grain size composition and total Hg (THg). Mercury (Hg) speciation analysis was applied as well on a subgroup of samples which were selected following both statistical and geographical criteria.

Sand is the most common mean grain size in the central sector of the investigated area whereas the eastern and western ends are dominated by the silty fraction. The concentration of THg in the sediments varies widely, ranging overall from 0.16 to 59.1  $\mu\text{g g}^{-1}$ . Overall, the highest concentrations of THg were observed in the sediments showing a prevalent very fine sand fraction, most likely due to the occurrence of detrital form of Hg (cinnabar particles). This evidence was confirmed by the speciation analyses which identified cinnabar ( $\alpha\text{-HgS}$ ) and metacinnabar ( $\beta\text{-HgS}$ ) as the main Hg species in sediments thus testifying to a generally scarce mobility of the element present as a sulphide. This evidence supports the hypothesis that the effects of a resuspension event would be negligible in terms of increase of dissolved Hg in the water column and we could expect a rapid settling back of Hg to the sea bottom in association with the sediment particles.

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## May mercury availability to methylation in contaminated sediments be reduced by using biochar as an amendment? Preliminary evidences from laboratory experiments

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*Keywords:* mercury, biochar, sediment.

Among potentially toxic trace elements introduced in the environment by both natural and anthropogenic sources, mercury (Hg) is a contaminant of major concern due to its toxicity and relatively high bioavailability of its most toxic chemical form, methylmercury (MeHg). Indeed, sediments may act as a sink for Hg but they can also be considered a secondary source of contamination due to resuspension events and geochemical processes at the sediment-water interface with subsequent release of Hg species into the overlying water column. In semi-confined aquatic systems, limited water circulation, elevated production of organic matter and hypoxia/anoxia events may promote Hg methylation and MeHg production which can lead to potential MeHg bioaccumulation in the aquatic biota thus posing a risk to marine life and human health. Against this background, sustainable sorbent amendments may represent a cost-effective and environmentally sustainable way to reduce the amount of bioavailable mercury that can be methylated (Gilmour et al., 2013; 2018).

The Marano and Grado Lagoon (northern Adriatic Sea, Italy) has been contaminated with Hg from the second largest Hg mine worldwide (Idrija, Slovenia) and from a decommissioned chlor-alkali plant. Although there has been extensive research on the biogeochemical behavior of Hg in this area (Covelli et al., 2007; 2012), there is still a lack of key information to evaluate whether in situ sustainable remediation can be successfully employed to mitigate Hg mobility in porewaters and potential MeHg production, promoting preservation and restoration of the lagoon environment with the reuse of the sediments, which are considered an important natural resource for the future management of the lagoon.

The purpose of this study is to evaluate the potential application of vineyard pruning residues biochar on Hg contaminated sediments at a selected fish farm in the lagoon, which is one of the most productive sites for aquaculture. Leaching tests were conducted on biochar to assess the release of major and potentially toxic elements in solution. To characterize porewaters and sediments, two short sediment cores were collected and the surface sediment layer (0-5 cm) was extruded under an inert atmosphere. One core was amended with biochar (3% w/w) whereas the other was untreated and used as a control sample. In both cases, sediment was divided into different aliquots which were incubated for different time intervals up to 6 months. Periodically, porewaters were extracted from both untreated and amended sediment samples and the effects of biochar on the mobility of Hg and other major and trace elements were evaluated by means of chemical analyses on both solid and dissolved fractions.

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## **The complex handling of historical contaminated sites: the case of the world-class Mt. Amiata district (Italy)**

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*Keywords:* mercury legacy, monte Amiata, floodplain.

Global population growth and industrialization have driven the demand for material resources with a staggering growth in the decades after the World War II and at the beginning of 21<sup>st</sup> century. However, mining activities inevitably cause environmental degradation, including contamination of watersheds by mercury (Hg). Mercury affects human health as well as the terrestrial and marine biodiversity.

Close to historical mining sites, river self-restoration (i.e., without any management) is incompatible to human timescales, because Hg remains stored within floodplains for decades to millennia. In contrast, complete remediation of watersheds is often economically unsustainable because of the extent of contamination that crosses regional and national borders (e.g., Grygar et al., 2022). This paper presents results of recent studies on the Paglia-Tiber River (PTR, Italy) watershed, affected by a long and intense mining exploitation, as an example of environmental degradation due to lack of management strategies. The nature and the extent of contamination suggest that no clean-up strategies are feasible from an economic and social point of view.

The PTR receives part of the drainage from the world-class Mt. Amiata Hg district, where production ended in 1980s. Longitudinally, sediments of PTR are contaminated (Hg >1 mg/kg, as defined by the Italian law) for 200 km up to the city of Rome (Rimondi et al., 2019). Transversally, the Hg contamination area affects all the Paglia River floodplain, and extends up to the pre-anthropogenic Pleistocene fluvial terraces. Such distribution resulted from the interplay of Hg mining, that fed the floodplain with large amounts of Hg-contaminated sediments during the braided stage of the river (end of 1800-mid-1950s), and the subsequent morphological changes of the river after 1960, induced by anthropogenic activities like gravel mining, that led to the present-day single-channel morphology (Fornasaro et al., 2022). Most of Hg is now stacked in overbank sediments at a higher level than the present-day watercourse. Conservative estimates indicate that at least 60 tons of Hg are contained in the sediments of the first 40 km of the Paglia River course (Colica et al., 2019). Under high flow conditions, and especially in coincidence with intense rain events, large amounts of Hg stored in the overbank sediments are physically mobilized and redistributed along the PTR and eventually to the Mediterranean Sea. Extreme weather events, expected to intensify for climate change, will further exacerbate these processes. In similar settings, given the impossibility of total remediation, mitigation strategies must be found to guarantee that the coexistence between humans and Hg contamination occurs at minimum risk. With respect to the PRT, ongoing studies are evaluating the potential role of poplar trees plantation along the riverbanks to favour the physical retention of Hg-rich particles from the overbanks. A side benefit would be biomass recovery for energy production.

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## **The former Hg-mining area of Abbadia San Salvatore (Mt. Amiata, central Italy): geochemical investigation vs. remediation activities**

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*Keywords:* monte Amiata, mercury, remediation.

The mining activity of the Hg(HgS)-rich ore deposits in the Mt. Amiata district started at the end of the 19<sup>th</sup> century and terminated in 1982 since the demand of mercury dramatically collapsed, mostly because of the elevated toxicity of the various forms into which this element is found in atmosphere, hydrosphere, biosphere and pedosphere. The dismission of mercury basically started after the Minamata event. Among the many Mt. Amiata mining areas, that of Abbadia San Salvatore was the most important center of exploitation of cinnabar and production of liquid mercury. A lot of scientific studies and reports evidenced that the mining and industrial activity has caused a significant impact able to affect all the environmental matrices. To facilitate the activities in the mining concession (ca. 65 ha), the area was divided in 6 units according to the increasing concentration of mercury. Unit 6 is indeed the most critical, since it hosts the Gould furnaces and condenser lines, where gaseous elemental mercury (GEM) reaches concentrations even  $>50,000$  ng/m<sup>3</sup>, a multi-layer shallow aquifer strongly affected by the presence of dissolved and suspended mercury (up to 200 µg/L) and contaminated soils where the contents are up to 2%, likely deriving from the tailings stored in this area and the old furnaces. In the other units, the monitoring activity allowed to plan specific solutions to reduce the presence of high concentrations of GEM that, in most cases, were  $>2000$  ng/m<sup>3</sup>, i.e., well above the threshold limit required by regional authority to consider reclaimed a specific site by GEM, i.e., 300 and 500 ng/m<sup>3</sup> in outdoor and indoor environments, respectively. A pilot well is instead planned to verify which procedures are to be adopted to restore the concentration of mercury in the shallow aquifer below 5 µg/L, in order to discharge the Hg-low content waters into surface waters. Two different techniques were satisfactorily tested. As far as the soil matrix is concerned, there is no other option but to impermeabilize it to avoid any contact between the meteoric water and the Hg-rich soils.

In this study, we review the geochemical activity carried out in the environmental matrices inside the former mining area of Abbadia San Salvatore and adjacent areas as part of the remediation program aimed at restoring and allocating the area to an archeometallurgical museum and public park as a result of the 2008 agreement between the previous owner of the mining concession (ENI-Agip Division) and the Municipality of Abbadia San Salvatore.

## Mercury contamination in Italy: developing strategies for risk assessment

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Keywords: mercury contamination, GEM volatilisation, risk assessment.

Mercury (Hg) occurs naturally or as an anthropogenic contaminant in the environment, posing serious threats to ecosystems and human health due to its mobility, toxicity, and bioaccumulation potential.

Mercury contamination in Italy is due both to past mining activities and to various industrial uses. Contamination from mining can be particularly extensive. In the case of the Mt. Amiata mining district, in southern Tuscany, remarkable amounts of Hg were released in the environment causing a widespread contamination of downstream ecosystems over at least 200 km along the Paglia-Tiber River system (Rimondi et al., 2015). For large areas of Friuli Venezia Giulia (NE, Italy), the high contamination recorded in soils and sediments is caused by the mining activity at Idrija (Western Slovenia). The relevance of mining activities for Hg contamination is confirmed also by the EU mapping of Hg in topsoils, identifying highest concentrations of Hg close to mining sites, including Mt. Amiata and Idrija (Ballabio et al., 2021).

In Italy, there are also several areas affected by the presence of Hg mainly used in the industrial manufacture of Cl products (Hg-cells). In 2020, after the Italian ratification of the Minamata Convention and the first official EU request on the Mercury European Regulation (EU 2017/852) implementation for contaminated sites, ISPRA collected relevant information from regional inventories identifying more than 240 Hg contaminated sites (i.e. posing significant risks), about half of which have been remediated.

The toxicity of Hg varies greatly with its chemical form and exposure pathway. In Italy, for evaluating human exposure, the amount of three different Hg forms is usually considered, accounting for different toxicity/mobility related to specific pathways: Methylmercury (organic form) for direct contact; Mercury Chloride (soluble form in water) for mobilization to water resources (groundwater) and Elemental Mercury (volatile form) for inhalation route. The latter represents, together with the organic form, the most critical for human exposure (Kim et al., 2016).

Substrates enriched in Hg due to anthropogenic contamination can release notable amounts of gaseous elemental mercury (GEM) into the atmosphere even years after the phase out of the contamination source, thus representing a health concern for exposure via vapour inhalation and requiring accurate measures of the GEM emissions to achieve a comprehensive risk assessment. An innovative measurement approach represented by an accumulation chamber coupled with a real-time GEM analyser, which allows rapid assessment of areal emissions (Floreani et al., 2023), has been tested for GEM fluxes estimation at the soil-air interface in some residential and agricultural areas within the contaminated site of Portoscuso (SW Sardinia). Diffuse GEM emissions were calculated and used as input in a new modelling approach for the estimation of outdoor and indoor human exposure.

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## **S12.**

### **New approaches in geochemical data analysis and mapping: from the urban scale to continental wide experiences**

*CONVENERS AND CHAIRPERSONS*

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*Domenico Cicchella (Università del Sannio)*

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## **Radiological risk proceeding from road paving and building materials in the downtown of Naples (Italy)**

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*Keywords:* radiological risk, EBK interpolation, Monte Carlo simulation.

Using a radionuclide identification device (RID), the handheld gamma-ray spectrometer ATOMTEX AT6102, 2548 measurements of ambient equivalent dose rate (ADER) were made in air at a distance of 0.2 m (ADER<sub>0.2m</sub>) and 1 m (ADER<sub>1m</sub>), respectively, from the ground along the street network of the downtown old sector of the city of Naples, in Italy.

Data were sorted and grouped according to the nature of the road paving at each measurement station to determine if a primary influence is exerted on local ADER by the materials used. At a first glance, paving made by natural volcanic rocks (lavas) proceeding from quarries located in the surrounding of the Mt. Somma-Vesuvius volcano show a markedly high ADER values compared to other natural rocks used and non geological materials (i.e. asphalt and concrete). The influence of vesuvian materials on ADER variability is also confirmed by the comparison of its values acquired at different distances from the road paving in the same location (at 0.2 and 1 m from the paved surface) since they show a constant increase as moving close to the ground.

ADER data were mapped through both discrete and interpolated methods. Interpolation of the data was performed by means of the Empirical Bayesian Kriging (EBK) in ArcGIS software.

To assess, in a deterministic way, the health risks proceeding from the low-dose ionizing radiation exposure originating from the paving materials, four indexes (i.e.: the Radium equivalent [Re], the dose rate in the air [D], the Annual Effective Dose Equivalent [AEDE] and the Excess Lifetime Cancer Risk [ELCR]) were used in this study in accordance with the European Commission (1999) and UNSCEAR (2000). In addition, the Monte Carlo simulation method was applied to assess ELCR including the uncertainty. The ADER<sub>1m</sub> data (1273 measurements) spatially separated on the basis of the urban districts falling in the study area were used as an input of the stochastic model. The percentage of certainty, that ELCR could exceed the world average value of 0.00029 proposed by UNSCEAR (2000) was calculated for each involved district showing a critical condition for almost all the downtown territory.

The situation is even more complicated if the stochastic ELCR is assessed including also the exposure proceeding from indoor sources since the dwellings of the Naples downtown have been generally built using Neapolitan Yellow Tuff (NYT) which is characterized by a high emission rate of natural gamma radiation.

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UNSCEAR (2000) - I Sources and Effects of Ionizing Radiation, United Nations Scientific Committee on the Effects of Atomic Radiation UNSCEAR 2000 Report to the General Assembly, with Scientific Annexes, UN, New York.

## The new environmental-geochemical atlas of rural and anthropized soils of Italy: preliminary elaboration of elemental data

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*Keywords:* geochemical atlas, Italy, anthropized areas.

A national wide project dedicated to the geochemical characterization of soils of Italy was jointly carried out by researchers from the University of Napoli Federico II (Campania), University of Sannio (Campania), University of Bologna (Emilia Romagna) and University of Cagliari (Sardinia). One hundred and thirty-nine (139) and one hundred and fifty-nine (159) topsoil samples were collected across Italy, in rural and urbanized/industrialized territories, respectively. Sampling was based on a regular grid with squared cells, each covering an area of about 2500 km<sup>2</sup>. In each cell, at least one sample was collected in correspondence with the territory hosting the main anthropized (urbanized/industrialized) area (avoiding potential contamination hotspots, where possible), and one sample was collected in correspondence with a rural land deemed representative of the sampling cell.

The soil was analyzed to determine its inorganic composition (including the near-total and bioavailable fraction of 54 elements) at Bureau Veritas Laboratories (Vancouver, Canada); the concentrations of several Polycyclic Aromatic Hydrocarbons (PAHs) and Organic Chlorine Pesticides (OCPs) were determined at the University of Geoscience (Wuhan, China), as well.

The data related to the inorganic composition of soils were georeferenced using geographical coordinates acquired during the field work. All the analytical values below detection limits were imputed by using K-Nearest neighbor (kNN) approach.

Following imputation, an exploratory data analysis (EDA) was performed, keeping separated the data related to rural areas from those collected in urbanized/industrialized areas.

Data were spatially processed in a GIS environment (using QGIS software) to generate discrete and interpolated maps of the geochemical variables for both types of samples. For each element and each sample type, a dot map and a spatially continuous raster map were generated. Dot map intervals were separated using the probability plot (PPlot) method by Sinclair (1974), which allows the geochemical data structure (and populations) to be considered. The IDW method was chosen to generate rasters since it is an exact interpolator capable of maintaining the singularities of original data which may represent anomalies relating to contamination processes. Raster map intervals were separated by using the Concentration-Area (C-A) plot.

All the statistical elaborations on discrete and raster data were performed in R software developing dedicated programming scripts.

For each element, a comparison among data from rural and anthropized areas was performed using several methods, as well. Elemental associations representative of the main geogenic or anthropogenic sources were determined by means of multivariate analysis (based on robust statistics).

All the results were graphically homogenized to be included in the "Environmental-geochemical atlas of rural and anthropized soil of Italy" whose preparation is in progress.

Sinclair A.J. (1974) - Selection of thresholds in geochemical data using probability graphs. *J. Geochem. Explor.*, 3, 129-149.

## **A hybrid knowledge-data driven method to build compositional indicators in geochemistry: an application to outline geochemical domains in Volturno River Basin (South Italy)**

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*Keywords:* principal balances, compositional indicators, geochemical domains.

The understanding of most of the processes underlying the geochemical evidence arising from environmental media can be supported and improved by using statistical methods. This work aims at identifying areas with common geochemical characteristics (geochemical domains) and to assess, for these areas, specific geochemical background values to be used as a reference to determine the degree of the impact locally exerted by human activities on the natural environment. For this purpose, we combine some of the most advanced techniques developed in the frame of compositional data analysis (CoDa) with available geological information to reduce the uncertainty in the interpretation of the sources when dealing with geochemical patterns featured by significant spatial variability. A geochemical database including the concentration of 16 chemical elements in 887 stream sediment samples was used. The data refers to an area of 5500 km<sup>2</sup> roughly corresponding to the catchment basin of Volturno River (Southern Italy) which is characterized by significant lithological heterogeneity. The proposed method is based on two main subsequent phases:

- selection of a subset of samples (end-members) with a very high probability of being strongly influenced by one of the lithologies outcropping in the catchment basin (knowledge-driven phase);
- application of the principal balances technique (based on the CoDa approach) to create compositional indicators of natural sources (data-driven phase).

Sample catchment basin (SCB) and machine learning (ML) techniques were used to define the catchment area of each sample and to group the samples according to the values of compositional indicators, respectively.

In the Volturno catchment basin, it was possible to distinguish four geochemical components: 1) predominant carbonatic component (PCC); 2) predominant siliciclastic component (PSC); 3) predominant pyroclastic component (PPC); 4) predominant volcanic component (PVC). The PCC includes sediments enriched in Ca, Mg, and Sr and depleted in Th, La, Ba, Ga, K, Na, and Al, originated by both Triassic limestones and Pliocene and Quaternary sedimentary deposits; PPC and PVC include sediments generally enriched in Th, La, Ba, Ga, K, Na, Al with pyroclastic deposits enriched in high mobility elements (K, Na, Mg, Ca) and older volcanic rocks enriched in low mobility elements (Th, La, Ti, Ga, Mn), respectively. The PSC is characterized by a relative enrichment in Co, Ni, Fe, and Mn.

Finally, the natural background reference values were calculated for the four geochemical domains using the ProUCL software. All the elements show substantial compositional differences among the defined geochemical domains; this is significant for the good performance of the proposed method. Further investigations on geochemical data proceeding from different prospecting areas are needed to demonstrate the scalability of the proposed method.



## **Geochemical speciation, ecological risk and assessment of main sources of potentially toxic elements in stream sediments from Nile River in Egypt**

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*Keywords:* potentially toxic elements, compositional data analysis, bioavailability.

Although the Nile River is one of the main sources of water supply in Egypt, there are not many works on the concentration of potentially toxic elements (PTEs) in its stream sediments. In recent decades, the anthropic pressure caused by industrial and agricultural activities has been intense and the PTEs emissions have accelerated considerably. Moreover, the geological setting of the region fosters favourable conditions for the natural enrichment of PTEs. The combination of natural and anthropogenic effects contributes to explain the high concentration of PTEs in Nile sediments and put the ecosystem at serious risk. This study aims to evaluate the level of contamination by PTEs of the stream sediments of the Nile River. The results reveal that elements such as Cr, Mn, V and Fe are found in high concentrations in almost all the studied samples. They have a natural origin and are connected to the Oligo-Miocene basalts, black shales, iron oxide deposits, ophiolites and granite of the Nubian shield. Moreover, the concentrations of Cu, Ni, Co and As are linked to both natural and anthropogenic processes. Basalts and ophiolites are the natural sources of Cu, Ni and Co, while sulphides and granites of As; industrial activity represents their main anthropic source. Atypical concentrations of Mn, Zn and Pb are mainly of anthropogenic origin. Sequential extraction shows that Mn, Co, Ni and, in some sites, Cu and Zn are the most bioavailable elements. These elements present a high risk of toxicity, while the remaining elements imply a low to moderate risk. Although chromium is the element with the highest enrichment factor found in the sediments, this element is not very bioavailable and, therefore, it has little impact on the degree of toxicity of the sediments.

## Major elements concentration in soils. A case study from Campania Region (Italy)

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*Keywords:* background concentration, robust principal component analysis, geochemical mapping.

In this study, 500 bottom soils and 7,300 topsoils samples were collected to determine the major elements concentrations and to evaluate the correspondence of soil chemical contents and the local geology and to better identify background values. The < 2 millimetres fraction of each sample was analysed for a total of 52 elements combining ICP-MS and ICP-ES techniques. This study focuses on the concentration and distribution of major elements: Al, Ca, Fe, K, Mg, Mn, Na, P and Ti. A combined methodological approach, which involved compositional data analysis, multifractal data interpolation, as well as enrichment factor analysis, was applied to the geochemical dataset. Results indicate that the compositional approach in the multivariate data analysis allows to better interpret the behaviour of elements in natural environment and in geochemical processes as compared to raw data and to improve the quality of related maps. The study has shown that the soils of the Campania region generally contain higher concentrations of investigated major elements than those assessed for European and Italian agricultural soils. In Campania, both bottom soils and topsoils contain higher concentrations of Al, K, Na, P and Ti in volcanic areas. Limestone and dolostone are responsible for higher Ca and Mg contents, while soils formed on siliciclastic deposits generally contain higher levels of Fe and Mn. P and Na concentrations are higher in volcanic soils, but the contribution of fertilizers, which is evident in some areas, should not be underestimated. Weathering processes play an essential role in the distribution of elements in soils, and this appears very evident mostly in volcanic areas. The observations are consistent with the results of the enrichment factors analysis.

## Implemented robust CoDA balances describe geochemical variability of heterogeneous catchments

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*Keywords:* geochemical variability, compositional data, river catchments.

In order to obtain generalizable insights into river catchment geochemistry, the need is to explore the organizing principles that might underlie their heterogeneity and complexity moving beyond the current status of explicitly characterize local watersheds with very complex models. In this regard, it is crucial to conduct comparative studies and implement robust methods capable of exploring the sources of catchments' variability across different scales. In this work, we propose an improved robust methodology for the analysis of variance of isometric coordinates (called balances) obtained with the sequential partition method that successively maximizes the explained variance in the data set (Martin-Fernandez et al., 2018). Robust orthonormal coordinates are created based on hierarchical clustering and robust estimation of the variation matrix and implemented in the open-source R software environment.

Using the newly developed methods, we compare the hydrochemical variability of the rivers pertaining both to the Alpine region and two of the widest catchments in central Italy (Arno and Tiber basins). The balance explaining the highest variance is the same for the three case studies and it is characterized by two groups of variables: the first one, dominated by  $F^-$ ,  $SO_4^{2-}$ ,  $Mg^{2+}$ ,  $HCO_3^-$ ,  $Ca^{2+}$  and the second one, by  $NO_3^-$ ,  $K^+$ ,  $Cl^-$  and  $Na^+$ . This index could represent the contrast between the carbonates cycle (and associated variables) versus that governed by silicates and anthropogenic inputs. The analysis of balances with the lowest variance ( $Cl^-/Na^+$  and  $HCO_3^-/Ca^{2+}$ ) suggests that processes affecting Arno and Alps water chemistry are mainly influenced by random fluctuations. On the contrary, in the Tiber basin, interconnections seems to play a fundamental role highlighting complexity when variance increases (power law distribution). The shape of the frequency distribution of the balances is further analyzed jointly with spatial distribution maps to investigate which of them may be associated with a more resilient behavior in the different geological and geomorphological contexts of the Alpine and Mediterranean areas.

Martin-Fernandez J., Pawlowsky-Glahn V., Egozcue J. & Tolosana-Delgado R. (2018) - Advances in principal balances for compositional data. *Math. Geosci.*, 50, 273-298. <https://doi.org/10.1007/s11004-017-9712-z>.

## The Langelier-Ludwig square diagram through a new compositional lens

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Keywords: Langelier-Ludwig diagram, compositional data, water chemistry.

The idea of representing water's chemical composition with a simple graphical tool dates to Langelier & Ludwig (1942), who proposed the well-known “square” diagram. Suitable groupings of cations and anions are chosen and plotted as a percentage of milliequivalents, with the sums of those cations and anions on the y- and x-axes, respectively. In geochemistry, the Langelier-Ludwig (LL) diagram is commonly used to identify hydrogeochemical facies of water samples. Even so, it displays relative ratios rather than absolute concentrations and the sample space in which the data are represented is given by the simplex. Incorrect conclusions may be drawn when the compositional nature of geochemical data is not considered, for examples: i) a change in one value in one component affects all other values due to the constant sum constraint of the measured chemical elements; ii) correlations are influenced by the presence of negative bias in the covariance structure and iii) linear or nonlinear patterns can be misinterpreted.

In this work, we propose a new compositional version of the LL diagram based on a well-chosen coordinate representation. Results for the classical and the updated version of the diagram were compared for two datasets representing the groundwater chemistry in different areas of central Italy. The advantage of the revised diagram is that all the information is contained in the log-ratios describing the intricate relationship between chemical species in aqueous solutions. The geochemical interpretation of this new diagram, based on the relative dominance of major ions and distance from the (robust) barycenter of the data, provides a better and unbiased understanding of water-environment interactions and the detection of triggering factors for water composition. Advancements in water research rely on this knowledge to protect water ecosystems and biodiversity from anthropogenic and climate-related impacts. As an additional aid to interpretation, (robust) tolerance ellipses show the correlation structure in the new LL diagram and clustering algorithms can be applied to divide the data into groups beforehand. Several plotting options and interactive representations complete the implementation in the free open-source software. The presented methods are available through the function “LLdiagram” in the R package *robCompositions* (Templ et al., 2022).

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Templ M., Gozzi C. & Bucciante A. (2022) - A new version of the Langelier-Ludwig square diagram under a compositional perspective. *J. Geochem. Explor.*, 242, 107084. <https://doi.org/10.1016/j.gexplo.2022.107084>.

## Self-Organizing Maps for soil geochemical data analysis

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Keywords: soil, contamination, SOM.

Contaminants occur naturally in soils due to geological and pedological processes without anthropogenic influence. In this case, the pedological elemental concentration is called “natural background” and is referred to a specific soil at a specified place and time (Reimann & Garrett, 2005). Natural soil background concentrations are variable, depending on the mineralogical composition of the soil parent material and on the pedogenetic processes (Kabata-Pendias & Pendias, 2001). Conversely, the so-called “baseline concentration” in soils represents the amount of the elements introduced into the environment from an anthropogenic activity. Risks to the environment and human health can result if the contaminants are present at concentrations that can be toxic for living organisms. Therefore, understanding background/baseline concentrations of contaminants is important when characterising the degree of environmental harm and for determining whether site contamination exists. Various analytical methods are implemented for analysing data and discriminating the different sources of elemental concentrations. Among them, there are the so-called visual techniques in which the Self-Organizing Maps (SOM) technique (Kohonen, 1982) must be highlighted as the most representative. It, through data visualization, allows to understand high dimensional data by reducing the dimensions of data to a map. More precisely, it compresses the information of high-dimensional data into geometric relationships onto a low-dimensional representation and, jointly, represents clustering concept by grouping similar data together. Therefore, it reduces data dimensions and displays similarities among data. In this research, this technique was employed for the assessment of background/baseline concentration in topsoil of the municipalities of Cosenza and Rende (Calabria, southern Italy). Soil samples were collected from 149 locations, comprising urban and peri-urban areas, for the determination of 25 major and trace elements by XRF and ICP-MS. Concentration data were projected onto a two-dimensional grid and the geometric relationship of the projected vectors was subsequently used to perform a cluster analysis. The results of the model are visualized in versatile 2D maps in which similar samples are mapped close together on a grid. Seven clusters, five geogenic - (I) Cr, Co, Fe, V, Ti, Al; (III) Y, Zr, Rb; (IV) Si, Mg, Ba; (V) Nb, Ce, La; (VI) Sr, P, Ca, and two anthropogenic - (II) Ni, Na; (VII) As, Zn, Pb - were identified. The first ones are related to soil elemental associations, which are controlled by chemical and mineralogical factors of the study area parent material and by soil-forming processes, and the second ones are influenced by anthropogenic input. The most contaminated areas were identified in urban soils compared to peri-urban soils of the study area. This study demonstrates that SOM represents a promising approach for delineating pollution patterns of soil.

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## Occurrence and distribution of silver, gold, palladium and platinum resulting from the high-resolution soil geochemical survey in Campania Region (Italy)

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**Keywords:** rare and precious metals, geochemical sources, compositional data analysis.

Natural processes and anthropogenic influences determine the occurrence of rare and precious metals (RPMs) in a region. Among the natural sources, volcanism, rock weathering, riverine transport, sea-salt spray and the deposition of extra-terrestrial matter contribute to elements amount (Mitra & Sen, 2017). Sen & Peucker-Ehrenbrink (2012) performed a study in which it is stated that the Earth's surficial anthropogenic fluxes for RPMs exceed natural fluxes. Anthropogenic sources of RPMs include their use as catalytic converters in exhaust gas with the aim to reduce the emission of hydrocarbons, carbon monoxide and nitrogen oxides, electronics, drugs, catalysts in the chemical industry, jewellery, thick-film circuits printed on ceramic substrates, in glass and glass-fibre manufacture (Cicchella et al., 2003; Zuzolo et al., 2018).

The main objectives of the present study were: i) assessing the soil RPMs concentrations; ii) identifying RPMs background/baseline and geochemical anomalies in soils of the study area; iii) evaluating the RPMs spatial distribution and input sources; iv) examining data according to CoDA method and defining the best data analysis approach.

For this purpose, RPMs concentrations were explored in the 5735 topsoil samples in the Campania Region (Southern Italy). They were analysed by inductively coupled plasma mass spectrometry (ICP-MS) after an aqua regia digestion. The elemental concentrations ranged from 0.001 to 2.061 mg kg<sup>-1</sup> for Ag, from 0.0001 to 0.4188 mg kg<sup>-1</sup> for Au, from 0.005 to 0.296 mg kg<sup>-1</sup> for Pd and from 0.001 to 0.014 mg kg<sup>-1</sup> for Pt. The mean values for Ag, Pd and Pt are above the bulk continental crustal abundances. A robust compositional computation analysis was applied on the selected elements. It showed that RPMs geochemical anomalies can be ascribed both to geology-related volcanic and anthropogenic sources. The central-western part of the region, characterized by volcanic rocks, more influences the RPMs concentrations than areas characterized by silico-clastic and carbonate deposits, occurring mostly in the southern and eastern part of the region. More precisely, the concentration of Ag and Au reproduces differences in the origin of their source material in the volcanic products of northern (Roccamonfina) and central Campania (Campi Flegrei, Vesuvius). In addition, a clear relationship exists between the abrasion of automobile catalytic converters and the higher concentrations of Pt and Pd in soil, such as one between Au and Ag concentrations and the main urban areas (Napoli, Salerno, Caserta, Benevento, Avellino). Evidence from this study showed that compositional data transformations such as clr transformation could help to avoid artefacts better than the use of raw data.

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## **A multimedia geochemical prospecting project in Basilicata region: the activities carried out on soils and stream sediments of the Cavone and Basento River basins**

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*Keywords:* soils, stream sediments, statistics.

In 2020, a sub-regional scale geochemical prospecting project started following a scientific collaboration agreement between the Department of Earth, Environment and Resources Sciences (DiSTAR) of the University of Naples Federico II (UniNa) and Eni S.p.A. Southern District (DIME). The main goal was the determination of the geochemical background/baseline values for different media (i.e., stream sediments, soils, and groundwaters) in an area covered by the catchments basins of the Basento and Cavone Rivers in the south-eastern sector of the Basilicata region (Southern Italy).

For this purpose, three working units were activated: 1) The "Environmental Geochemistry" (GEOCHEM) unit, dedicated to the characterization of solid surficial media (i.e., stream sediments and soils) collected in the median sector of the Basento River basin and the entire Cavone River basin; 2) The "Hydrogeochemistry" (IDROGEOCHEM) unit, dedicated to the groundwaters of the middle valley sectors of both rivers; 3) The "Geology" (GEO) unit, aimed at the creation of a geological model in support of the GEOCHEM and IDROGEOCHEM units activities.

The Environmental Geochemistry Working Group (EGWG) at DiSTAR led the activities of the GEOCHEM unit. Specifically, during spring-summer 2021, 190 topsoil samples (at an average depth of 10-15 cm from the surface) and 185 composite stream sediment samples were collected in an area of about 1400 sqkm. In addition, during June 2022, 10 bottom soils (at an average depth of 80-100 cm from the ground surface) were collected, as well.

All the samples (both soil and stream sediments) were analyzed at OMAC Laboratories Ltd (Loughrea, Ireland). Samples underwent an Aqua Regia digestion followed by ICP-MS to determine the quasi-total concentrations of 53 chemical elements (Au, Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, Ge, Hf, Hg, In, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Pd, Pt, Rb, Re, S, Sb, Sc, Se, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V, W, Y, Zn, Zr).

A further aliquot of the 190 topsoils and 10 bottom soils was analyzed at the Life Analytics S.r.l. laboratory (Battipaglia, Italy) through ICP-MS following the acid digestion reported in the UNI EN 13657:2004 + UNI EN ISO 17294-2:2016 methods, considered mandatory by the national Italian guidelines to determine concentrations of potentially toxic elements (As, Be, Cd, Co, Cr, CrIV, Cu, Hg, Ni, Pb, Sb, Se, Tl, V, Zn) in a contaminated site. Concentrations of SO<sub>4</sub> in soils were also determined at the Life Analytics S.r.l.

The generated datasets were georeferenced and processed using statistical univariate and multivariate techniques and multifractal methods. A wide set of graphs (including boxplots, histograms, and probability plots) and maps (showing the discrete and interpolated distribution of raw, anomalous, and background values) was prepared for each geochemical variable allowing a comprehensive analysis of the natural and anthropogenic processes affecting the study area.

## Factors influencing the bioavailability of some selected elements in the agricultural soil of a geologically varied territory: the Campania region (Italy) case study

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*Keywords:* bioavailability, geochemical mapping, regression analysis.

Bioavailability of some major and trace elements was evaluated in 1,993 agricultural topsoil samples collected across Campania region (Southern Italy). Samples were analysed by an ammonium nitrate leaching prior to ICP-MS and ICP-ES analysis. The study aimed primarily at comparing the distribution of the bioavailable concentrations of selected elements with their pseudo-total concentrations, determined using a modified Aqua Regia digestion.

Geochemical maps of the pseudo-total and bioavailable concentrations were generated using a multifractal inverse distance weighted (MIDW) interpolation. In addition, the spatial distribution patterns of the percent bioavailability of elements, based on the ratio among the bioavailable and pseudo-total fractions, were determined.

A main focus was made on Al, Ca, K, Mg, Cu, Tl since they are linked, albeit for different reasons, to agriculture. The median value of the percent bioavailability showed the order  $Ca > K > Mg = Tl > Cu > Al$  and that represents a positive finding in terms of both agricultural productivity and environmental quality.

A linear regression was applied to data to unveil any dependence between the bioavailable fraction and the pseudo-total content of elements. Furthermore, a multiple linear regression was then applied including in the model also the grain size distribution (i.e., clay, silt, sand) and organic matter content of samples, to evaluate their possible role in promoting the environmental availability of elements.

The pseudo-total concentrations of Al, Ca, K, and Mg alone resulted to be poorly able to predict the variability of the bioavailable fraction whereas for Tl and, above all, Cu resulted to be more capable to forecast the patterns of the bioavailable concentrations. The addition of the grain size distribution and organic matter content to the models expanded the predictive capability of Ca, K, and Mg, whereas a marginal improvement was showed by Al, Cu, and Tl suggesting that other unknown factors probably exert a major influence on their mobility.

As regards Tl, Cu, and other potentially toxic elements the results obtained suggest that the use of total or pseudo-total concentrations, when dealing with the assessment of risks deriving from consumption of agricultural products, should be of limited significance. It was demonstrated, in fact, that further factors, probably related with physical-chemical characteristics of soils, could influence the real amount of these elements transferable from soil to plants.

This study represents a methodological contribution to a better understanding of the processes underlying the spatial variability of chemical elements in soil. Considering the positive outcomes obtained, further researches are planned to include more factors (e.g., soil pH, redox potential, content in Fe and Mn oxides, etc.) in the predictive models.

## Stream sediments and environmental contamination assessment: a case study from southern Italy based on the Sample Catchment Basin approach

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*Keywords:* stream sediments, sample catchment basin, enrichment factors.

As part of a monitoring project jointly carried out by University of Naples "Federico II" and Eni S.p.a., the spatially omogeneous sampling of 185 stream sediments was performed across the catchment basins of Basento and Cavone rivers in Basilicata region (Southern Italy). Potential toxic elements (PTEs) were analysed using the ICP-MS method after samples were treated by mean of an Aqua Regia solution. The geochemical prospecting of stream sediment is a reliable tool for investigating the influence of geology and evaluating the presence of natural and/or anthropogenic anomalies within river catchment basins. It is well known that sediments produced by weathering processes are transported by surficial runoff toward lowest areas of a catchment areas. So, this type of samples is representative of upstream and the whole basin which they originate. To separate the geochemical signals generated by surficial processes from the geological background contribution, it's necessary to consider that the abundance of an element in a stream sample is the result of several enrichment and dilution steps taking place during transport. The dilution effect can be modelled and corrected to improve the geochemical signals and better locate the source of anomalies. For this purpose, the Sample Catchment Basin (SCB) approach was used, where the correction of elements concentrations at sample point can be based on a-posteriori definition of an area upstream of sampling location, characterized by specific geomorphological and hydrogeological features, which outlines the region which directly affects the downstream sample (Albanese et al., 2013; Najafian et al., 2020). This method tries to estimate the background concentration of elements in different lithological units as well as the background value for every SCB. By mean of this technique, it was then possible to define the enrichment factors (EFs) for each basin compared to the value of the chemical concentrations of the different PTEs analysed. The EFs were useful for defining the level of anthropogenic impact on the area and in turn were used to identify associations of elements that could potentially correspond to natural and/or anthropogenic sources that condition the geochemical variability across the basins. The results show that where urban and industrial centres are present, anthropogenic anomalies are more evident.

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## **Risk assessment from Radon-222 following tap water consumption (and showers) in Campania region (Italy)**

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*Keywords:* tap waters, human health risk, radionuclides.

The composition of groundwaters mainly depends on the geological features of their reservoir. Naturally occurring radionuclides (NORs) such as K-40, U-238, and Th-232 (including their decay products) and other radionuclides of cosmogenic origin can be found in water following their contact with some rock types such as those of igneous nature. Radon-222, a noble gas and a radioactive isotope belonging to the decay chain of U-238, may also be present in groundwaters following contact with volcanic materials or active structures. The decay of Radon-222 into its daughter products can occur in the human body following water ingestion or inhalation, which represent some of the primary sources of exposure to Ionizing radiations and can be a severe threat to human health.

Legislative Decree No 28/2016 establishes an upper guideline value for Rn-222 of 100 Bq/l for tap waters in Italy. In contrast, a good amount of scientific literature shows that applying a risk assessment-based approach to waters can lead to a higher degree of public health safety protection compared to the mere use of guidelines. WHO (2004) and the EU Council (European Commission, 2001) do not consider the "guideline approach" as a suitable method and suggest assessing health risk for Rn-222 by determining the Indicative Dose (ID). This latter is the dose of radiation an individual assumes through ingestion and/or inhalation due to environmental exposure.

Different lithologies in the Campania region (Southern Italy), including volcanic and sedimentary rocks, can influence the concentration of metals and gases in groundwaters mostly used for drinking. This work is based on the data proceeding from a large scale Rn-222 monitoring made on tap waters in Campania. Specifically, a total of 181 measurements were completed on different sections/points of the regional water supply system, including public fountains (98), water tanks (52), wells (21), and springs (10). A stochastic risk assessment was performed for homogeneous areas supplied by specific hydrogeological units, and the probability for the local population to be exposed to an unacceptable risk from Rn-222 resulted to be considerably high for those areas totally or partially supplied by waters proceeding from the regional volcanic domains (E.g.: Mt. Somma-Vesuvius, Mt. Roccamonfina, etc.).

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WHO (2004) - Guidelines for drinking-water quality, Third Edition. World Health Organization, Geneva.

## **$^{87}\text{Sr}/^{86}\text{Sr}$ spatial distribution in Italy: geocomputational tools to track the geographical origin of biological samples**

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*Keywords:* strontium, isoscape, provenance.

Reconstructing the geographical origin, the provenance and the movements of biological samples is key in many fields of study, including food science/security, ecology, archaeology and forensic anthropology/medicine. To this end, Sr isotope tracers have historically played a central role due to their link with the lithological and geological features of the landscape. Yet, to accurately interpret provenance through isotope systematics, it is paramount to have reference datasets of geobiological/environmental samples from the area of interest as comparison. Such data can be spatially modelled through geostatistical and machine learning techniques, to obtain continuous maps of isotope distribution, i.e. isoscapes. In addition, these maps can be ‘queried’ e.g. by Bayesian methods to obtain estimated probability of geographical origin and possibly overcome ‘eyeball’ approaches. Here, we present the current state of the Italian Sr isoscape (Lugli et al., 2022) and novel freely available online-tools that can be used to test the geographical origin of biological samples. Specifically, we will show flaws and merits of traditional interpolation methods (e.g. Kriging), compared with novel automated learning algorithms such as Random Forest (Bataille et al., 2018), and we will demonstrate how sample provenance can be defined numerically by combining isoscapes, related spatial uncertainties and Bayesian inversion methods (Ma et al., 2020). Overall, these approaches can strengthen our interpretation of sample provenance, within a robust statistical framework.

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Ma C., Vander Zanden H.B., Wunder M.B. & Bowen G.J. (2020) - AssignR: an R package for isotope-based geographic assignment. Methods Ecol. Evol., 11(8), 996-1001. <https://doi.org/10.1111/2041-210X.13426>.

## Elemental and isotope geochemistry as a tool for geographical origin identification: the case study of red chicory in Massenzatica (Ferrara, NE, Italy)

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Keywords: geochemistry, food traceability, isotopic analysis.

Determination and authentication of the geographical origin of food products have recently become relevant in investigations against fraud for consumer protection. Studies on territoriality are based on the hypothesis that chemical elements detected in plants and their products reflect those contained in the soil. Geographical features of the production area are considered relevant factors affecting the specific designation such as the composition of the parent rock, soil-forming process, climate, topography, and land use. Since in a biomass, the inorganic component tends to be more stable than the organic one, for some years several studies have been examining trace elements, suggesting their potential application for the determination of geographical origin. An accurate analysis of the elemental composition, including trace elements and stable light isotopes, can possibly support the identification of quality features and territoriality of crops and their derived products.

Red chicory (*Cichorium intybus* L., Asteraceae) is a common crop in the southern Po Delta area, where it grows in sandy soils up to close to the coast. The local economy aims at valorizing the local red chicory, assuming that several generations of cultivation may have selected special characters which, e.g., would differentiate it from the same varieties cultivated elsewhere. The two inspected red chicory cv. (long-leaved “Treviso” and round-leaved “Chioggia”) were cultivated in a well-defined area sited near Massenzatica (Municipality of Mesola, Province of Ferrara, NE Italy) (Bergantin et al., 2017). Two different fields were selected for comparison, one located inside the area of the Consorzio Uomini di Massenzatica, the other not very far from this but closer to the seacoast. Samplings of soils and plants (leaves and roots) were performed in the period of plant vegetation from the late autumn. The comparative geochemical data were obtained using XRF, ICP-MS and EA-IRMS techniques. A first comparison regarded the specificity of the two cultivars with respect to the same soil: to this aim, chlorophyll fluorescence parameters were recorded in the field and correlations with the elemental data were sought. Subsequently, the elemental compositions of the two varieties in two fields were compared to establish a method to identify the geographical origin, particularly to test its sensitivity, the soils being overall very similar to each other. The results confirm that some major and trace elements could be used as geochemical markers according to the geological areas. These elements therefore could be proposed for the geochemical fingerprint of red chicory in the coastal area near the Po Deltas. The method, applied for testing the origin of red chicory sold in the market, can help create a protected designation of origin label.

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## Transfer factors of potentially toxic elements from soil to agricultural products in Campania region, southern Italy

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*Keywords:* environmental geochemistry, transfer factor, potentially toxic element.

The introduction into the soil of potentially toxic elements (PTEs) originating from anthropogenic sources is a concern for living beings. When PTEs are not bound to the crystalline lattice of soil, they can easily migrate from the geological to the biological compartment (Jarup, 2003). The knowledge of the natural geochemical composition of the soil allows us to determine contamination levels due to active anthropic sources, assess hazards and risks, and minimize negative impacts on living organisms (Reimann et al., 2005).

Several studies have already investigated the distribution patterns of PTEs in soil within the Campania region of southern Italy (De Vivo et al., 2022); however, little is known about the transfer processes of contaminants from soil to agricultural products.

Here, we present the results of a new study aimed at determining the transfer factors (TFs) of PTEs from soil to agricultural products commonly grown in the Campania region. Given this territory's complex geological and geomorphological settings and the historical anthropization associated with industry, agriculture, and urbanization, we determined the TFs for a significant number of fruit and vegetable samples (1300 specimens) collected throughout the entire region. The goal was to detect behavioral differences between analyzed agricultural species and to highlight spatial changes in TFs patterns for individual species.

The TFs were calculated by comparing concentrations of PTEs in products with both the quasi-total (based on Aqua Regia leaching) and the bioavailable (based on ammonium nitrate leaching) concentrations of the same elements in regional soil.

Preliminary results indicate that TFs vary in space and amount for different agricultural species, independent of the original soil elemental concentrations. High TFs values were found in areas with low PTEs concentrations in soil and vice versa. These findings suggest that, apart of their content in soil, more factors could influence the uptake of PTEs to the plants. Hence, sophisticated statistical approaches such as multiple regression and multivariate analyses were applied to investigate whether additional chemical and physical characteristics of soil (such as pH, grain size, and organic matter content) could play a role in determining the quantity of contaminants migrating from soil to plants.

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Jarup L. (2003) - Hazards of heavy metal contamination. *Brit. Med. Bull.*, 68, 167-182.

Reimann C. & de Caritat P. (2005) - Distinguishing between natural and anthropogenic sources for elements in the environment: regional geochemical surveys versus enrichment factors. *Sci. Total Environ.*, 337(1-3), 91-107.

## Environmental impact of wildfires on soil geochemistry: a case study of two fire events in Campania region (southern Italy)

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*Keywords:* environmental geochemistry, wildfires, enrichment factor.

In recent years, climate change and intentional illegal burnings has significantly increased the number of worldwide wildfires. These normally generate dusts which are dispersed by wind and can accumulated into soil following fall-out (Dimitrios, 2020). As a consequence, wildfires has become a problem of global concern since human beings may be exposed to potentially toxic elements (PTEs) after breathing dusts released during combustion or resuspended from soils.

The geochemical characteristics of ashes depend on the nature of the burnt material (Dermibas et al., 2003), as well as other factors such as the intensity of combustion, the composition of underlying soils and the type of bedrock. Furthermore, several studies have demonstrated that the PTEs in deposited ashes can modify the chemical and physical properties of the receiving soil, thus influencing the development and growth of microorganisms and vegetation (Raison, 1979).

The purpose of this study was to investigate the environmental impact associated with two fire events that occurred during the 2017 summer season in the Campania region (Southern Italy): a) a wildfire at the volcano slopes within the Vesuvius National Park; b) a fire at a waste disposal site (named Iside) within Caserta province. The variations of PTE concentration occurred in the topsoil which received the ashes were examined and the significance of the changes detected was evaluated by means of robust statistical methods. Finally, a potential interpretation of the results was provided.

In total, 120 topsoil samples were used for the study. Specifically, for each site, 30 samples were available from a pre-event prospecting activity, and 30 samples were intentionally collected after the fire events. To favor the comparison, the "post-fire" samples were collected at the location of the "pre-fire" sampling sites along the main wind directions which were recorded at the time of the fires.

To investigate the potential elemental contamination of soil due to the fire events, the Enrichment Factor (EFs) of a selected group of PTEs was determined and mapped for each sample. Furthermore, a combined application of multivariate statistical analysis and geospatial analysis was performed on the calculated EFs.

For the Iside site, the association of Hg, Tl, Cu, and Co was identified as the primary factor responsible for data variability suggesting that special and electronic wastes were burned. For the Vesuvian area, the association of Hg, Cu, and Cr was found to be quite strong, possibly due to the burning of forest biomass. A relevant enrichment of Hg was observed in both areas.

This study highlights the distinct chemical evidence left by fires in the environment, depending on the nature of the burnt materials. Moreover, the findings demonstrate that even the burning of biomass from natural areas can introduce PTEs into the environment, potentially increasing the degree of environmental hazard.

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## Developing a hydrogeological conceptual model of Central Chile's coastal fractured rocks

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Keywords: hydrogeology, fractured rocks, saltwater intrusion.

Central Chile is currently experiencing water scarcity due to the overuse of water resources exacerbated by a prolonged Megadrought (Garreaud et al., 2017; 2019). Such context reveals the need for efficient water resource management depending on a deep understanding of the hydrogeological systems. Chile is a mountainous country with a ~6,500 km long coastline mainly composed of intrusive rocks. Despite the vast coastal area, no hydrogeological studies exist yet there. A hydrogeochemical (physicochemical parameters, anions, cations, trace elements) and isotopic study ( $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ ) from 8 springs and 15 wells is conducted to develop a conceptual model of Central Chile's coastal hard rock hydrogeological systems for the first time. The study is focused on Laguna Verde (~33°S), a peninsula composed of Jurassic granitoid strongly affected by regional-scale faults (Gana et al., 1996) under a mediterranean climate with mean annual precipitation of ~500 mm/year.

Preliminary results show 341-5500  $\mu\text{S}/\text{cm}$  electrical conductivity values, temperature 16-25°C, and pH 6.4- 8.1. Groundwater composition shows  $\text{Cl}^-$  and  $\text{Na}^+$  enrichment from the highest topographical areas to the sea. While  $\text{HCO}_3^-$ - $\text{Ca}^{+2}$  hydrogeochemical facies dominated inland,  $\text{Cl}^-$ - $\text{Na}^+$  facies were concentrated along the coastline. Binary plots suggest that plagioclase dissolution partially explains the groundwater composition in Laguna Verde. Given that groundwater samples were taken over sea level (~300 m a.s.l), the coastal fog is a plausible dissolved ions source to explain the observed  $\text{Cl}^-$  and  $\text{Na}^+$  enrichment towards the coast.

To complement the isotopic and hydrochemical analysis, statistical analyzes were performed in order to understand the dynamics and chemistry of the groundwater. The results of the hierarchical analyses reveal three main composition of water, while the factorial analysis indicates a strong control of Na, Cl, Br and  $\text{HCO}_3^-$  in the composition of groundwater.

This work is funded by CAPTA-CORFO 19CTIGH-12134. Simunovic's Ph. D. studies are funded by ANID-Beca Doctorado Nacional/2021 21211312.

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## Stochastic geochemical atlas: a tool to predict uncertainty in local elemental background evaluation

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*Keywords:* geostatistics, stream sediments, heterogeneity.

Last decades have shown that regulation and planned technical procedures addressed to manage the environment through elemental background evaluation clashed sometimes up to unreasonable scenarios.

Availability of a geochemical information widely spread over a large area and integrating uncertainty should help regulatory Agencies engaged in remediation procedures or institutions in charge of drafting regulatory acts. Particularly stream sediments long term compositional stationarity has the capability to describe the mean upstream basin geochemistry. This happens through an averaging elemental contribution of the different outcropping lithotypes by mixing processes. Interestingly stream sediments' domain of existence is coincident with the interface between surface water and river deposits called hyporheic zone. That thin geological body is the frontier among main spheres featuring Earth (atmo-, hydro- geo- and bio-sphere) thus the site where biotic and abiotic phenomena evolve and interfere.

The variability of what we can expect to be found in the hyporheic zone is highly dependent on geology, geomorphology, and catchment management through the climate tuning. This leads to very distant scenarios from lower up to highly low-scale heterogeneity and thus toward high-frequency variability of elemental concentrations. That panorama can induce an over- or under-evaluation respect to a threshold value.

The highly short-scale geological heterogeneity as found in Ligurian Alps and Apennines catchments calls an urgent change of strategy in the description of the spatial distribution of environmental parameters. Thanks to that uncertainty-based integration of geochemical data regolith, local variability has been detected and formalized toward a "geochemical compatibility". The Geochemical Numerical Model of Liguria (GNM-L) based on stream sediments is created by ad-hoc implementation of spatial stochastic methods. The aim was finalized to create a flexible and highly adaptive tool supported by a geostatistical approach.

Taking care of geomorphology, geology and statistical features, 8 digital layers representing statistics parameter related to 34 chemical elements (SiO<sub>2</sub>, TiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, CaO, MgO, MnO, K<sub>2</sub>O, Na<sub>2</sub>O, As, Ba, Co, Cr, Cu, Ga, Hg, La, Ni, Pb, Sb, Sc, Sr, Th, U, V, Y, Zn, Zr, Tl, Sn, Br, Cd, Be) the GNM-L was recently released as a public tool. The enhancement of the information's density for each single element present in GNM-L routinely updatable over the a term, allows decision- and policy-makers to understand more deeply the environment with the help of a tool more adherently to the uncertain local reality.

The predictive capability of the GNM-L is shown and performed through the use of independent geochemical dataset (as from FOREGS, or released by local Agencies) enabling the user to compare how the element present in a specific geological matrix (mainly stream sediments but also soils) can be considered compatible or not respect to a reference stochastic image of the environment.

## **S13.**

### **Petrological and geochemical tools to investigate recycling processes: new insights and future directions**

#### *CONVENERS AND CHAIRPERSONS*

*Martina Casalini (Università degli Studi di Firenze)*

*Francesco Narduzzi (Università degli Studi di Trieste)*

*Enrico Cannaò (Università degli Studi di Milano Statale)*

*Mattia Bonazzi (Consiglio Nazionale delle Ricerche, Pavia)*

*Vincenza Guarino (Università degli Studi di Napoli Federico II)*

*Davide Berno King Abdullah (University of Science and Technology, Arabia Saudita)*

## **Trioctahedral micas in xenoliths related to Plinian eruptions from the Somma-Vesuvius volcanism (Italy): composition, structure, and genetic implications**

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*Keywords:* phlogopite, crystal chemistry, Vesuvius.

The present work is part of a systematic mineralogical and petrographic characterization of mica-bearing xenoliths from Somma-Vesuvius volcano (Roman Magmatic Province). Skarns, composite skarns-marbles and cumulates from Pompeii Plinian eruption (AD 79), and skarns and syenite from Avellino eruption (3945 ± 10 cal yr BP) were investigated to define the crystal chemistry of the Somma-Vesuvius trioctahedral micas and to draw inferences on petrogenetic processes they were subjected. Xenoliths were characterized by means of polarized optical microscopy, SEM-EDS, XRPD and bulk-rock geochemical analyses. Mica crystals were studied through electron microprobe analysis and single crystal X-ray diffraction. Micas from skarns are variably associated with Mg+Ca silicates (clinopyroxene, vesuvianite, humite, clinohumite, chondrodite, forsterite, garnet), other sporadic silicates (anorthite, sodalite, titanite, britholite), apatite, calcite, various types of oxides, as well as rare sulfides and halides. In composite skarn-marble rocks, the mineral assemblages show some differences compared to skarns, as lack of clinopyroxene and the presence of dolomite. Cumulate samples consist of mica and clinopyroxene, whereas syenite is mainly composed of mica, K-feldspar, feldspathoids and clinopyroxene. Together with mica, apatite occurs in all the lithotypes. Trace element arrays are scattered for skarn and composite skarn-marble samples. The REE patterns have a general enrichment in light (La, Ce, Pr, Nd) and medium (Sm, Eu, Gd, Tb, Dy) REEs. Cumulate samples generally have low amounts of Ba, Sr, Zr and Th, while syenite exhibits low concentrations of trace elements, except for Rb, Cs and Tl. Mica crystals occurring in the studied xenoliths are phlogopite with different Al and Mg content at the octahedral site, a negligible tetraferriphlogopite component and variable dehydrogenation degree. All samples belong to the 1M polytype (C2/m and C2 space group) and have a wide range of unit cell parameters, especially of the c axis [ $5.3055(1) \leq a \leq 5.3218(1) \text{ \AA}$ ,  $9.1893(1) \leq b \leq 9.2188(4) \text{ \AA}$ ,  $10.1803(2) \leq c \leq 10.2951(2) \text{ \AA}$ ]. The shortest c cell parameter pertains to dehydrogenated phlogopite from Avellino skarn whereas OH-rich phlogopite from Pompeii composite skarns-marbles has a c cell parameter which approximates that of the endmember phlogopite.

Overall, it is observed that the crystal chemistry of the micas of the present study extend the known range of the other Vesuvian micas from literature. The Ti-depletion and the wide degree of dehydrogenation of phlogopites from skarns and composite skarns-marbles suggest that the studied samples originated under variable pressure conditions. In addition, the presence of humite in the mineral assemblage seems to indicate the occurrence of devolatilization reactions. The scarce mica occurrence in cumulate and mainly in syenite, instead, may depend on pressure conditions in the magma storage system exceeding the mica stability.



## The exotic accessory minerals within mantle metasomatic domains: new insights of the sources of orogenic magmas

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Keywords: ultramafic xenolith, felsic veins, accessory minerals.

The petrographic and mineralogical investigation of ultramafic xenoliths is fundamental for our understanding of the nature and evolution of the upper mantle. These xenoliths are commonly brought to surface by the eruption of alkaline basic magmas in intraplate settings. On the contrary, in convergent settings, their occurrence is rare and usually associated with post-collisional anorogenic volcanism, being of paramount importance since they represent the supra-subduction mantle sources. A particular case is represented by the ultramafic xenolith occurrence in the Betic Cordillera of southern Spain, where decimetre-sized metasomatised mantle xenoliths (lherzolites and harzburgites) were brought to the surface by the eruption of post-orogenic Na-alkaline basalts of the Cabezo Negro de Tallante volcano. Interestingly, a few of them are also crossed by felsic veins and veinlets which have been interpreted as the interaction of crustal-derived melts released in the mantle wedge and peridotite during the subduction (Avanzinelli et al., 2020; Dallai et al., 2022). Petrographic and mineral chemistry analyses show that these veins and veinlets are mainly made up of plagioclase, orthopyroxene and quartz, or by phlogopite/amphibole, diorite and gabbro-norite. In centimetric veins the parageneses include sporadic pargasite amphibole, whereas the network (apophysis) of millimetric veinlets contain a large variety of accessory minerals such as amphibole, phlogopite, apatite, zircon, rutile, Fe-Ni(Cu-Zn) oxides and sulphides and peculiar mineral phases pertaining to the apatite, monazite, huttonite/thorite and thorianite-uraninite solid solutions. Preliminary investigation with SEM and EMPA revealed that the compositional range of huttonite/thorite is SiO<sub>2</sub> 15-18 wt%, ThO<sub>2</sub> 69-85 wt%, P<sub>2</sub>O<sub>5</sub> 1-5 wt%, La<sub>2</sub>O<sub>3</sub> 0-3 wt%, Ce<sub>2</sub>O<sub>3</sub> 2-6 wt%. Uraninite-thorianite mineral phases have UO<sub>2</sub> 17-46 wt% and ThO<sub>2</sub> 41-78 wt% contents. Apatite contains Cl up to 6 wt%. Fe-Ni sulphides contain NiO up to 75 wt%. The rutile compositional data indicate that this mineral dominates the budget of Ti (TiO<sub>2</sub> 80-100 wt%) and Nb (Nb<sub>2</sub>O<sub>5</sub> 5-13 wt%). Further major and trace elements analyses will be performed to better constrain the composition of these mineral phases. These xenoliths will offer valuable information about the nature and composition of the metasomatic agents in subduction-related mantle sections, as well as the element redistribution in the metasomatic parageneses through the interaction with the mélange mantle wedge. This is of great importance because they represent the unique (or very rare) direct explanation for the observed geochemical signature of orogenic magmas.

Avanzinelli R., Bianchini G., Tiepolo M., Jasim A., Natali C., Braschi E., Dallai L., Beccaluva L. & Conticelli S. (2020) - Subduction-related hybridization of the lithospheric mantle revealed by trace element and Sr-Nd-Pb isotopic data in composite xenoliths from Tallante (Betic Cordillera, Spain). *Lithos*, 352-353, 105316. <https://doi.org/10.1016/j.lithos.2019.105316>.

Dallai L., Bianchini G., Avanzinelli R., Deloule E., Natali C., Gaeta M., Cavallo A. & Conticelli S. (2022) - Quartz-bearing rhyolitic melts in the Earth's mantle. *Nat. Commun.*, 13, 7765. <https://doi.org/10.1038/s41467-022-35382-3>.

## New insights into the evolution of Triassic-Jurassic alkaline magmatism in the Southern Alps: evidence from trace and isotopic composition of dyke zircons

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Keywords: dykes, Zircon, Finero complex.

Triassic magmatic activity is widely documented in various sectors of the Southern Alps, including the Dolomites, the Brescia Alps and the Ivrea-Verbanò area (IVZ). However, the evolution of this activity remains poorly constrained. In recent years, extensive evidence of Triassic magmatism has been reported in the Finero Complex (northernmost tip of IVZ; Zanetti et al., 2013; Schaltegger et al., 2015).

This contribution focuses on the alkali magmatism documented by the discordant intrusion in the Finero mantle peridotite of swarms ranging from ultramafic (hornblendites) to evolved dykes (from diorites to albitites). These dykes show different mineralogical, chemical and isotopic compositions, indicating a mixing of mantle and recycled crustal components.

An important tool for defining the geochronological and geochemical characteristics of parent melts is the zircon survey. Zircon is a common accessory mineral in evolved igneous rocks and can contain numerous trace elements, such as Hf, REE, Nb, Ti, U and Th.

The zircons separated by Finero dikes are anhedral to sub-anhedral. The CL features show that the primary magmatic textures were mostly overprinted by homogeneous and bright irregular domains.

The zircons of the dykes were fully characterized by determining the concentration of trace elements as well as the isotopic compositions of U-Pb and Lu-Hf by LA-ICP-(QQQ/MC)MS.

Zircons are characterized by low concentrations of REE (70-160ppm), Th (15-150ppm), U (20-200ppm), Nb and Ta (both are always < 2ppm). The U-Pb zircon ages indicate a complex evolution showing few concordant ages ranging from ~190 to ~216 Ma, with several weakly concordant ages in the similar time range.

The variability of U-Pb ages is not related to the internal structure of the CL. Furthermore, the mean  $\epsilon_{\text{Hf}}(t)$  values of +9 and +3 suggest the presence of distinct zircon populations, segregated by melts derived from mantle sources containing variable amounts of crustal component.

The comparison between our U-Pb data and the literature data suggests the development of multiple melt pulses on a broad time horizon at Triassic-Jurassic boundary.

These data allow to better understand the transition of the geochemical affinity of the Southern Alps magmatism from orogenic to anorogenic, linked to changes in the tectonic regime triggering a regional uplift of a metasomatized asthenosphere.

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Zanetti A., Mazzucchelli M., Sinigoi S., Giovanardi T., Peressini G. & Fanning C.M. (2013) - SHRIMP U-Pb Zircon Triassic Intrusion Age of the Finero Mafic Complex (Ivrea-Verbanò Zone, Western Alps) and its Geodynamic Implications. *J. Petrol.*, 54, 2235-2265.

## Elevated Nb/Ta, SiO<sub>2</sub> undersaturated magmas, and the recycling of carbonate-rich sediments in subduction zones

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*Keywords:* CO<sub>2</sub>, HFSE, subduction.

Understanding the recycling of CO<sub>2</sub> in subduction zones is crucial to constrain the global carbon cycle and to reveal the source of a volatile compound that plays a key role determining the explosivity of volcanism. During subduction of carbonate-rich lithologies, the release of CO<sub>2</sub> strongly affects the mantle chemistry and mineralogy, eventually producing, upon melting, SiO<sub>2</sub> undersaturated magmas (Wendlandt & Eggler, 1980). However, the degree of SiO<sub>2</sub> saturation is also influenced by other factors, such as the degree and pressure of partial melting. In this work we use a novel proxy, the Nb/Ta ratio, which is rather constant in most geological reservoirs, but shows extremely elevated values in carbon-rich fluids/melts such as carbonatites (e.g., Green, 1995; Bragagni et al., 2022). Thus, we test if this ratio can be sensitive to subduction-derived CO<sub>2</sub> rich fluids/melts.

High precision HFSE concentration were obtained via isotope dilution on samples from the Italian plio-quadernary magmatism. The SiO<sub>2</sub> (over)saturated Tuscan magmatism (Radicofani) shows unfractionated Nb/Ta, indistinguishable from that of the ambient mantle, represented by Tyrrhenian sea basalts. Instead, SiO<sub>2</sub> undersaturated magmas of the Roman Magmatic province (Latium and Vesuvius districts) have elevated Nb/Ta. This is consistent with previous studies that identified two different lithologies in the subducting beneath the Tuscan and Roman magmatic provinces, being silica-rich in the first one and carbonate-rich (marl) in the second one (e.g., Conticelli et al., 2015). Notably, in the Roman magmatic province, the degree of SiO<sub>2</sub> undersaturation, expressed as Feldspathoid Silica-Saturation Index, is negatively correlated with Nb/Ta.

Combining our new data with published ones, we highlight a link between elevated Nb/Ta, SiO<sub>2</sub> undersaturated magmatism, and sediment melts from subducting carbonates, occurring in circum-Mediterranean localities (Italy, Macedonia, Bulgaria, Turkey) and in the Sunda arc. Therefore, we propose that the Nb/Ta ratio can be used to trace the recycling of subducting carbonates.

Bragagni A., Mastroianni F., Münker C., Conticelli S. & Avanzinelli R. (2022) - A carbon-rich lithospheric mantle as a source for the large CO<sub>2</sub> emissions of Etna volcano (Italy). *Geology*, 50, 486-490. <https://doi.org/10.1130/G49510.1>.

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Green T.H. (1995) - Significance of Nb/Ta as an indicator of geochemical processes in the crust-mantle system. *Chem. Geol.*, 120, 347-359. [https://10.1016/0009-2541\(94\)00145-X](https://10.1016/0009-2541(94)00145-X).

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## Trace element and $\delta^{11}\text{B}$ evolution of the Asùt Tesoru mud volcano (Mariana forearc, IODP Exp 366): evidence for shallow slab devolatilization and element recycle

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*Keywords:* boron isotopes, serpentinites, subduction zones.

The development of hydrated forearc mantle regions is considered one of the major outcomes of chemical recycling in convergent margins, influencing the geochemical signatures of volcanic arcs (Savov et al., 2005) and sustaining the deep microbial ecosystems (Plümper et al., 2017). We focus our attention on the serpentinite clasts from the Asùt Tesoru mud volcano in the Mariana forearc (18.06°N and 147.06°E, IODP Exp 366) as a proxy to unravel the active geochemical exchanges between the upper mantle and slab-derived fluids at shallow depths. We provide new in-situ trace element concentrations and boron (B) isotope compositions ( $\delta^{11}\text{B}$ ) employing a laser ablation microprobe coupled with an ICP-MS and a multi-collector ICP-MS, respectively, for a suite of well-studied samples for which major and trace element whole rock compositions are available, together with their bulk  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  and Fe-O isotopic signatures (Debret et al., 2019; 2020). The Asùt Tesoru mud volcano is located about 70 km from the Mariana trench and 18 km above the slab, where temperatures at the slab-mantle interface are estimated at 250°C. The analyzed serpentine polymorph in the serpentinite clasts span from lizardite- to antigorite-end members. Preliminary results document enrichments in B (from 10 to 150 ppm) and other fluid-mobile and redox-sensitive elements (e.g., Ba, Sr, As, W, Mo). Boron isotope composition range between -5 and +21‰ and shows a positive correlation with the B concentrations. Remarkably, the  $\delta^{11}\text{B}$  signatures evolve from positive to negative values from lizardite-bearing samples towards the antigorite-bearing ones. Higher B, Sr, Ba, W and Mo contents in lizardite-bearing samples compared to antigorite-bearing ones indicates a selective devolatilization for these elements during the early stage of subduction at relatively oxidized conditions. Increasing of the W/Ba ratio from lizardite- to antigorite-serpentines also suggests an influx of slab-derived fluids with an increase of a sedimentary pelagic-like component during the serpentinization of the forearc mantle throughout the serpentine phase transition. The slab-fluid influx is associated with a significant decrease in the  $\delta^{11}\text{B}$  (up to 15‰), which agrees with the expected  $\delta^{11}\text{B}$  imprint of the fluids released by the downgoing slab during shallow burial.

Our preliminary results highlight the strong influence of the shallow slab devolatilization on the geochemical and redox evolution of the hydrated forearc mantle, which may further impact the cycle of elements in convergent margins.

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## Polybaric fractional crystallization and open-system processes in the Cixerri amphibole-rich domes (SW, Sardinia, Italy)

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*Keywords:* amphibole, Sr-Nd isotopes, Cixerri.

The igneous rocks outcropping in the form of lava domes in the Cixerri half-graben, in south-western Sardinia, are calcalkaline basaltic andesites and andesites with orogenic chemical signature (peaks at Pb, K, Rb, Ba, Sr; troughs at Nb, Ta and Ti). They are an expression of the subduction-related igneous activity developed in Sardinia during the Upper Eocene-Middle Miocene (38-12 Ma; Lustrino et al., 2009 and references therein), as confirmed by <sup>40</sup>Ar/<sup>39</sup>Ar age determinations on a Cixerri andesite (21.31 ± 0.05 Ma). This age indicates that these domes were emplaced during the peak of activity of the subduction-related magmatic cycle in Sardinia (~22-18 Ma). At this time, the N-NW directed Apennine-Maghrebide subducting slab had reached the 80-120 km dehydration depth, triggering metasomatism of the mantle wedge (Carminati et al., 2012 and references therein). The investigated domes are porphyritic with zoned amphibole, plagioclase and minor clinopyroxene phenocrysts included in a groundmass made up of the same phases plus alkali feldspar, quartz and opaque oxides. The bulk-rock major and trace element variations compared to the phenocryst composition, and the mass balance calculations are consistent with magmatic evolution driven by fractional crystallization of amphibole and plagioclase, with minor clinopyroxene and magnetite. The significant abundance of amphibole in the Cixerri rocks, differently from the typical two-pyroxene andesites of the neighboring Sulcis district, can be explained by the high calculated H<sub>2</sub>O content (up to 9 wt.%) and oxygen fugacity (NNO+1-NNO+2) in the Cixerri magma. The calculated pressure of amphibole crystallization (~2-4 kbar and ~6-9 kbar) and the bulk rock isotopic variations (<sup>87</sup>Sr/<sup>86</sup>Sr = 0.70701-0.70786 and <sup>143</sup>Nd/<sup>144</sup>Nd = 0.512328-0.512436) indicate that the Cixerri magma evolved in a polybaric and open plumbing system with a low degree of crustal assimilation (r = 0.1-0.2). Oscillatory and reverse zoning of plagioclase and amphibole could be related to magma recharge/mixing/crustal assimilation, or to pressure decrease and H<sub>2</sub>O increase in the evolving magma during its ascent in the crust. The flat HREE patterns of the Cixerri rocks and the lower concentration in HREE than typical N-MORBs point to a magma source in the spinel stability field located in a mantle wedge depleted in incompatible elements prior to the enrichment by slab and sediment derived fluids and melts.

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## Framing the temporal evolution of the Mid-Triassic magmatism in the Southern Alps (Italy): clues from U-Pb dating of titanite in phonolitic dykes from the Dolomites area

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*Keywords:* Dolomites area, phonolites, mid-Triassic magmatism.

Due to their excellent state of preservation, the Permo-Triassic magmatic rocks of the Southern Alps (Italy) offer the opportunity to reconstruct the geodynamic evolution at the Gondwana-Laurasia boundary. During the Mid-Triassic, the acme of the volcano-plutonic activity produced magmas with orogenic-like affinity, and was pre- and post-dated by the emplacement of small volume of melts, nowadays cropping out as dyke swarms intruded into the plutonic bodies and/or the overlying volcanites. Here, we present a detailed geochemical and geochronological study of phonolitic dykes ( $\text{SiO}_2 = 56.8\text{-}57.8$  wt.%;  $\text{Na}_2\text{O} + \text{K}_2\text{O} = 11.1\text{-}15.3$  wt.%) intruded into the basaltic to trachyandesitic Mid-Triassic lavas in proximity of Predazzo (Dolomites area). The phonolites have porphyricity index <10%, and are constituted by clinopyroxene, sanidine, sodalite, plus accessory titanite, apatite and magnetite phenocrysts embedded into a microcrystalline to glassy matrix. Clinopyroxene has diopsidic to hedenbergitic composition, and displays concentric zoning with significant variation in the Mg# [ $\text{MgO}/(\text{MgO}+\text{FeO}_{\text{tot}})$  mol%], Mn, Ti, Al and Na contents. Titanite has a highly variable U-Th concentration (U from 24 to 478 ppm and Th from 170 to 4328 ppm) and is characterized by a chondrite-normalized REE pattern with a convex-upward shape ( $\text{La}/\text{Yb}_N = 19\text{-}42$ ) with enrichment in LREE and depletion in HREE. Zr-in-Titanite thermometry (Hayden et al., 2008) indicate crystallisation temperatures between 860 and  $943 \pm 57^\circ\text{C}$ . In-situ, U-Pb dating on titanite phenocrysts performed by laser ablation-inductively coupled-mass spectrometry (LA-ICP-MS) shows that the age of phonolite dykes is comprised between  $240.4 \pm 3.2$  Ma and  $242.0 \pm 3.6$  Ma, partially overlapping with the emplacement of the Middle-Triassic plutonic bodies of the Dolomites ( $238.190 \pm 0.050$  -  $238.075 \pm 0.087$ ; Storck et al., 2019). This age is markedly different from that of other younger alkaline manifestations cropping out in the same area (i.e. lamprophyre dykes dated at  $219.22 \pm 0.73$  Ma; Casetta et al., 2019), which also show a different chemical signature. These results provide new insights into the timing of the Middle Triassic magmatic event in the Southern Alps, fostering the debates about the temporal and chemical evolution of the magmatism in between the Variscan orogeny and the opening of the Alpine Tethys.

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## **Subduction-legacy and olivine monitoring for mantle-heterogeneities of the sources of ultrapotassic magmas an overview from the Central Western Mediterranean basin**

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*Keywords:* Central Italy, ultrapotassic volcanic rocks, olivine chemistry, mantle metasomatism.

Subduction drags a large amount of CO<sub>2</sub> into the Earth's interior, which is partly returned to the atmosphere by arc volcanism. Processes involved in the recycling of subducted carbon within the upper mantle are mainly related to mineralogical transformation. Subducted CO<sub>2</sub> may dramatically affect the equilibria among peridotitic minerals (olivine vs. pyroxenes) changing their stability fields and thus their modal abundances. This process is accompanied by a subduction-induced change in the budget of some incompatible trace and major elements (e.g., K, Ca, HFSE), whereas it has a minimal effect on the mass balance of compatible elements (e.g., Ni). Here, we report an overview on olivine chemistry, major and trace, and when present stable isotopes, in subduction-related mafic alkaline ultrapotassic rocks from Western Mediterranean basin. Olivine is used as a proxy to define mantle wedge mineralogy and metasomatic processes. Minor element concentrations, and in particular the high Li and low Ti in olivine, confirm a major role for recycled sediment in the generation of Western Mediterranean ultrapotassic magmas. The distinct contents of Ni, Mn, and Ca in olivine reflect the bimodal character of silica-rich and silica-poor ultrapotassic Italian rocks and constrain two distinct mineralogical reactions between metasomatic agents and peridotite. In the most silica-poor ultrapotassic mafic rocks (i.e., kamafugites) three genetically different olivine groups are recognised: phenocrysts, melt-related xenocrysts, and skarn-derived xenocrysts. The melting and crystallization conditions of Italian kamafugites and lamproites indicate compositionally heterogeneous mantle sources on very small scales. Distinct geochemical features of the olivine macro-crystals observed in kamafugite, point to a range of processes occurring both within the magma storage and transport system. Diversity of metasomatic agents was involved in mantle processes on local scales, coupled with magma mixing and/or the uptake of xenocrysts during magma ascent.

## Fingerprinting the subduction factory in the Neogene magmatic activity of central and eastern Anatolia

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**Keywords:** Anatolia, subduction, isotope composition.

Arc-like magmas are characterised by trace elements and isotopic fingerprints thought to reflect fluid/melts derived either from subducted oceanic lithosphere or sediment in the involvement of magma genesis. These volcanic rocks show high LILE/HFSE ratios, as well as high  $^{87}\text{Sr}/^{86}\text{Sr}$  and low  $^{143}\text{Nd}/^{144}\text{Nd}$ , and also associated to excess  $^{207}\text{Pb}/^{206}\text{Pb}$ . Volcanic rocks with clear subduction signatures are also generated by magmas originated during post-collisional settings, in which different tectonic episodes (strike-slip faulting or lithosphere delamination) trigger magma production and their ascent to surface from mantle sources previously metasomatised by subduction events.

In Central and Eastern Anatolia, abundant magmatic activity occurred during the Neogene to Quaternary in response to the ocean-continent subduction and continent-continent collision of the Eurasia, Africa, and Arabia plates, followed by post-collisional strike-slip dynamics. In Sivas-Malatya and Elazığ-Tunceli areas, arc-volcanic activity started during the Early Miocene at Yamadağ (19.5-13.6 Ma) and Kepez Dağ (16.4-13.5 Ma) volcanic complexes, overlapping with the activities in the Mazgirt (16.0-15.13 Ma) and Pertek (16.2-15.7 Ma) areas. These magmas are characterised by typical subduction-related geochemical affinities, with high LILE/HFSE ratios (e.g., Ba/Nb = 13-77), and variable  $^{87}\text{Sr}/^{86}\text{Sr}_i$  (0.7040-0.7077) and  $^{143}\text{Nd}/^{144}\text{Nd}$  (0.51245-0.51287) isotope ratios, suggesting an origin from partial melting of a mantle wedge delimited by the subduction of the last oceanic branch of Neotethys. Coeval Na-alkaline basaltic activity erupted during the Early-Middle Miocene (16.7-13.1 Ma) in Sivas, and later, during Late Miocene (11.4-11.0 Ma) in Tunceli fields. Although these magmas show typical intraplate OIB-like features, trace element abundances (Ba/Nb = 5-35), as well as isotope compositions of  $^{87}\text{Sr}/^{86}\text{Sr}$  (0.7039-0.7068) and  $^{143}\text{Nd}/^{144}\text{Nd}$  (0.51256-0.51284) imply the possible interaction with subduction-related reservoirs.

The amount of the “subduction” component declined in Na-alkaline products erupted during the Middle-Late Miocene (15.9-8.9 Ma) in Arguvan and the Pliocene (5.9-4.0 Ma) in Kangal fields, as well as in magmas emplaced during the Pliocene Karakoçan (4.1 Ma) and Pleistocene Elazığ areas (1.6 Ma). These latter are characterised by lower LILE/HFSE ratios (e.g., Ba/Nb = 7-28), with isotope ratios overlapping typical OIB-like magmas ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.7033-0.7052$  and  $^{143}\text{Nd}/^{144}\text{Nd} = 0.51263-0.51287$ ).

On the contrary, younger magmatism in Cappadocia (3.6-0.1 Ma), central Anatolia, has coeval calc-alkaline and Na-alkaline products. Notably, here most of the Na-alkaline products show an arc-type distribution of trace elements (Ba/Nb = 12-37),  $^{87}\text{Sr}/^{86}\text{Sr}$  (0.7036-0.7055) and  $^{143}\text{Nd}/^{144}\text{Nd}$  (0.51263-0.51289). Here, true intraplate-like magmas are absent, and the genesis of these basaltic magmas is ascribed to mixing between deeper within-plate (OIB-like) and shallower calc-alkaline subduction-related magmas.

## Petrology and geochemistry of the Eocene-Oligocene subduction-related Lar igneous complex (SE, Iran)

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*Keywords:* Lar igneous complex, shoshonitic/ultrapotassic magmatism, sisthan suture zone.

The Lar Igneous Complex represents an Eocene-Oligocene igneous event located in the South Eastern Iran, along the Sistan Suture Zone. Such a suture belongs to the Alpine-Himalayan orogenic belt that started to form during the Cretaceous, due to the closure of a branch of the Neo-Tethys and the subsequent collision of the Lut and the Helmand (Afghan) block.

The Lar complex is made of intrusive and hypabyssal igneous rocks characterised by shoshonitic to ultrapotassic petrological affinities, variable degrees of silica saturation, and with a clear orogenic geochemical fingerprint.

Alkaline silica-undersaturated igneous rocks include lamprophyres, nepheline-syenite and phonolitic dykes, on one side, and silica-saturated and -oversaturated rocks represented by syenitic to trachytic dykes and monzonitic bodies, on the other one.

Lamprophyres and nepheline-syenites show symplectitic domains involving nepheline and K-feldspar, and minor kalsilite, recalling pseudoleucite textures, a peculiar petrographic feature typical of intrusive conditions. Lamprophyres are characterized by cumulus olivine (Fo content up to 91) and clinopyroxene (Mg# up to 0.83). The latter are characterised, in most of the samples, by abundant phlogopite inclusions.

Primordia Mantle-normalised incompatible trace element patterns show LILE enrichments and HFSE depletions, typical of subduction-related magmas, with the alkaline potassic and silica-undersaturated rocks characterised by higher LREE/HREE ( $La_N/Yb_N$  from 12 to 22) than silica-saturated and -oversaturated rocks ( $La_N/Yb_N$  from 10 to 12).

The Sr-Nd-Pb isotopic composition of the less differentiated samples from the Lar suite displays an almost homogeneous signature, suggesting a common mantle source. The occurrence of continental crustal contamination processes coupled to crystal fractionation affects only the most differentiated products. An isotopic-based geochemical modelling highlights a mantle source metasomatized by partial melts from carbonate-rich (over subordinate carbonate-poor) recycled sediments within the upper mantle.

## The crystallization and mineral assemblages of F-disilicates in peralkaline trachyphonolites from Ischia, Phlegrean Fields and Sardinia

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Keywords: F-disilicates, peralkalinity, REE.

The F-disilicates are a complex group of minerals that cannot be defined by a single composition. These discrete phases are a chemical solution of a number of different end members. Their classification is made here according to the cationic occupancy at each site, following structural information, and using discriminant diagrams to which are added the reference compositions of the rinkite and wöhlerite groups are added, taken from the Handbook of Mineralogy and MINDAT web sites. These phases are subdivided into rinkite and wöhlerite groups, and typically crystallize in peralkaline rocks, being enriched in Mn, Zr, Nb, REE and F, and very low in Al<sub>2</sub>O<sub>3</sub> and MgO. Their presence is strongly related to peralkalinity, silica, chlorine, fluorine, water activity,  $f_{O_2}$ , Zr, Nb and REE during their crystallization (Marks & Markl, 2017 and references therein; Guarino et al., 2021), but the actual composition and mineral assemblages are far from being firmly established from a thermodynamic point of view.

Magmatic F-disilicates have been identified in several trachytic rocks at Ischia (e.g., the Zaro lava, the Mt. Vico and Castello Aragonese domes), Phlegrean Fields (e.g., the Cuma dome; Melluso et al., 2012), and at Montiferru, Sardinia (the trachyphonolitic domes in the summit region; Fedele et al., 2007). The main types of F-disilicates identified are: kochite (rinkite group) and hiortdahlite and låvenite (wöhlerite group) at Phlegrean Fields, hainite, kochite and rosenbuschite (rinkite group) and hiortdahlite, normandite and låvenite (wöhlerite group) at Ischia, and hainite and kochite (rinkite group) and baghdadite/hiortdahlite (wöhlerite group) at Montiferru. The F-disilicates are associated with several additional phases (fayalite, hedenbergite-aegirine, aenigmatite, fluorite, britholite, various feldspathoids and baddeleyite, pyrochlore, titanite, etc.), indicating a very high degree of magmatic differentiation.

The presence of F-disilicates suggests that the peralkaline liquids were variably enriched in incompatible elements such as HFSE, REE and F (less in H<sub>2</sub>O and Cl). Their variability is closely related to the complex and enriched system from which they crystallize. The F-disilicates begin to crystallize after the crystallization of fluorite, which corresponds to the maximum of fluorine activity. Another peculiarity of these localities is the positive correlation between Mn<sup>2+</sup> and Fe<sup>2+</sup>. This suggests that the cation Mn<sup>2+</sup> plays an important role in the field of stability of the F-disilicates.

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## Fluid redox fingerprint of the $\text{CaCO}_3$ +antigorite dehydration reaction in subducted metacarbonate sediments

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*Keywords:* antigorite dehydration, redox, electrolytic fluid thermodynamic modelling.

Antigorite dehydration is a process able to release, in comparison with other minerals, the highest amount of  $\text{H}_2\text{O}$  from a subducting slab. The released fluid delivers critical elements (e.g., S, Cu, and REE) to the overlying subarc mantle, modifying the mantle source of arc magmas and related ore deposits. Whether antigorite breakdown produces oxidising or reducing fluids is debated. Whereas previous studies have investigated antigorite dehydration in serpentinites (i.e., in a (C)AMFS- $\text{H}_2\text{O}$  system), this contribution is devoted to the CMFS-COHS carbonate system, which is representative of the metacarbonate sediments (or carbonate-dominated ophiocarbonate rocks) that sit atop the slab. Thermodynamic modelling is used to investigate the redox effect of the carbonate-buffered antigorite dehydration reactions (i.e., brucite breakdown and antigorite break-down) on electrolytic fluid geochemistry as a function of P-T- $f\text{O}_2$ . The influence of P-T- $f\text{O}_2$  conditions on the solubility of C and S, solute-bound  $\text{H}_2$  and  $\text{O}_2$ , fluid pH, the average valence states of dissolved C and S, and the fluid redox budget indicates that, in metacarbonate sediments, the  $\text{CaCO}_3$ +antigorite reaction tends to produce reducing fluids. However, the redox state of such fluids is buffered not only by the redox state of the system but also, most importantly, by concomitantly dissolving redox-sensitive minerals (i.e., carbonates, graphite, pyrite, and anhydrite). A qualitative correlation between the redox state of the system and the possible depth of fluid release into the mantle wedge is also derived.

## Source and mobility of mercury in continental magmatic systems: the STECALMY Project

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Keywords: Hg in the Earth's crust, Hg loss, sesia magmatic system.

Active volcanoes emit significant amounts of mercury (Hg) into the atmosphere, thus playing a key role in its cycling on the Earth. Being highly toxic, Hg enrichment in sedimentary rocks is often used to link major ancient bio-climatic crises to massive volcanic eruptions. Therefore, the Hg cycle from its degassing upon accumulation in marine and terrestrial environments is widely studied. Critically, it remains uncertain what is the concentration of Hg in magmas prior to degassing. Degassing and/or partitioning of Hg into the Earth's core could explain its low concentrations in basalts. Conversely, differentiation and/or crustal assimilation could increase Hg concentrations in igneous and volcanic rocks (Deng et al., 2022). However, these observations remain ambiguous for the following reasons: i) the analyzed rocks are not from the same magmatic system, and, more importantly, ii) the results could be biased by unintentional under- or overestimation of Hg caused by analytical challenges related to its high volatility and extremely low concentration (< 100 ng/g) in crystalline rocks.

The STECALMY project investigates the source and mobility of Hg in the Earth's crust using as a study case the Sesia Magmatic System (SMS; Western Southern Alps, Italy), an exposed continental magmatic system that can be traced from its deepest roots to its volcanic products (Tavazzani et al., 2020 and references therein). Here, we first developed a rigorous sample preparation and analytical procedure to optimize Hg analyses in crystalline rocks. Different igneous rocks were pulverized with agate mortar and a planetary mill equipped with agate and tungsten carbide jars. Powders obtained with these three approaches were analyzed with Direct Mercury Analyzer (DMA-80) and, after total acid dissolution, with Cold-Vapour-Atomic-Fluorescence-Spectroscopy. The first results show that up to 80% of Hg can be lost during powdering with tungsten carbide jars. With this new rigorous protocol, we aim to analyze the Hg concentration in granites from the Valle Mosso pluton of the SMS, since it exposes to surface pre- to syn-eruptive features and forms the uppermost part of a magmatic plumbing system of a large Permian caldera-forming volcanic eruption (Tavazzani et al., 2020 and references therein).

Deng C., Gou J., Sun D., Sun G., Tian Z., Lehmann B., Moynier F. & Yin R. (2022) - Mercury isotopic composition of igneous rocks from an accretionary orogen: Implications for lithospheric recycling. *Geology*, 50(9), 1001-1006. <https://doi.org/10.1130/G50131.1>.

Tavazzani L., Peres S., Sinigoi S., Demarchi G., Economos R.C. & Quick J.E. (2020) - Timescales and Mechanisms of Crystal-mush Rejuvenation and Melt Extraction Recorded in Permian Plutonic and Volcanic Rocks of the Sesia Magmatic System (Southern Alps, Italy). *J. Petrol.*, 61(5), ega049. <https://doi.org/10.1093/petrology/egaa049>.



## The olivine-minette dykes from the Julian Alps, NE Italy: age, geochemistry and geodynamic implications

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**Keywords:** Olivine-minette dykes, U-Pb apatite geochronology, Julian Alps.

Here we present new petrographic, geochemical, and geochronological results on the olivine-minette dykes from the Rio Colan Valley, Julian Alps, NE Italy (Narduzzi et al., 2023). Dykes are ~ 60 cm wide and crosscut an upper Triassic sedimentary sequence. No crustal contamination is seen at the contact with the host rocks. Dykes consist of phenocrysts of olivine (serpentinized), biotite-phlogopite, and diopside. Accessory minerals are apatites, forming needles in the matrix and within micas and clinopyroxenes, opaques, rare feldspars, and chromites. The same minerals forming the phenocrysts constitute the groundmass. They are immersed in an ialocrystalline to a holocrystalline matrix showing intergranular texture. Furthermore, petrographic observations indicate that olivine+biotite-phlogopite+diopside+apatite±opaques are in equilibrium, implying the dykes are primitive minette. This is consistent with their high Mg#, high Cr and Ni contents, and flat HREE profiles. These geochemical features suggest that these magmas are derived from a depleted peridotite having, likely, garnet and olivine as residual minerals. Based on the high concentrations of K<sub>2</sub>O and incompatible elements, together with superchondritic Nb/Ta ratios, we propose that the peridotitic source also had phlogopite and rutile in its mineralogical assemblage. We argue that this mineralogical assemblage reflects the recycling of crustal material and carbonatitic metasomatism related to an older orogenic event and rutile-rich metasomatism linked to the Pangea breakup. Also, our geochemical results show that these olivine minettes are geochemically hybrid products between lamprophyres and lamproites once compared with similar Mediterranean volcanics. Eventually, since apatites are not of secondary origin (i.e., hydrothermalism), they were separated from two dykes and dated by LA-MC-ICP-MS U-Pb geochronology. Dating yielded differences between forced and unforced discordia ages up to ~ 45 Ma, which we argue is likely due to the adopted initial <sup>207</sup>Pb/<sup>206</sup>Pb correction. However, since the forced discordia and weighted mean ages yielded similar results, we argue that these olivine minette dykes intruded and crystallized at ~ 67 Ma. Both the age and anorogenic character of these magmas are consistent with the extensional tectonics that the Julian Alps were experiencing during this time due to the advance of the external Dinaric front following the eastward subduction of the Adria plate.

Narduzzi F., Ponton M., Marelllo M., de Castro MP, Queiroga G. & De Min A. (2023) - Geochemical characterization, U-Pb apatite geochronology, and geodynamic significance of olivine minette dykes from the Julian Alps, NE Italy. *Geol. Mag.*, 1-16. <https://doi.org/10.1017/S0016756823000183>.

## Hf isotopic variability of Early Mesozoic magmatism in the Ivrea-Verbano Zone and Dolomites: Implications on the geodynamic evolution and correlation of the Southern Alps

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**Keywords:** magmatism, Dolomites, Southern Alps.

Trace elements, geochronological and Nd-Sr isotopic characterization of volcano-plutonic sequences in the Dolomites have differentiated the Early Mesozoic magmatism of the area into two distinct groups: i) the Middle Triassic high-K calc-alkaline to shoshonitic series; and ii) the Late Triassic to Early Jurassic alkaline series. To the west, in the Ivrea-Verbano Zone (IVZ), Triassic to Jurassic aged dykes belonging to these two series also intruded mantle and lower crustal rocks. To further decouple and correlate the different pulses of magmatism in the eastern and westernmost sectors of the Southern Alps, we characterize some shoshonitic lavas from the Dolomites and alkali-rich dykes from the IVZ for their Hf isotopic composition. Whole-rock of the Middle Triassic shoshonitic lavas from the Dolomites are characterized by  $\epsilon\text{Hf}_{(238)}$  from  $-2.8$  to  $+3.8$ . In the IVZ, HFSE-depleted amphiboles from some hornblendite and sapphirine-bearing gabbroic dykes with similar trace-element and Nd-Sr isotopic affinity to the Dolomitic shoshonites provide  $\epsilon\text{Hf}_{(225)}$  from  $+0.9$  to  $+5.8$ . Late Triassic alkaline dykes with HFSE-rich amphiboles from the IVZ, however, show significant Hf isotopic variability with respect to different domains within samples and relative to the Middle Triassic magmatic rocks. Amphiboles from the melanocratic domains and zircon from the leucocratic patches of some IVZ Late Triassic alkaline dioritic dykes show  $\epsilon\text{Hf}_{(200)}$  from  $+5.3$  to  $+7.6$  and from  $+6.4$  to  $+15.4$ . Magmatic zircon with perfect oscillatory zoning and U-Pb age of 200 Ma from an alkaline anorthosite dyke sample from the IVZ also provided relatively lower  $\epsilon\text{Hf}_{(200)}$  from  $-0.4$  to  $+4.3$ . Our Hf isotopic data indicate that the eastern and westernmost sectors of the Southern Alps are most likely characterized by similar tectonomagmatic events during the Early Mesozoic. The Middle and Late Triassic magmatism in the two sectors were probably derived from variably metasomatised mantle sources containing subduction-derived crustal components. The emplacement of the IVZ dykes into mantle peridotites suggests that crustal assimilation during transport and/or emplacement is limited. The variability in the Hf isotopes characterizing the Late Triassic alkaline magmatism in the IVZ could be related to the injection of multiple pulses of Nb-Ta-rich melts from different mantle domains containing different amounts of slab-derived components. The 200 Ma alkaline magmatism with low  $\epsilon\text{Hf}$  indicate that the mantle sources beneath the Southern Alps was enriched and continuously generated mantle melts with variable crustal signatures, probably since the end of the Variscan times up to the Late Triassic-Jurassic.

## Subduction zone recrystallization of the oceanic lithosphere by hydration of brittle structures

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*Keywords:* subduction, eclogitization, fluids.

Metamorphism causes major changes in the mineralogy and rheology of the Earth's lithosphere, provided that mineral reactions are triggered by fluid access. In absence of coupled deformation and fluid flow, the unaltered lithosphere remains long time stiff and metastable, thus sustaining large differential stresses. This is relevant to subduction of the oceanic lithosphere, where fluid presence vs absence affects seismicity and rock eclogitization. Hydration of oceanic plates mostly occurs in oceans, with formation of top-slab reactive rock volumes prone to deformation and accretion to the subduction interface. In such domains, pressurized fluids cause full rock eclogitization and seismic rock embrittlement. Differently, the behavior of the unaltered lithosphere from the inner slab is much less known, although these domains also host earthquakes and their eclogitization can drive the slab pull. Aim of this contribution is showing the role of brittle structures in driving fluid influx and eclogitization of unaltered domains of fossil oceanic lithosphere.

The ophiolitic gabbro-peridotite of the Lanzo Massif (W. Alps) largely escaped Alpine subduction metamorphic recrystallization due to poor oceanic hydration. This made these rocks dry, stiff asperities in the subduction complex, which locally developed pseudotachylyte-bearing faults at intermediate-depth depths and widespread meso- to micro-faulting. In the field, thin, flat-lying metric faults cause centimetre-scale offset of gabbro dykes: such faults contain a (sub)micrometric-sized “annealed” fault gauge of fresh olivine and pyroxene only locally overgrown by secondary chlorite. Cataclastic plagioclase is progressively altered into high-pressure zoisite+paragonite+garnet up to become the most intensively eclogitized mineral domain in the studied samples. The fault planes thus developed at dry conditions in the olivine stability field; localized access of externally derived fluids promoted fault hydration, massive plagioclase replacement by high-pressure assemblages and trace element influx/redistribution. This implies that subduction zone eclogitization is promoted by fluid access along pervasive fault discontinuities and reactive minerals. We discuss the deformation features of the Lanzo rocks in the frame of the rheology and seismicity of a subducting oceanic plate. They could be associated to minor slip events in domains of the Lanzo lithosphere close to areas of faulting and pseudotachylyte formation during major regular earthquakes.

## A novel methodology for quantitative analysis of sulfur volatile species from HP-HT experiments

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*Keywords:* sulfur, subduction, dehydration experiments.

Subduction zones are key locations of chemical transfer occurring between the Earth's surface and the inner reservoirs. Here, the release of aqueous fluids mediates elemental exchange from the downgoing slab to the overlying mantle wedge, triggering hydrous melting and melt production. Influx of slab-derived oxidizing fluids and melts into the mantle wedge peridotite is commonly invoked to explain the higher oxidation degrees recorded by arc magmas compared to magmas from other geodynamic settings. However, the actual oxidizing agents and the mechanisms of transfer from the subducting slab to the mantle wedge remain hotly debated issues.

Among the most controversial and poorly understood components, sulfur is thought to play a pivotal role in mantle redox conditions, as well as ore-forming processes. Contrasting lines of evidence for the behavior of sulfur in subduction environment mostly arise from petrological observations on mantle xenoliths, high-pressure sulfide-bearing rocks, and thermodynamic models (Schwarzenbach et al., 2018; Piccoli et al., 2019). However, the lack of experimental works limits considerably our knowledge on sulfur release and speciation in slab-derived fluids.

To bridge this knowledge gap, we present a novel methodology for quantitative analysis of sulfur species ( $H_2S$  and  $SO_2$ ) in fluids produced during HP-HT dehydration experiments conducted at conditions of geological interest. In contrast to previous works (e.g. Iacovino et al., 2020), our new approach allows for the first time a quantitative determination of volatile species dissolved in experimental fluids. Volatiles will be analyzed by means of a capsule-piercing device connected to a quadrupole mass spectrometer (Tiraboschi et al., 2016), using gas mixtures of known composition as calibration standards.

We expect that this technique will contribute significantly to our understanding of sulfur behavior and speciation in subduction settings. Constraining sulfur species that are predominant at fixed P-T-redox conditions will also allow providing stronger constraints on the role of sulfur-bearing fluids as effective oxidizing agents of the mantle wedge.

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## **Molecular hydrogen solubility in quartz at subduction conditions: insights from redox-buffered experiments at 2 GPa and 700°C**

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*Keywords:* hydrogen, subduction, quartz.

In the Earth's interior hydrogen is commonly exchanged between the different reservoirs as water or hydroxyl groups through reactions involving minerals, fluids and melts. However, especially at reduced conditions hydrogen can also exist in its molecular form ( $H_2$ ), which has the peculiar capability of diffusing through a multitude of materials. In particular, the mobility of  $H_2$  in mantle minerals is thought to influence their dD signature and to be responsible of redox reactions that can eventually result in partial melting of ascending mantle plumes. Whether and how  $H_2$  is transported back into the mantle through subduction zones and which are the minerals possibly involved in this process is still obscure.

To tackle this topic, we experimentally investigated the solubility of hydrogen in quartz, an ubiquitous mineral in subducted rocks, at 2GPa and 700°C and redox state comprised between DFMQ  $\sim$ -1.5 and DFMQ  $\sim$ -7. High P-T conditions were achieved by means of a rocking end-loaded piston cylinder apparatus and oxygen fugacity was buffered by using the double capsule technique. In each experiment the inner capsule was filled with a mixture of powdered ultrapure quartz calcinated at 1000°C and pure water, while the outer capsule contained a mineral assemblage capable of buffering the hydrogen fugacity (from more oxidizing to more reducing: fayalite(ferrosilite)-magnetite-quartz, cobalt-cobalt oxide, wüstite-magnetite, iron-wüstite, quartz-iron-fayalite). After every run the quenched volatiles trapped in the inner capsules were extracted and analyzed by quadrupole mass spectrometry.

Concentrations of up to 0.1 moles of  $H_2$  per mole of quartz ( $\sim$  4000 ppm by weight) can be attained at DFMQ  $\sim$ -5.5 and  $\sim$ -7, with  $H_2$  solubility decreasing towards more oxidized conditions. These concentrations greatly exceed those predicted by thermodynamic modeling for an aqueous fluid equilibrated at the investigated redox condition, this being apparent for relatively oxidized fluids when  $H_2$  concentration is theoretically negligible, indicating an effective sequestration of hydrogen by quartz grains. Moreover, the dissolution process seems to be largely reversible upon cooling and/or depressurization, this being compatible with a bulk diffusion mechanism of molecular hydrogen, perhaps coupled with physisorption on quartz grain surfaces. Nevertheless, further experiments are needed to better constrain the main factors affecting  $H_2$  solubility and diffusivity in quartz.

In a broader sense our preliminary results suggest that quartz can promote hydrogen sequestration from subduction zone fluids at high pressure and, by releasing it during exhumation, can possibly perturbate the redox state of subduction channel rocks and, eventually, of mantle wedge.

## The link between subducted marine microalgae and volcanic arc emissions

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*Keywords:* COH fluids, stable isotopes, experimental petrology.

Ocean sediments consist mainly of calcium carbonate and organic matter (phytoplankton debris). Once subducted, some carbon is removed from the slab and returns to the atmosphere as CO<sub>2</sub> in arc magmas. Its isotopic signature is thought to reflect the bulk fraction of inorganic (carbonate) and organic (graphitic) carbon in the sedimentary source. Tumiati et al. (2022) challenged this assumption by experimentally investigating model sediments composed of <sup>13</sup>C-CaCO<sub>3</sub> + <sup>12</sup>C-graphite interacting with water at pressure, temperature and redox conditions of an average slab–mantle interface beneath arcs. We demonstrated that oxidation of graphite is the main process controlling the production of CO<sub>2</sub>, while CO<sub>2</sub> derived from carbonate decomposition/dissolution is negligible. The isotopic composition of CO<sub>2</sub> reflects therefore the CO<sub>2</sub>/CaCO<sub>3</sub> rather than the bulk graphite/CaCO<sub>3</sub> (i.e., organic/inorganic carbon) fraction. Tumiati et al. (2022) also provided a mathematical model to predict the arc CO<sub>2</sub> isotopic signature on the basis of the fluid–rock ratios and of the redox state in force in its subarc source. In order to test the model in a carbonate + graphite system characterized by natural isotopic compositions, we replicated the experiments using dried cultured coccolithophores instead of marked compounds. Coccolithophores, which constitute the best part of open ocean sediments above calcite compensation depth, are able to provide at the same time calcium carbonate (coccoliths) and organic matter (cell material), which become aragonite and graphitic carbon, respectively, at the run conditions of 3 GPa and 700°C. We demonstrated that the model published by Tumiati et al. (2022) fits well the new experimental data, and it confirms to be valid to predict the isotopic composition of CO<sub>2</sub> emitted by arc volcanism even for low amount of graphite < 1 wt%, which is the assumed to be the average abundance in marine sediments.

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## **S14.**

# **The continental crust through space and time: unraveling igneous, metamorphic and mineralization processes**

*CONVENERS AND CHAIRPERSONS*

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## In situ U-Pb dating of low-U minerals: challenges and opportunities

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Keywords: LA-ICPMS, geochronology, U-Pb.

Laser-ablation ICP-MS U-Pb dating has proven to be of great value for many geoscience disciplines. For a long time, this technique has primarily been used to date accessory minerals such as rutile, monazite, and especially zircon. Recently, this technique has been applied to rock-forming minerals with low U and high common-Pb concentrations such as garnet or carbonates.

Carbonate dating is the most developed field with a few tens of publications per year from an increasing number of different laboratories. The applications of carbonate dating are manifold and encompass, e.g., the dating of sedimentation or fossilization processes (e.g. Montano et al., 2022), which can be combined with stable or clumped isotopes studies, or structural studies that investigate calcite fibres and vein formation related to folds and thrusts (Muñoz-Lopez et al., 2022). In the case of garnet dating, two areas of research should be distinguished. Skarn garnet, with U concentrations of ca. 2 to 70  $\mu\text{g/g}$ , has proven a fruitful target for U-Pb dating (e.g. Reinhardt et al., 2022). In turn, garnet from igneous or metamorphic rocks, including metasomatic garnet from the subcontinental lithospheric mantle, is much more challenging due to abundant inclusions and/or extremely low U concentrations (usually  $<1 \mu\text{g/g}$ ). However, recently developed methodologies overcome this issue of dating garnet with ca. 1 ng/g U and significantly widen the application of the U-Pb geochronometer in garnet (Beranoaguirre et al., 2022). Finally, dating mineralization-related minerals, like cassiterite, columbite, wolframite or scheelite is also an emerging field developed in the last couple of years. Providing a temporal framework for such minerals may give important insights into the understanding of the formation and evolution of the main ore bodies and thus guide exploration efforts on a local and regional scale.

This contribution highlights the potential, feasibility and limitations of the cutting-edge technique of in-situ U-Pb dating of low-U minerals.

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## Trace elements behaviour and Nd isotopic ratios in REE-bearing accessory minerals from greenschist facies to crustal anatexis

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**Keywords:** crustal anatexis, Nd isotopes, REE-bearing minerals.

The study of accessory phases (e.g., trace elements concentrations and radiogenic isotopes) is nowadays a powerful tool for the understanding of geological processes such as crustal differentiation. They are the main carriers of incompatible elements in crustal rocks and play a major role in the enrichment of these elements from the lower towards the upper crustal levels. However, the impact of high-grade metamorphism and crustal anatexis on the chemistry of these accessory phases and the remobilization of their incompatible elements to higher crustal levels is not well constrained yet.

Here, we present new results acquired on samples from the Chugach Metamorphic Complex (CMC) in Alaska, an Eocene accretionary prism where metapelitic and metagraywacke rocks experienced Low Pressure-High Temperature (LP-HT) metamorphism. Metamorphic ages (55-50 Ma) and P-T conditions of the CMC are well constrained (Gasser et al., 2012) with a systematic N-S metamorphic gradient going from greenschist facies in the north (phyllites, 400–550°C) to amphibolite facies (schists, ~500–650°C) and to upper amphibolite facies (migmatites, ~650–750°C) in its southernmost part (Bruand et al., 2014). Migmatites found in the CMC experienced anatexis >650°C under water saturated melting conditions. In this study, we have investigated a dozen of samples collected along this metamorphic gradient to study the impact of increasing metamorphic grade up to anatexis on REE-bearing accessory minerals. In this study, we present trace element concentrations of apatite, monazite, allanite and titanite along the P-T gradient. Preliminary results show in particular that variations in some trace elements in apatite (e.g. HREE) would be more prone to record the CMC P-T gradient and partial melting process while composition of monazite is homogeneous throughout the gradient. Both whole-rock and in-situ Nd isotopic compositions on monazite and allanite in schists and migmatites were also analysed by (LA)-MCICP-MS. We found no significant difference in  $\epsilon_{\text{Nd}}$  between monazite, allanite and whole-rock, regardless of the type of rock analysed. This suggests (i) an overall homogeneity of the Nd isotopic composition above 550°C up to crustal anatexis conditions and (ii) a mineral to whole-rock isotopic equilibrium.

Finally, these results will be compared to preliminary data acquired on migmatitic samples from the lower calabrian crust (Italy, Serre massif).

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## Titanite from metacarbonate: a “complementary” petrochronological tool for deciphering the P-T-t evolution of the continental crust (Ivrea-Verbano Zone, Italy)

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Keywords: titanite, petrochronology, metacarbonate.

Titanite (CaTiSiO<sub>5</sub>) is a common accessory mineral in metacarbonates and metabasites. It contains several important geochemical elements, such as REE, Pb, U, Zr resulting a useful petrological and geochronological tool (Kohn, 2017). The possibility to combine the trace element composition with U-Pb dating offers the possibility to gain information about the timing of metamorphic reactions or deformation events.

We performed a geochemical and petrological characterization of titanite within metacarbonate rocks occurring at different levels of the Variscan continental crustal section exposed along the Valle Strona di Omegna, Ivrea-Verbano Zone. The crustal section consists mainly of middle-high grade metapelites/metapsammities and metabasites, with numerous lenses of metacarbonate rocks. The crustal section is characterised by a progressive increase of temperature conditions, from amphibolite to granulite facies, with increasing crustal paleo-depth (toward NW). Metacarbonates contains mostly calcite, with local occurrence of dolomite, and ranges in composition from impure marble to calc-silicates. Clinopyroxene, feldspar, amphibole and epidote are common in amphibolite facies rocks whereas scapolite, garnet and olivine appear in granulitic samples.

Major and trace elements were determined for titanite from metacarbonates with different mineral assemblages along the crustal profile. The chemistry of titanite shows interesting correlations with lithologies, mineral assemblages and titanite modal abundance. In order to constrain temperature, we adopted the Zr-in-titanite thermometer (Hayden et al., 2008) by considering Pressure estimates from adjacent coexisting metamorphic rocks well characterized by previous works (e.g., Redler et al., 2012; Kunz & White, 2019). The obtained temperatures are in the range of 600-900°C and are coherent with the high temperature conditions recorded by surrounding metapelites/metabasites during regional metamorphism at Upper Carboniferous – Lower Permian interval (e.g., Redler et al., 2012; Kunz & White, 2019). The titanite U concentration ranges from about 20 to 300 ppm without apparent correlation with metamorphic grade and/or mineral assemblages. U-Pb Titanite dating was only performed for samples where the U concentration of titanite was higher than 100 ppm. Preliminary U-Pb dates range from Middle to Upper Triassic suggesting a decoupling between titanite petrogenesis, based on microstructures and trace element composition, and U-Pb system.

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## Elemental mapping and in-situ microanalysis of accessory minerals: an essential petrochronological tool

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*Keywords:* accessory minerals, electron microprobe, WDS mapping.

Minor and trace elements determinations in accessory minerals, such as silicates, oxides and phosphates, are commonly performed using LA-ICP-MS for petrochronological applications (Kohn et al., 2017).-

Monazite, titanite, zircon and rutile are common accessory minerals within magmatic and metamorphic rocks. Their U, Th and Pb content are commonly used in LA-ICP-MS to date significant geologic events. Other key elements such as REE in monazites, REE and Zr in titanites or Zr in rutiles are used as valuable tools to disclose information about the petrologic evolution of the host rocks. These methods have been commonly used from several decades with an increase of interest by the scientific community, thanks to the robust information they can provide in a wide range of geological environments. In particular, the determination of Zr in rutiles and titanite is a quite recent straightforward methodology which give affordable temperature estimates in different petrologic settings, due to the widespread occurrence of this accessory mineral among different rock types.

However, one of the more challenging aspects in measuring such elements is the small size of the phases that sometimes makes difficult (or impossible) to carry out analyses by laser ablation, due to the size of the laser beam. The EPMA can be thus an optimal alternative as investigating tool, as the size of the electron beam is smaller and less invasive than the laser. Furthermore, WDS analysis is able to correct X-ray peaks overlapping (i.e. REE, Ti-V). Moreover, high resolution elemental maps of minerals can be easily performed, attaining important details about zoning, useful to interpret the evolution of rocks in which they are hosted. Maps are also fundamental in addressing LA-ICP-MS investigations and, eventually, to get correct interpretations of age data. The use of these two analytical methodologies are thus complementary, but the obtained data should be previously tested and compared.

The EPMA joined laboratory of the UNIFI-DST and CNR-IGG of Firenze hosts a JEOL JXA-8230 microprobe, equipped with 5 spectrometers and 12 analyser crystals. Specific protocols for the analysis and mapping of monazites, titanites, zircons and rutiles were defined and applied on metapelites (monazite and rutile), amphibolites and calc-silicates (titanite) from lower crustal rocks of the Ivrea-Verbano Zone (northern Italy) and Serre Massif (central Calabria). The different methods were set taking into account several variables, such as calibration standards, accelerating voltage, beam current, beam diameter, counting times, matrix correction method, correction of overlapping peaks in order to get the lowest detection limits (few tens of ppm) of analyzed elements (e.g. Zr, Th, U, REE) and the most accurate results. Peak overlaps (e.g. Nd La vs Ce La for titanites and monazites, U Ma vs Th Ma for monazites, V Ka vs Ti Ka for rutiles) were considered and corrected through the use of suitable doped glasses.

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## Pressure-Temperature evolution and U-Pb geochronology of biotite-cordierite gneiss from the Boulder Creek batholith (Front Range, Colorado, USA)

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Keywords: Paleoproterozoic, migmatite, microstructures.

The Boulder Creek batholith is a Paleoproterozoic intrusion within the Front Range in Colorado (USA) made by: (i) the Boulder Creek granodiorite (BC; 1714±5 Ma; Premo & Fanning, 2000) and (ii) the Twin Spruce Quartz Monzonite (ca. 1700 Ma; Gable, 1980). The emplacement of this batholith is syntectonic to the regional deformation of the surrounding rocks. The Boulder Creek rocks probably originated from partial melting of the upper mantle and lower continental crust (Gable, 1980; Mahan et al., 2013). Recent field observations suggest that a local occurrence of Bt-gneisses within the BC batholith are an older unit with evidence for multiple episodes of foliation development, contrasting previous mapping reports, in which the Bt-gneiss are instead part of a shear zone affecting Boulder Creek granodiorite.

Our work provides microstructural analysis of a Bt-Crd gneiss collected at the W of Boulder (USA). Our observations highlighted the presence of microstructures of partial melting processes (i.e., melt films at grain boundaries, twinned plagioclase, peritectic cordierite). In detail, two tectono-metamorphic stages are recognized: (i) pre-melting stage defined by the isorientation of plurimillimetric Bt and minor white mica defining the main foliation; (ii) the migmatitic stage corresponds to neosome crystallization (Pl+Qz+Bt+Kfs±Crd) within microdomains parallel to the main foliation.

P-T conditions related to the first stage range between 600-650°C and ~4.5 kbar. Preliminary U-Pb zircon geochronology has nearly concordant dates that are similar to those obtained for the granodiorite at ~1700 Ma (Premo & Fanning, 2000), which would be consistent with partial melting of the gneiss having occurred near in time to batholith emplacement. However, the data also display evidence for multiple re-openings of the isotopic system that led to Pb loss, making the interpretation complicated. Nevertheless, the high degree of U-Pb system disturbance in our zircon data compared to much more well behaved zircon U-Pb data from prior BC batholith studies (Premo & Fanning, 2000) supports our interpretation that the Bt-Crd gneisses are not part of the BC batholith but rather are probably older wallrock.

Our study represents a starting point to address the question about the role of these high-grade partially melted rocks within the BC batholith, particularly their relationships with migmatized rocks near the outer margin of the batholith, and the BC granodiorite itself. Further studies (e.g., field studies, U-Pb geochronological and isotopic analyses) will be fundamental to understand whether these biotite-cordierite gneisses are the source of the melt from which the Boulder Creek granodiorite originated or if they are instead xenoliths belonging to the country-rock; Also, they will ease the reconstruction of the tectonic processes involved in the Paleoproterozoic accretion of the earlier continental crust (e.g., Baird et al., 2022 and references therein).

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## Assessing thermal history of the prograde metamorphic sequence in the Kinzigite Formation (Ivrea-Verbano Zone) through monazite-xenotime thermometry

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*Keywords:* kinzigite, xenotime, monazite.

The Ivrea-Verbano Zone (IVZ) represents a part of the tilted Palaeozoic basement located in northern Italy and southern Switzerland. The deep crustal rocks of the IVZ record lower Palaeozoic accretion, metamorphism and magmatism, overprinting during the Variscian orogeny, post-Variscan magmatic underplating and associated lithospheric stretching and thinning, as well as Mesozoic extension and final Alpine tilting. The regional lithology has been subdivided into supracrustal rocks of the Kinzigite Formation and the base comprising mantle peridotites and mafic igneous complex of Permian age. The lowest grade rocks, in upper amphibolite facies, appear along the SE margin of the IVZ (Kinzigite Formation) with the metamorphic grade increasing towards the NW to granulite facies. The amphibolite facies rocks of the Kinzigite Formation consist of metapelites and metapsammites and subordinate metacarbonates and metabasites. Metapelites and metapsammites, also known as kinzigites, form a uniform 3-4 km wide tract, interpreted as a Palaeozoic accretionary complex.

To better understand the thermal history in the Kinzigite Formation, we undertook a continuous sampling every 500 m along the Strona River (NE part of the IVZ). This study aimed at using REE-phosphates monazite and xenotime as adequate thermometers in amphibolite facies. If monazite is in compositional equilibrium with xenotime, the partitioning of Y and HREE between these phases is temperature sensitive and may also be applied as a geochronometer (Heinrich et al., 1997; Gratz & Heinrich 1997; 1998).

To this end, we characterised these accessory minerals in a prograde, upper amphibolite to granulite facies metapelite sequence with respect to their petrological, textural, and chemical properties. We selected only garnet-free kinzigites, since the geothermometer to be applied has been calibrated only in garnet-free systems and the role of garnet as Y-HREE sink might produce unreliable results. Detailed textural characterisation was performed using scanning electron microscopy, whereas electron microprobe analysis revealed major element + REE + Y composition of the phosphates and, in some cases, paragenetic rock forming minerals.

Based on criteria for textural and compositional equilibrium between coexisting monazite and xenotime, we identified monazite-xenotime pairs suitable for applying thermometry. Analyses of nearly 200 grains revealed different homogenous or complex textural and compositional types of phosphates (in agreement with observations by Williams et al. (2022)), yielding populations formed in excess of 550°C, but also at low temperatures (< 400°C). We will further correlate these thermal profiles with Raman spectroscopy of carbonaceous material.

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## Contact metamorphism of pelitic country rocks constrains the depth of emplacement of the Re di Castello intrusion (Adamello Batholith)

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*Keywords:* Adamello, contact metamorphism, thermobarometry.

We have studied the contact metamorphism in the Lozio shale graphitic metapelites cropping out in the upper Caffaro Valley (southern Adamello). The samples are located at variable distance (max 500 m) from the intrusive contact with the Re di Castello quartz diorite.

Near the contact the hornfelses display the mineralogical assemblage K-feldspar-cordierite-biotite-muscovite-plagioclase-quartz-graphite, with rare needles of fibrolitic sillimanite in only one sample (LOZ1). Andalusite was never observed throughout the aureole. Cordierite is the most prominent mineral in the hornfelses and forms sector twinned crystals <0.5 mm and/or dendritic porphyroblasts reaching 2 cm. Its abundance affects the reactive bulk composition of the hornfelses and explains the presence of K-feldspar rather than Al<sub>2</sub>SiO<sub>5</sub> associated with muscovite and quartz.

Thermometry based on Raman spectroscopy of carbonaceous materials (RSCM) on sample LOZ1 provided ~610-620°C as maximum temperature recorded at the intrusive contact.

The thermodynamic modelling of the same sample in the TiNCKFMASH system and in the presence of graphite failed at predicting a stability field for the mineral assemblage (Kfs-Crd-Bt-Ms-Pl-Qz-Sil-Gr) observed in all samples. Conversely, calculated assemblages predict a wide P-T region of stability of Al<sub>2</sub>SiO<sub>5</sub>-bearing assemblages before the Ms+Qz breakdown, and K-feldspar only after it. This discrepancy is probably due to uncertainties in the thermodynamic properties and solution models for cordierite, which plays a major role in the studied rocks.

The P-T conditions recorded by LOZ1 were thus constrained by an alternative bathograd-like approach, considering phase relationships in the simplified KNASH-C system. In order to form sillimanite only as product of the incomplete Ms-Qz breakdown - divariant for the presence of Na in Ms and Kfs and shifted to lower T due to the presence of graphite - an isobaric path typical of contact metamorphism must have crossed above the Ms<sub>ss</sub>-Qz-Kfs<sub>ss</sub>-Sil-And-fluid invariant point, i.e., at P>3.3 kbar. The same univariant point also constrains the minimum temperature at the intrusive contact, which was >615-620°C.

Assuming an average crust density of 2.7 g cm<sup>-3</sup>, the estimated pressure corresponds to a minimum paleo-depth of emplacement of 12.2 km.

## Garnet and monazite U-Pb dating of metasomatic effect around a mafic intrusion

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Keywords: U-Pb dating, garnet, monazite.

Emplacement of melts and the associated metamorphic and metasomatic effects in mid/low continental crust may increase the rheological heterogeneities at the meter scale that are not easily detectable on the field. The fluid-induced metasomatic effects are more apparent when the composition of the intrusion and host rocks differs significantly. Host rocks may develop mineral assemblages useful for reconstructing the thermal history of the emplacement event. These mineral assemblages could provide a good opportunity to date the mafic intrusion that can be hardly dated due to the lack or rare occurrence of reliable geochronometers (e.g., zircon).

This is the case of a gabbroic body, i.e., the Anzola gabbro, that intruded the lower continental crust of the Ivrea-Verbano Zone in the Italian Southern Alps.

The intrusion of this mafic body (up to 800 m thick) is interpreted as one of the main factors increasing the rheological heterogeneity at its boundary that promoted the localization of the adjacent shear zone (i.e., the Anzola shear zone; Corvò et al., 2022). The age of the mafic intrusion, as well as its relationships with the Anzola shear zone, are unknown, mostly because of lack of suitable geochronometers (zircon, titanite) in the mafic intrusives. At the rim of the gabbro, we discovered and characterized metasomatic patches, which escaped shearing, but rather experienced de-hydration reactions (coronitic garnet replacing amphibole), skarn-like mineralization (marbles, calc-silicates, garnet and hedenbergite pockets) and corundum growth (Smith et al., 2015; Yakymchuk & Szilas, 2018). In this domain, we performed U-Pb LA-ICP-MS dating of garnet and monazite. Cm-sized garnet occurs within pockets also containing plagioclase and amphibole and developed between the gabbroic rocks and a metacarbonate. Monazite was observed within corundum-bearing paragneisses made of K-feldspar, corundum, biotite, garnet, plagioclase, and spinel. The origin of this corundum assemblage can be related to the metasomatic exchange between the mafic intrusion and the metapelites (e.g., Yakymchuk & Szilas, 2018).

The U-Pb in-situ dating of garnet from the pockets between the metacarbonate and the gabbro provides lower intercept ages in the range of 250-240 Ma, in agreement with the <sup>40</sup>Ar/<sup>39</sup>Ar age (~247 Ma) obtained on hornblende from the Anzola gabbro (Brodie et al., 1989). U-Pb dating on monazite corundum-bearing paragneisses recorded a main coeval age peak (250 Ma), which is interpreted as dating the metasomatic process due to the mafic intrusion and thus providing the timing of the intrusion itself. Our results show the potential of garnet U-Pb to constrain metasomatic processes, and more in general the indirect dating of a mafic intrusion by studying its contact metamorphic and metasomatic aureole.

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## **Melferite: formed by high-strain melt transfer through sub-solidus rocks**

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*Keywords:* melt-present deformation, melt migration.

Melt transfer and migration occurs through both supra- and sub-solidus rocks. Mechanisms of melt transfer include dyking, mobile hydrofracturing and diffuse porous melt flow where melt flow may or may not be channelized via instabilities or into high-strain zones of active deformation. Here, we highlight the microstructural- and outcrop-scale signatures of syn- deformational melt-migration pathways through high-strain zones that cut sub-solidus rocks. High-strain zones with high proportions (> 10%) of macroscopic, internally undeformed, felsic or leucocratic material are readily interpreted as important melt-migration pathways and are most common in supra-solidus host rocks. However, it is challenging to recognise high-strain melt-migration pathways through sub-solidus rocks; these pathways may lack noticeable felsic or leucocratic components at the outcrop scale and share many macroscopic features in common with ‘classic’ sub-solidus mylonite, such that the two are generally conflated. We contrast field and microstructural characteristics of ‘classic’ mylonite originating from solid-state deformation with those of high-strain zones that also cut sub-solidus rocks yet have microstructural indicators of the former presence of melt. We compile several features allowing one to distinguish solid-state from melt-present deformation in high-strain zones that cut sub-solidus rocks. Our aim is to encourage geologists to assess such high-strain zones on a case-by-case basis, in view of sub-solidus (i.e., mylonitic) versus melt-present deformation. Such assessment is crucial as (1) rocks deformed in the presence of melt, even small percentages of melt, are orders of magnitude weaker than their solid-state equivalents, (2) melt-rock interaction in such zones may result in metasomatism, and (3) such zones may sustain long-lived melt migration and ascent enabling chemical differentiation at a crustal scale.

## Temperature estimates from the lower continental crust exposed in Calabria: application of the Zr-in-rutile thermometer to migmatites and granulites

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**Keywords:** lower crust, peak metamorphic temperature, Zr-in-rutile.

Rutile (TiO<sub>2</sub>) is a common accessory mineral in many metamorphic rocks and is stable over a wide range of P-T conditions. It provides a single-phase thermometer when crystallised in a Zr-saturated environment, the maximum Zr content in a given rutile population is a good indication of the minimum peak metamorphic temperature of a sample (e.g., Zack & Kooijman, 2017).

Rutile contains significant amounts of several trace elements and is one of the classical minerals used for U-Pb age determination. It has been extensively adopted for reconstructing the T-t evolution of the lower crustal rocks exposed in the Ivrea-Verbano Zone (e.g., Ewing et al., 2015).

Here we present temperature estimates based on the Zr content in rutile from granulites and migmatites exposed in the northern part of the Serre Massif, central Calabria. This massif is exceptional as it represents an almost complete continental crust section of the Variscan belt (e.g., Schenk, 1989). The exposed lithostratigraphic sequence consists mostly of granulites, at the bottom, and migmatites towards the top. The P-T conditions in the lower crust have been constrained mostly by conventional geothermobarometry (e.g., Schenk, 1989; Acquafredda et al., 2008).

Rutile occurs within felsic granulite interlayered with mafic rocks at the base of the lower crust ( $P > 7.5$  kbar). Here, rutile is characterised by numerous exsolution lamellae of baddeleyite, zircon and srilankite (ZrTi<sub>2</sub>O<sub>6</sub>), a common property of rutile from (U)HT granulites (Zack & Kooijman, 2017). Rutile also occurs within felsic granulites and cordierite-bearing migmatitic paragneisses upwards in the lower crustal section.

The Zr content of rutile has been determined by LA-ICP-MS. It ranges from 442 to 4579 ppm within felsic granulites, resulting in a large spread of temperature ( $763 \pm 79^\circ\text{C}$ ). Going upward, close to the boundary with migmatitic paragneisses ( $P \approx 6.5$  kbar), the Zr content of rutile from felsic granulites shows a narrower range (2436-3085 ppm), providing an average temperature of about  $861 \pm 11^\circ\text{C}$ . Finally, approaching the top of the lower crust ( $P \approx 5.5$  kbar), the Zr content of rutile from cordierite-bearing migmatitic paragneisses ranges from 1353 to 2227 ppm, yielding an average T of  $794 \pm 19^\circ\text{C}$ .

Contrary to expectation, Zr-in-Rutile thermometry provides the lowest temperature for granulites at the base of the lower crust. Indeed, rutile from these rocks shows evidence for a significant Zr loss, as documented by Zr-rich phases occurring as exsolution lamellae or as satellites around rutile and by the large spread of Zr content. Thus, the average temperature is underestimated. Anyway, except for this problematic sample, the temperatures obtained for intermediate and upper levels of the lower crust are significantly higher than those provided until now. This suggests that the thermal perturbation within the Variscan crust has been particularly pronounced as reported for other sectors of the Orogen (e.g., Ewing et al., 2015).

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## Identifying evaporitic protoliths in metasedimentary sequences of collisional orogens: implications for ore deposits prospection

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*Keywords:* meta-evaporites, magnesite, ore deposits prospection.

The identification of evaporitic protoliths in metamorphic terrains has become increasingly important in recent years due to their association with a wide range of ore deposit types (Morissey & Tomkins, 2020), either syn-sedimentary or syn-orogenic. Metamorphosed evaporite-bearing sedimentary sequences have been described in several orogenic belts. Common characteristics of these evaporite-bearing metasedimentary sequences are (Warren, 1997): (i) their Proterozoic age, (ii) the systematic association with stratabound metallic mineral deposits (e.g. Pb-Zn and Cu-Fe sulphide deposits), (iii) the association with gemstone bearing lithologies and/or gems (e.g. rubies, emeralds, lapis lazuli), and (iv) the local occurrence of magnesite deposits. Despite their potential importance for ore deposits exploration, the identification of evaporitic protoliths in orogenic belts is not straightforward.

Here we present the results of a geochemical, petrographic, minero-chemical and petrological study focusing on peculiar magnesium-rich assemblages occurring in the upper part of the Lesser Himalayan Sequence (LHS), central Nepal. The lithologies studied include muscovitic-, phlogopitic-, talc-, chlorite-phlogopite- and chlorite-talc schists, whose assemblages reflect high amounts of MgO, Al<sub>2</sub>O<sub>3</sub> and K<sub>2</sub>O, balanced by low amounts of CaO in the bulk rock compositions. The assemblages observed are: muscovite + phlogopite + kyanite + plagioclase + epidote; phlogopite + kyanite + orthoamphibole + hornblende + garnet + cordierite; talc + phlogopite + kyanite + orthoamphibole + plagioclase; chlorite + phlogopite + kyanite + hornblende + orthoamphibole; chlorite + talc + orthoamphibole. The protolith assemblages of two of these lithologies are reconstructed from the measured bulk rock compositions; it is shown that these lithologies are derived from the metamorphic transformation of magnesite-bearing protoliths in an internally buffered system.

We interpret these magnesite-bearing protoliths as evaporitic sediments, suggesting that the entire Upper-LHS metasedimentary sequence represents the metamorphic product of a carbonate-evaporite-pelite sequence deposited during the Proterozoic. The occurrence of: (i) stratabound Pb-Zn sulphide deposits, associated with (ii) dolomitic marble layers locally hosting ruby deposits, and (iii) a large magnesite + talc deposit approximately 10 to 100 km to the east of the studied samples, further supports our interpretation.

The demand for base metals is likely to increase in the near future as they are required as essential components of most clean energy technologies. The results of this study may provide important clues to guide mineral prospecting in the future, i.e. Mg-rich metamorphic rocks characterised by unusual mineral assemblages may be good candidates for being derived from magnesite-bearing evaporitic protoliths, even if they no longer contain carbonates.

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Warren J.K. (1997) - Evaporites, brines and base metals: fluids, flow and "the evaporite that was". *Aust. J. Earth Sci.*, 44, 149-183. <https://doi.org/10.1046/j.1440-0952.2000.00781.x>.



## The contribution of dolomitic and magnesitic rocks to orogenic degassing

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Keywords: orogenic CO<sub>2</sub> degassing, decarbonation reactions, dolomite and magnesite.

The continental crust is emerging as a relevant source of carbon dioxide (CO<sub>2</sub>); in hot collisional orogenic settings, CO<sub>2</sub> is produced at depth mostly through decarbonation reactions and can ascend to the surface along fault and fracture networks, eventually being released into the atmosphere, thus linking deep crustal processes with near-surface ones.

Calcite-bearing sediments (calcareous pelites, marls, impure limestones) are among the most investigated sources of CO<sub>2</sub> in collisional settings (e.g. Groppo et al., 2021; 2022). However, dolomite- and magnesite-bearing sediments can also be important components of evaporitic sequences deposited along passive margins and involved in collisional orogenic processes. To date, decarbonation reactions in dolomitic and magnesitic rocks have been poorly studied and their contribution to the orogenic carbon cycle has been largely neglected.

In order to understand the influence of dolomitic and magnesitic lithologies on orogenic degassing, we have undertaken a petrological study of metasediments derived from dolomite and magnesite-bearing protoliths exposed in the upper part of the Lesser Himalayan Sequence (Upper-LHS), central Nepal, whose P-T evolution is constrained by data from associated metapelites (Tamang et al., 2023). The aim of the study is threefold: (i) to characterise the main assemblages and microstructures of metasediments derived from protoliths containing different types and amounts of carbonate minerals; (ii) to investigate the most relevant decarbonation reactions for each of them; (iii) to estimate the P-T conditions under which the decarbonation reactions took place, the composition of the fluids released by these reactions, and the amounts of CO<sub>2</sub> released per unit volume of reacting rocks.

We show that the CO<sub>2</sub> productivity of dolomitic and magnesitic pelites and marls is significant, at least in terms of CO<sub>2</sub> produced at depth, and is similar or even higher than that of calcareous pelites and marls sensu stricto. Irrespective of the type of carbonate in the protolith, maximum CO<sub>2</sub> production is systematically recorded by sediments originally containing 20-25% of carbonate, whereas for carbonate contents above 50-60% CO<sub>2</sub> productivity is negligible, unless aqueous fluids infiltrate from the outside and trigger decarbonation reactions. Depending on the ability of the CO<sub>2</sub>-rich fluids to ascend to the Earth's surface without interacting with the host rocks (Groppo et al., 2022), dolomitic and magnesitic lithologies, which are quite abundant in the Upper-LHS, could be relevant sources of CO<sub>2</sub>, possibly contributing to the diffuse Himalayan CO<sub>2</sub> degassing currently observed (e.g., Girault et al., 2018).

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## **Exposed young granites as a gauge for exhumation rate: an example from the pluton of the Giglio Island (Tuscany)**

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*Keywords:* Zircon U-Pb, Apatite (U-Th)/He, granite exhumation.

The presence of recently intruded granites at Earth surface suggests that their exhumation may have occurred rapidly (Spencer et al., 2019). They provide a means of quantifying the process in the upper crust which brought them up to the surface in a relatively short time. This is feasible if the level of emplacement, the emplacement age and the timing of exhumation can be constrained. The Neogene granites of the Tuscan Magmatic Province (Italy), emplaced in the upper crust during a period of extensional tectonics (Acocella & Rossetti, 2002) are ideal for determining and quantifying the exhumation process. The peraluminous monzogranite of Giglio Island in the northern Tyrrhenian Sea (Barrese et al., 1987; Westerman et al., 1993) is characterized by the presence of roof pendants, xenoliths and miarolitic cavities. The depth of emplacement (6.4-10 km) is constrained using the reaction sequence of xenoliths and xenocrysts deriving from wall and roof rocks of the pluton. The emplacement age of the granite, as revealed by U-Pb dating of zircon, occurred during latest Messinian ( $5.7 \pm 0.4$  Ma). Exhumation, constrained by apatite (U-Th)/He ages, was essentially complete in 0.9 Myr and took place at a minimum rate of 6 mm/yr. This requires rapid tectonic unroofing, isostatic rebound and thermal softening activity, weakening the upper crust by the upward doming of the brittle-ductile transition, thereby favouring exhumation at a previously undocumented velocity.

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## Modelling SiO<sub>2</sub> solubility over wide P-T conditions: open problems and advances

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Keywords: SiO<sub>2</sub> solubility, thermodynamic modelling, mass transfer.

Fluids in the Earth's crust and upper mantle constantly change chemically, physically, and catalyze different processes, such as mass transfer, with implications for large-scale geodynamics. Silica solubilization has profound implications for mass transfer over a wide range of geologic environments, from upper crustal levels down to the deepest portion of subducting slabs and at the hot base of large orogens. Here I investigate, by using electrolytic fluid thermodynamic modelling, the solubility and speciation of SiO<sub>2</sub> in H<sub>2</sub>O at 100-1400°C and 0-10 GPa, with a particular focus on the geothermal gradients typical in subduction zones and collisional orogens. Comparison with experiments highlights how modelling is likely to under-estimate above 700-800°C experiments by roughly 10 wt%. I show how SiO<sub>2</sub> solubility strongly increases with temperature, reaching dissolved loads between 5 wt% and >70 wt%, within subducting slabs. Results indicate that fluids with dissolved SiO<sub>2</sub> ranging from 3 to 57 wt% along Barrovian and Buchan-type P-T gradients, strongly question the long-standing assumption of the isochemical nature of regional metamorphism. A by-product of this investigation is the tracking of the source of mineralizing fluids responsible for widespread quartz veins back to the deeper and hotter roots of orogens where amphibolitic to granulitic-facies conditions are encountered

## Deformation-induced changes in the metamorphic record along rheologically contrasted boundaries

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*Keywords:* HT shear zone, HP metamorphism, Alps.

One of the main challenge in the metamorphic studies, is the presence of contrasting pressure and/or temperature records preserved by the mineral assemblage of rheological boundaries. Their mineral assemblages are commonly considered to form under lithostatic pressure and near-equilibrium regional geothermal gradients, possibly influenced by transient fluids. Hence, the resulting metamorphic histories based on the estimation of the pressure and temperature conditions represent the major tool for tectonic reconstruction as proxies of the burial and exhumation history of the rocks during subduction-exhumation phases. The occurrence of ultrahigh-pressure and/or high-temperature rocks embedded within significantly lower grade metamorphic rocks rises a major challenge for developing a consistent geodynamic model for exhumation of such deep-seated rocks. Subduction zones are, in fact, efficient player driving material from the surface down into the Earth's mantle. However, the mechanisms to exhume part of this material (and particularly the denser oceanic rocks) back to the shallow crust are still highly debated. Scientists generally invoke either mechanical decoupling within a tectonic mélangé or variable metamorphic re-equilibration during the retrograde path. Alternative explanations highlight the role of deformation in promoting the coexistence of multiple local equilibria, which cease to correlate with lithostatic conditions and thus burial depths. In this view, the non-hydrostatic stress and the local temperature deviations are accounted as important components potentially modifying the metamorphic system. In this contribution, we integrate structural, petrological and thermochronometric data from classic occurrences of ultra-high pressure and high temperature outcrops of the Adula and Cima Lunga nappes of the Central Alps. The wide dataset comprises new field mapping covering the entire nappes extension (several hundred square kilometres) and structural-petrochronological analyses at the meso- to micro-scale. Our results show the highly variable pressure-temperature-time-deformation paths experienced by the compositionally heterogeneous rocks of the Cima Lunga and Adula nappes. We present evidence of contrasting metamorphic records among the rocks of these nappes, potentially contradicting the assumption of a purely lithostatic gradient, as well as of an undisturbed regional geothermal gradient. New findings provide arguments to discuss pros and cons of tectonic overpressure and shear heating as reliable mechanisms to explain these contrasting metamorphic records.

## Origin of underplated gabbroic crust: insights from the lower Mafic Complex of the Ivrea-Verbano Zone

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Keywords: amphibole gabbronorites, ultramafic rocks, trace elements.

The magmatic processes controlling the accretion of the lowermost continental crust are fundamentally unidentified, mostly due to the inaccessibility of the deep crustal levels. The lower crustal section of the Ivrea-Verbano Zone (IVZ), Southern Alps, encases the Mafic Complex, a ~8 km thick gabbro-dioritic intrusion formed during the post-Variscan transtensional tectonics. The present study wishes to elucidate the processes driving the chemical differentiation of mantle-derived magmas emplaced in the lowermost continental crust. For this purpose, we carried out a petrological-geochemical investigation of the lower Mafic Complex, which constitutes the southwestern sector of the intrusion.

The lower Mafic Complex mostly consists of amphibole gabbronorites (Sinigoi et al., 1991) and minor ultramafic bodies locally known as Rocca d'Argimonia sequence (Tribuzio et al., 2023). The amphibole gabbronorites include concordant pyroxene hornblendite levels that are up to 1 m thick. The Rocca d'Argimonia sequence is discordant to the amphibole gabbronorites and consists of two ~400 m thick rock bodies displaying up to 100 m thick peridotite-pyroxenite alternations. The peridotites (dunites and harzburgites) are crosscut by amphibole-poor gabbronorite dykes.

The chondrite-normalized Rare Earth Element (REE) pattern of clinopyroxene and amphibole from the amphibole gabbronorites and the included pyroxene hornblendites displays medium REE (MREE) enrichment compared to light REE (LREE) and heavy REE (HREE). The REE patterns of clinopyroxene and amphibole from the Rocca d'Argimonia pyroxenites and gabbronorite dykes differ in the nearly flat MREE- HREE and the slight LREE depletion compared to MREE. Available Nd-Sr isotopic data from the literature reveal an enriched signature for the amphibole gabbronorites, with initial  $\epsilon_{\text{Nd}}$  of -4 and initial  $^{87}\text{Sr}/^{86}\text{Sr}$  of 0.707. The Rocca d'Argimonia rocks have initial  $\epsilon_{\text{Nd}}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  typically ranging from +2 to -1, and from 0.705 to 0.706, respectively.

A two-stage process is envisioned for the development of the lower Mafic Complex:

(1) Mantle-derived H<sub>2</sub>O-rich magmas intruded the lowermost continental crust, thereby crystallizing the amphibole gabbronorites and the included pyroxene hornblendites. These magmas were likely derived from mantle sources isotopically enriched in Nd-Sr. Involvement of similar magmas was also reported for other sectors of the IVZ, like in the Finero area (Giovanardi et al., 2020).

(2) The amphibole gabbronorites were intruded by mantle-derived H<sub>2</sub>O-poor magmas with a relatively depleted Nd-Sr isotopic signature, thereby giving rise to the peridotite-pyroxenite sequence of Rocca d'Argimonia.

New Nd-Sr-O isotopic analyses are currently in progress to substantiate the involvement of two distinct primary magmas in the building of the lower Mafic Complex, and to unravel the potential role of crustal contamination in their magmatic evolution.

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## The potentialities of kyanite as a petrogenetic indicator in migmatites

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Keywords: anatexis, trace elements, CL zoning.

The kyanite potentiality as a petrogenetic indicator in metapelites has been recently investigated by several studies, highlighting how its variation in trace elements concentration can be recorded during the kyanite growth history (e.g., Kendrick & Indares, 2018; Peterman et al., 2021; Phillips et al., 2023). When observed under cathodoluminescence (CL) microscopy, changes in kyanite colour intensity derive from different concentrations of Fe, Ti, Cr, and other elements (hundreds to thousands of ppm).

In anatectic metapelites, kyanite can grow through (i) metamorphic reactions at sub-solidus conditions (i.e., subsolidus Ky1), (ii) muscovite dehydration melting reactions (i.e., peritectic Ky2), and (iii) back-reactions between melt and solid phases (e.g., garnet, K-feldspar) during cooling and melt crystallization (i.e., magmatic Ky3). These episodes of kyanite growth can be separated by episodes of kyanite consumption (e.g., kyanite is a reactant of the biotite dehydration melting reactions).

A petrochemical study combined with phase equilibrium modelling performed on biotite + kyanite + garnet migmatites from the Lower-Greater Himalayan Sequence exposed in eastern Nepal Himalaya highlights a link between the trace elements chemical zoning of kyanite and the consumption vs. growth of the main minerals acting as reservoirs/sinks for those elements (e.g., muscovite, biotite, garnet), and ultimately to specific growth stages of kyanite (i.e., Ky1, Ky2, Ky3). The complexity of kyanite porphyroblasts textures and their relation to its growth history can shed light on the evolution of continental crust undergoing partial melting and, more generally, on the metamorphic processes (mineral reactions and rock-melt interactions) occurring at depths.

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## Investigating the effect of oxygen fugacity on magnetite-melt Fe isotope fractionation at high-pressure and high-temperature: an experimental approach

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*Keywords:* experimental geochemistry, Fe isotopes, oxygen fugacity.

Iron is a major element in the Earth's crust and mantle, as well as in the silicate melts formed by partial melting of rocks in these reservoirs. Iron is a polyvalent element that can exist in its metallic (Fe<sup>0</sup>), ferrous (Fe<sup>2+</sup>) or ferric (Fe<sup>3+</sup>) states, the proportions of which control the oxygen fugacity (fO<sub>2</sub>) of a particular system. The fO<sub>2</sub> of magmatic systems regulates the formation of mineral phases, and in turn, the differentiation of silicate melts and the evolution of magmatic series.

Importantly, Fe has four stable isotopes (<sup>54</sup>Fe, <sup>56</sup>Fe, <sup>57</sup>Fe and <sup>58</sup>Fe) that can be used as a powerful geochemical tracer to investigate the physicochemical controls on the evolution of magmatic systems and planetary reservoirs. Technological advances in mass spectrometry (i.e., the advent of the multi collector inductively coupled plasma mass spectrometry MC-ICP-MS) allow us to precisely determine the Fe isotopic composition of minerals and melts (to within 0.05‰). Resolvable, systematic differences in their isotopic compositions have been shown to reflect the redox conditions at which they formed. Even though the study of Fe isotopes allows to shed light onto magmatic systems, the processes governing Fe isotopic fractionation are not fully understood and mainly rely on the study of natural specimens that are often affected by alteration, metasomatism or disequilibrium. Therefore, to fully comprehend Fe isotope systematics of natural systems, it is paramount to determine the factors controlling mineral-melt fractionation, and especially the role of fO<sub>2</sub>.

In this work we employed an experimental approach to provide new constraints on mineral-melt Fe isotope fractionation at high-pressure/temperature conditions replicating natural magmatic systems. Using an end-loaded piston cylinder press, we synthesized magnetite in equilibrium with granitic melt at 1 GPa and 800°C in a double capsule configuration that allowed the fO<sub>2</sub> to be controlled during the experiment. Once the experiments were conducted (with durations up to 3 days), the charges were recovered and nearly-pure mineral and glass separates were obtained. The separates were dissolved in acids, purified using anion-exchange chromatography and analyzed for Fe isotopes by MC-ICP-MS.

The experiments provide new constraints on the effect of fO<sub>2</sub> on magnetite-melt Fe isotope fractionation factors that will permit a quantitative understanding of the Fe isotope systematics of natural igneous systems.

## **<sup>40</sup>Ar/<sup>39</sup>Ar Jurassic apparent age from biotite petrochronology in the Valpelline Unit (Dent-Blanche Tectonic System, Austroalpine Domain, Western Italian Alps)**

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Keywords: migmatitic gneiss, biotite, <sup>40</sup>Ar/<sup>39</sup>Ar petrochronology.

The Valpelline Unit represents a fragment of the continental crust of the Adria/Africa plate that experienced a migmatite-partial melting stage during the Permian (Pesenti et al., 2012; Kunz et al., 2018). Now it is part of the Austroalpine Domain within the axial sector of the Alpine chain. This unit is made by High Temperature (HT) metamorphic rocks such as migmatite-gneiss, sillimanite-gneiss, acid granulites, amphibolites, marbles/calcsilicates and pegmatite dykes (Dielh et al., 1952; Manzotti & Zucali, 2013). Meso- and microstructural analysis allowed us to reconstruct three main deformation phases that produced the S2 regional-scale foliation related to the HT evolution. Zircon and monazite U-Pb geochronology constrains the age of HT metamorphism as Permian, associated with large melt-producing migmatite domains. The meso- and microstructural analysis shows that the S2 foliation is marked by biotite shape preferred orientation in migmatite gneiss and occurs as a relict within large garnet porphyroblasts. <sup>40</sup>Ar/<sup>39</sup>Ar stepwise heating was applied to biotite from microdomains of three main lithotypes: pegmatites, Crd-bearing and Grt-bearing migmatite and sillimanite-gneiss. Biotite was separated by crushing, sieving (which yielded 150-250 µm and 250-500 µm size fractions), magnetic separation, handpicking, and ultrasonic cleaning in ultra-pure H<sub>2</sub>O. For each sample (fine and coarse) we analyzed ca. 10 mg biotite, irradiated at the McMaster nuclear reactor in Ontario (Canada) for 5 h, carefully avoiding Cd shielding. All samples showed bimodal age, Cl/K and Ca/K distributions, evidence of two biotite generations, Bt1 and Bt2; both grain sizes contained Bt1 and Bt2, whereby the fine fractions had equal or slightly older ages than the coarse fractions. A well-defined Jurassic apparent age was observed in most samples, identified as Bt2 by its Ar isotopic signature; Bt2 overprints an older Bt1, which might have crystallised during the development of the regional fabric. <sup>40</sup>Ar/<sup>39</sup>Ar stepwise-heating results were compared with textural and minero-chemical variations to fully characterize the different generations of biotite by means of EPMA X-ray mapping and combined point analysis.

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## From floor to roof of a late Variscan batholith: geology and petrography of the north-eastern Serre Batholith (Calabria, southern Italy)

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*Keywords:* geological map, composite batholith, magmatic relationships.

Granitoid rocks make up a significant portion of the continental crust and, therefore, the study of granitoid complexes is of primary importance to reconstruct the processes leading to its generation and evolution. In this respect, field and petrographic data still represent essential basic information to unravel the architecture and build-up mechanisms of such complexes. We present here an original geological map of the north-eastern Serre Batholith, together with new field and petrographic data of its main five granitoid units (Russo et al., 2022). This study provides a portrait of a c. 13-thick floor-to-roof batholith exposure, focusing on the relationships between the main magmatic units, which were sequentially emplaced at decreasing depth from c. 23 to c. 6 km, during the latest stages of the Variscan Orogeny in southern Europe (Caggianelli et al., 2000; Langone et al., 2014; Fiannacca et al., 2017). Main findings indicate: a) intensity of foliation in strongly to moderately foliated Am-Bt tonalites (ABT) and strongly to weakly foliated Bt tonalites (BT) representing the oldest and deepest granitoids, increases toward the contact with lower crustal migmatitic host rocks. Structural features, coupled with microstructural evidence of suprasolidus deformation, are consistent with emplacement of the earliest granitoids along an active shear zone and a minor tectonic influence during solidification of the upper levels of the BT unit; b) the passage from BT and overlying two-mica porphyritic granodiorites and granites (MBPG) is locally marked by intrusive contacts. Rounded to angular blocks of BT in the MBPG indicate that the latter intruded the tonalites when they had already achieved a rigid state. Rare oriented fabric marked by alignment of K-feldspar megacrysts and occurrence of narrow shear zones in the MBPG close to the contact with the underlying BT suggest shear zone activity also during solidification of the basal MBPG; c) the contact between MBPG and overlying two-mica equigranular granodiorites and granites is gradational, over a c. 500 m wide band, reflecting partial homogenization of MBPG granitoids from the roof of the unit with the freshly emplaced MBG magmas. Lack of visible oriented rock fabric in the whole MBG unit implies negligible shear zone activity during or following magma emplacement; d) gradational contacts, over a band wide up to 1.5 km, also occur between the MBG and the Bt granodiorites (BG) that make up the batholith roof. BG locally show a visible oriented fabric that, together with deformation microstructures indicate possible shear-zone involvement during magma emplacement. The new geological map and related data provide a valuable addition to the existing knowledge of the Serre Batholith and, at the same time, a new starting point for further in-depth multidisciplinary investigations aimed to better understand the architecture and construction mechanisms of post-collisional batholiths.

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## Sr isotope stratigraphy of the Finero Complex (Ivrea Verbano Zone)

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Keywords: Sr isotope, mantle, lower crust.

The Finero Complex in the northern Ivrea-Verbano Zone is one of the most enigmatic cross-sections through the mantle-lower continental crust. A mantle peridotite (Phlogopite Peridotite) consisting of a pervasively metasomatized spinel-harzburgites with abundant phlogopite and amphibole (e.g., Cannaò et al., 2022) is in contact with a lower crustal mafic complex consisting of three different units: i) the Layered Internal Zone (LIZ-consisting of lherzolites, garnet-hornblendites, pyroxenites, anorthosites and garnet-gabbros); ii) the Amphibole Peridotite and iii) the External Gabbro (EG), which is in contact with the Kinzigite Formation (Siena & Coltorti, 1989). The effective relationships between the mantle and the crustal units are still not completely understood as well as the genetic relationships between the different crustal units.

We carried out the trace element characterization and the *in-situ* Sr-isotopes characterization of amphibole, plagioclase and clinopyroxene in the different lithologies of the whole Finero Complex with the aim of identifying chemical and isotopic disequilibria that could be witness of multiple and genetically distinct igneous events. *In-situ* trace element and Sr-isotope determinations were carried out at the Geochemistry, Geochronology, and Isotope Geology laboratory of the University of Milano. Trace elements were determined with a 193 nm laser ablation microprobe (Analyte Excite Teledyne Photon Machines) coupled with a single collector quadrupole ICP-MS. *In-situ* Sr isotope determinations were carried out with the same laser ablation microprobe coupled to a Neptune XT (ThermoFisher) multi collector (MC-)ICP-MS.

In all the analyzed lithologies, except for the anorthosites, amphibole and clinopyroxene yield within error <sup>87</sup>Sr/<sup>86</sup>Sr ratios. Strontium isotope composition in plagioclase is generally more radiogenic than in amphibole and clinopyroxene except in the External Gabbro, where <sup>87</sup>Sr/<sup>86</sup>Sr ratios are significantly lower. Strontium isotopic data in clinopyroxene and amphibole in the Phlogopite Peridotite confirm the high crustal signature of the metasomatic agent. In the LIZ <sup>87</sup>Sr/<sup>86</sup>Sr values for amphibole and clinopyroxene identify two different isotopic clusters: i) a less radiogenic cluster pertaining to the lherzolites and websterites approaching the composition of the depleted mantle; ii) a more radiogenic cluster with the higher values pertaining to the anorthosites. In the Amphibole Peridotite the <sup>87</sup>Sr/<sup>86</sup>Sr values of amphibole and clinopyroxene are slightly more radiogenic than in those from the LIZ.

The trace element composition of mineral phases in the different units as well as the occurrence of Sr isotopic disequilibria between minerals, suggest that the Finero mafic Complex may be the result of multiple infiltration of variably enriched melts into a pre-existing complex characterized by a depleted Sr isotopic signature.

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## Modelling the chemical potential landscape of garnet–sillimanite restites from Catena Costiera (Calabria, southern Italy)

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Keywords: restites, chemical potentials, diffusion.

Forward thermodynamic modelling of reaction microtextures of rocks metamorphosed under granulite facies conditions is key to gain information on high-temperature processes such as melt extraction and solid-state diffusion during the peculiar P–T path experienced (White et al., 2008; White & Powell, 2011; Mitchell et al., 2020). In particular, depending by the availability of intergranular melt during exhumation and/or cooling, the rock equilibration volume can vary, becoming smaller and smaller with solid-state diffusion dominating when temperature decreases. This turns into incomplete reaction microtextures such as symplectites. Nevertheless, these microtextures record chemical potential gradients and can allow us to track the evolution of the equilibration volume while melt was drained out and P and T changed. To this aim, we have investigated garnet–sillimanite restites from Catena Costiera in Calabria, wherein complex cordierite–spinel–corundum symplectites between garnet and sillimanite were observed by Piluso & Morten (2004). Our phase equilibrium thermodynamic modelling indicates that restites record T-peak conditions of 850–950°C at ~0.6 GPa when cordierite stabilised. At that stage, the molar volume fraction of melt was <5%, with cordierite formation that favoured further melt expulsion. We show, through calculated P/T– $\mu$  and  $\mu$ – $\mu$  grids that cordierite–spinel–corundum symplectites formed during the cooling path due to rising of  $\mu_{\text{FeO}}$ ,  $\mu_{\text{MgO}}$  and  $\mu_{\text{SiO}_2}$  chemical potential gradients. Finally, progressive decrease of  $\mu_{\text{SiO}_2}$  and immobility of  $\text{Al}_2\text{O}_3$ , turned into formation of corundum partially replacing spinel in the microtexture.

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## **S15.**

### **Exploring the interaction of surface processes and tectonics in coastal and fluvial systems**

#### *CONVENERS AND CHAIRPERSONS*

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## **Integrated approaches to support the hydrogeological coastal plain conceptualization (Metaponto, Southern Italy)**

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*Keywords:* coastal aquifer, salinization, conceptualization.

The integration of geophysical, geognostic and hydrogeological methods was implemented to support the conceptualization of a complex coastal aquifer to obtain a better understanding of the aquifer hydrodynamic. This approach involved the use of electrical resistivity survey, in terms of characterization and monitoring acquisitions, seismic survey and hydrogeological loggings. The integration of these techniques provided a more comprehensive understanding of the coastal aquifer system, helping to identify potential risks and opportunities for sustainable management. The integrated geophysical and hydrogeological approach was tested for understanding the coastal aquifer of the Metaponto plain with the final purpose of developing sustainable management strategies. Four geological formations and hydrogeological units can be schematically identified. They are, from the bottom to the top: the Argille Subappennine Formation (Subappennine Clays); the marine terraced deposits; the alluvial, transitional, and marine deposits, hereinafter the plain deposits); and the coastal deposits. The marine terraced deposits constitute the outcropping aquifer far from the coast; the plain deposits and secondly the coastal deposits constitute the aquifer along a wide coastal strip in the Metaponto plain, the Argille Subappennine is the deep aquifer bottom in both cases. This exemplification does not take into account the considerable variability in the granulometric characteristics of the deposits of the plain, which are determined by the succession of phases of erosion and deposition, variations in sea level, the position of the coastline as well as the extensive meandering of the main rivers of the plain, including the nearby Basento River. Inside the Metaponto coastal plain, which extends about 40 km along the Ionian coast, a test site was selected close to the Metaponto municipality, between the Cavone and Bradano Rivers (Southern Italy). In order to elucidate the effects of these complex geological events on the main hydrogeological attributes and thus improving knowledge of the plain's aquifer, an extensive survey campaign was conducted using a multi-methodological approach. Three electrical resistivity tomography (ERT) were realised, from inland to the coast, crossing test-site, of lengths ranging from a minimum of 940 m to a maximum of 1,820 m, integrated by thirty-four HVSr (Horizontal to Vertical Spectral Ratio) measurements. In order to make a comparison between geophysical and stratigraphical data, improving geophysical results, three boreholes were drilled. Every borehole was instrumented with an open pipe piezometer equipped with a permanent multipolar electric cable and electrodes along the vertical (every 2 meters), in order to investigate groundwater table and soil resistivity variations. Periodically (every three months), multi-parameter logs were carried out along the water column of piezometers by means of probes equipped with sensors for measuring temperature, electrical conductivity, pH, oxygen demand, and oxidation reduction potential. At the same time, surface-to-borehole ERT were acquired with electrodes spacing of 3 m. The ERT investigations, integrated with HVSr data, show excellent correlation with the geological information of the area and borehole coring data. The results highlighted the irregular geometries related to the morphological evolution of the coastal area as well as the geological and stratigraphic complexity of an area where the evolution of major rivers in their morphological dynamism, related to past geological events, have continuously influenced the current geometrical stratigraphical patterns and the grain size variability. The systematic and periodical use of multi-parameter logs integrated with surface-to-borehole ERT investigations, provided preliminary assessments of the spatial variability of chemical-physical characteristics of groundwater related to seawater intrusion phenomenon. Focusing on the risk of salinization for seawater intrusion, this approach can support conceptualization and numerical modelling, i.e., permitting the bounding of areas where saltwater intrusion is a potential risk and where some measures, such as groundwater recharge, may be needed to maintain the water supply.

## **Instability at Roca Vecchia: safeguarding a site of archaeological and naturalistic values along the Adriatic coast of Apulia, southern Italy**

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*Keywords:* cliff, karst, archaeology, instability, hazard.

The coastal sector of Melendugno municipality (Apulia, southern Italy) is among the most interesting on the Apulian Adriatic side, hosting several spots of peculiar beauty of the landscape and great archaeological value, which attract an increasing number of tourists every year. The site is largely characterized by cliffs with a maximum height of about 20 m, and often characterized by the presence of deep notches and large cavities modelled by marine processes and karst phenomena. In Apulia, cavities excavated by man in the soft calcarenite rocks have a great cultural, historical, archaeological and religious relevance, and have been object of scientific studies since many years. In detail, cave settlements present similar architectural elements even though they cover a long-time span, extending from the Middle Stone Age (Mesolithic - oldest phase), to the 17<sup>th</sup> century (1600 - most recent phase; Calò & Sammarco, 2020). As from the archaeological evidence found at the sites, the use of such caves was mainly as shelters and/or storage houses (Fonseca et al., 1979). In such a complex framework, the presence of religious places has been also documented, as at the Madonna di Roca sanctuary in Roca Vecchia, built on an ancient church which no longer exists. The area hosts also the Grotta della Poesia sinkholes system, one of the most beautiful sites for tourists in Apulia. It consists of two large sinkholes connected through channels, and in turn to the sea, by flooded passages. Recent surveys by scuba-divers have documented the possibility of further failures also within the submerged part of the system (Bertelmann et al., 2022).

Given the specific geological characters of the site, together with the marine action on cliff and the high density of artificial and natural caves, the whole coastline at Melendugno is affected by high degree of instability and sinkhole phenomena, that represent a serious hazard to both the local community and the tourists crowding the site, especially during the summer season. In order to improve the landslide knowledge at the site, Delle Rose & Parise (2005) documented several instability events over the years, by interpreting multi-temporal aerial photos from the fifties onward, highlighting significant changes in the coastal morphology. Recently, other geological surveys have been conducted along the Melendugno coast, in particular at Roca Vecchia, to evaluate the situations most prone to collapse or failure. Fragility of the area, combined to the high frequentation by tourists, require to proceed with monitoring actions, at the same time possibly regulating the number of visitors to safeguard these precious elements of the cultural heritage.

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## **Physical models of channel width in alluvial and bedrock rivers with implications for long-river profiles**

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*Keywords:* bedrock rivers, landscape evolution, climate-tectonic interactions.

The stream power incision model (SPIM), which gives the erosion rate of a bedrock river as a function of the shear stress on the river bed, is fundamental to tectonic geomorphology. It forms the foundation of current understanding of how tectonics and climate interact in active orogens, yet it is based on several empirical scaling laws, and is hard to validate with field observations. The SPIM depends on an assumption of steady open channel flow, a model of flow resistance due to the channel boundary, and an empirical channel width scaling. The channel width scaling in particular has a significant influence on the SPIM, however, there is currently no widely accepted model of what controls channel width in self-formed bedrock channels, and most of the models that do exist depend on other empirical scalings. The semi-empirical, unvalidated status of the SPIM prohibits it from becoming a predictive model of bedrock river incision.

Leveraging recent work on channel hydraulic geometry, I present an emerging framework for quantitatively describing how sediment transport and bedrock erosion form channels and long river profiles. The framework allows one to include a number of different processes and upscale their effects on river profile evolution to landscape evolution timescales in a rigorous way. This framework can also be used for alluvial channels, and I present results testing it against over 3000 alluvial river reaches where width varies by 3 orders of magnitude, and bankfull discharge varies by 7 orders of magnitude. Channel width is predicted to within a factor of 2 for 63% of reaches and to within a factor of 3 for 84% using just a single set of model parameters. The model inputs are simply bankfull discharge and representative grain size. This new work also allows the SPIM to be derived directly from the Navier-Stokes equation with minimal assumptions, putting it on firm theoretical footing, and making it easier to validate with field data.

## Morphometric characterization of the main lithologies in eastern Sicily

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*Keywords:* model Builder, quantitative geomorphology, eastern Sicily.

In recent decades, with the rapid development of the computing capabilities of PCs and with ever more precise and accurate digital elevation models (DEM), giant strides have been made in quantitative geomorphology, developing methods to numerically analyse the landscape evolution and to parameterize the active geomorphological processes.

In the present study, we explore the chance to find a semi-automatic procedure to discriminate different rock types by a morphometric approach. We apply different morphometric indexes, specifically those largely used in relief studies (e.g., topographic relief, hypsometric integral, topographic slope). We developed a complex working model, designed and built in ArcGIS Model Builder by connecting a series of already existing tools into new geoprocessing scripts. As essential input data for the model we used a detailed, 2x2m-resolution DEM. The analysis also benefits of the support of available (e.g., geological maps) and new geological data collected during geological-structural field surveys carried out in the Peloritani Mts. and Hyblean Mts., in eastern Sicily.

Since different rock types show similar values in certain morphometric indexes, we used a combination of these latter. This allowed us to generate a morphometric signature of each rock type, thus serving as foundational data to explore the role played by tectonic deformation vs. lithological factors in the regional- and local-scale landscape response.

## Soil-building resonance effect in the urban area of the city of Villa d'Agri (Southern Italy)

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Keywords: soil-building interaction, HVSR, resonance effect.

In this study we propose to evaluate the characteristics of built environment with urban soils according to an holistic approach (Gallipoli et al., 2020). The aim of this study is to evaluate the possible occurrence of double resonance effects between the first vibrational mode of all buildings located in the urban area of the city of Villa d'Agri (Basilicata, Italy) with the relative underlying soils. The single-station ambient noise measurements analysed through Horizontal-to-Vertical Spectral Ratio technique (HVSR; Nakamura, 1989; Gallipoli et al., 2010) have been used to estimate the vibrational characteristics both on soils and buildings. The soil main peak ( $f0\_s$ ), estimated through HVSR analysis over 105 points of measurements, mainly ranges between 0.8 and 3.7 Hz, with a median value equal to 2.1 Hz. In order to display sparse soil measurement as continuous fields in the space domain, isofrequency and isoamplitude maps have been obtained with IDW interpolation. The buildings measured have been chosen as to obtain a representative sample in terms of built typology, year of construction, height and soil foundation lithology. The frequency ( $f0\_b$ ) corresponding to the first vibrational mode of the 85 monitored buildings varies between 2.5 and 8.2 Hz, with a median value equal to 4.8 Hz. As expected, the main frequencies vary mainly with increasing of building height. This consideration allowed to estimate the relationship between the first vibrational period  $T$  (s) and the corresponding height ( $H$ ) through a simple linear model with zero intercept in the form  $T = 0,0167 \cdot H$ . Thanks to the availability of the heights for the whole building heritage of the city of Villa d'Agri, by using the estimated empirical relationship it has been possible to predict the main vibrational frequencies of all the buildings of Villa d'Agri (659) with a height between 6.5 and 19.8 meters. The estimated first vibrational frequencies ( $f0\_b$ ) ranged approximately between 2.5 and 9.8 Hz. In order to evaluate where the soil-building resonance effect occurs, the frequencies of 659 buildings have been compared to the interpolated frequency of the underlying soil. The analysis of this map displays that for 2 buildings (about 0.3%) there is a complete overlapping between soil frequency range and the main vibrational frequencies of this buildings; about 39% of the buildings (258) exhibit a partial overlapping between the two frequency ranges; lastly, 399 buildings (representing about 60% of the buildings) show no overlap between soil and building frequencies. The spatial information transmitted by these results is an extremely important element as it allows us to identify the most dangerous areas of the city, i.e. those parts where it is much more likely that the effect of soil-building resonance could increase a damage during an earthquake.

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## **A standard procedure for monitoring sandy beaches**

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*Keywords:* beach monitoring, sandy beach, sediment thickness.

The beach represents a variable environment where physical and biological processes interact with human activities. In this context, sandy beach investigation leads to gather sedimentological, geomorphological and geophysical data to study its evolution in space and time. This research suggests a standard procedure for monitoring the morpho-sedimentary processes of Torre Guaceto beach (Apulia Region, southern Italy) by analyzing the textural and compositional characteristics of the sands and quantifying the volumes involved in the coastal dynamics. The study area is a sandy pocket beach that can be considered representative of the coastal dynamics of a large sector of the northern Mediterranean Sea involving the southern Adriatic Sea. Sedimentological and ecological investigations allowed to describe the textural and compositional characteristics of the beach sands by interpreting their sand provenance and the physical/biological interactions within the beach. The topographic surveys carried out with a Terrestrial Laser Scanner and an Optical Total Station, aimed to quantify the variations of sediment volume over time. Lastly, the geophysical techniques which included Sub Bottom Profiler procedures, Ground Penetrating Radar investigation, and resistivity models enabled us to calculate the sand sediment thickness above the bedrock.



## Water leak detection via optical fiber and ground penetrating radar sensors: a laboratory experimentation

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*Keywords:* water leak detection, ground penetrating radar, optical fiber.

Leakage of water distribution networks is a relevant topic and, nowadays, deserve even more attention because, due to climate changes, the Earth suffers from drought and this makes necessary to move towards an effective and judicious usage of water resources. Moreover, water leaks can determine the instability of urban streets, material corrosion, and void formation thus increasing the risk of structural collapses that threaten people's safety. As a result, the effective usage of water resources is a relevant topic to move towards smart and resilient cities and it demands technologies designed to monitor water distribution networks, in order to avoid waste and ensure environmental safety (Puust et al., 2010).

Leak detection systems (LDS) can be divided into two main categories: Static and Dynamic. Static LDS are placed within the water network and allow continuous monitoring (e.g. fiber optic sensors), while the dynamic LDS are used on-demand, i.e. the investigation is carried out in the areas where moisture is observed or there is a suspicion of a water loss (e.g. electromagnetic sensors and infrared thermography). However, the early detection and non-invasive characterization of leak is difficult, if not impossible, to be achieved by means of a single sensor and the cooperative use of different sensors is of paramount importance.

This communication deals with the joint and cooperative use of the distributed optical fiber sensor based on the Brillouin scattering phenomenon (Bernini et al., 2004) and the ground penetrating radar (GPR) enhanced by microwave tomography (MWT) (Catapano et al., 2019; Catapano et al., 2022). The first sensor, if integral to the pipe, is able to detect temperature and/or thermal conductivity variations due to water leakages. Therefore, it is suitable to assure continuous monitoring and to provide low spatial resolution information about the leakage location. Conversely, GPR allows on-demand non-invasive surveys providing high spatial resolution images of the investigated scenario, provided that the collected data are processed properly.

In order to provide a proof of concept assessing the performances of each sensor and the advantages provided by their cooperative use, joint experimentation was carried out in an ad-hoc built experimental scenario reproducing a water leakage. The scenario is a scaled reproduction of a realistic test case and is made up by a plastic pipe filled by fresh water and buried in a river-sand terrain. The optical fiber sensor was integral with the pipe, while GPR data were collected along parallel and perpendicular survey lines with respect to the pipe. The results of the experimentation are encouraging and coherent with each other and support the joint use of the sensors in a holistic methodology for pipeline monitoring in urban areas.

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## Spatial and temporal monitoring of sea waves very close to the coastline using K-band radar

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Keywords: sea state monitoring, coastal zone, radar.

Coastal zones are important settlement areas that play an essential role for wealth of many countries. These areas are usually characterized by a strong identity, linked to their sea proximity, and by a great natural and cultural diversity. The most vulnerable coastal environments such as deltas, bays, and gulfs require continuous management and prevention actions, since they are exposed to several risk factors (coastal erosion, pollution, environmental disasters etc.) due to natural causes or the pressures of human activities. Climate change is exacerbating many of these risks (e.g. the ongoing rise in sea level, increased number of storms and flooding, etc.) and changing the frequency and magnitude of damaging events. In this framework, an accurate description of the wave dynamics in terms of dispersion, shoaling, and refraction effects induced by the seabed bathymetry and coastline, both in deep, intermediate, and shallow water conditions can reduce disaster risk and increase the resilience of coastal zones. Nowadays, prediction models, in situ sensors, remote sensing instruments, and their integration are useful tools to perform coastal risk analysis. However, remote sensing technologies (e.g. radars, video-monitoring systems) have attracted great interest thanks to their possibility to provide spatial and temporal information about sea state in a non-invasive way (Benetazzo et al., 2018; Ludeno et al., 2015; Mantovani et al., 2020). Among these, ground-based radar systems, such as High Frequency and X-band wave radar, have proven to be effective for measuring the wave spectra and retrieving the sea state information in coastal areas. However, both radar technologies have two disadvantages: i) they are blind in the near-shore region and so they are not able to retrieve the sea state information; ii) due to their weight, bulk, and necessity of high power supply, they are not easy to install and then cannot be considered portable systems.

This communication proposes an innovative short range K (SRK)-band radar to perform sea state monitoring very close to the coastline. SRK-band radars are complementary to the aforementioned ground-based systems for sea state monitoring (Ludeno et al., 2023). They are usually characterized by a small range coverage (e.g. up to a few hundred meters), which is useful for analyzing sea waves as well as the reconstruction of the sea surface current and bathymetry fields very close to the coast, river estuary, and in semi-closed areas (e.g. bay, harbor, etc.). Preliminary results referred to measurements carried out in real scenarios corroborate pros and cons of the proposed radar technology.

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## **Analysis of failure mechanisms and retreat rates of sea cliffs along the Campi Flegrei volcanic coastline, Italy**

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*Keywords:* sea cliff, retreat rates, Campi Flegrei.

Many sea cliffs worldwide are affected by severe retreat processes, mainly occurring with landslides, surface erosion and weathering processes. This represents a serious risk for living people, as well as for buildings, roads and railway networks. In Italy, nearly 2,850 km of coasts are occupied by rocky shores and cliffs which are directly in contact with the sea water and are exposed to landslides. The coastline of the Campi Flegrei active volcanic district is one of the rocky coastal zones more densely urbanized of Italy. Here, coastal cliffs are made by volcanoclastic deposits and include remnants of ancient volcanic edifices formed in the last 15 ka. Due to petrographic, geotechnical and geostructural properties of volcanoclastic deposits, these cliffs have been affected by rapid recession processes since their origin. A review of the analysis and monitoring activities, aimed at achieving a quantitative knowledge about retreat processes that are contributing to the geomorphic evolution of the Campi Flegrei rocky coast, is presented. The research is based on the use of geomatic techniques and focuses on the most relevant coastal cliffs in the area: Coroglio, Punta Epitaffio, Torrefumo and Baia dei Porci cliffs, located in different sectors of the Campi Flegrei area. Mass wasting processes are effectively contributing to the dismantling of coastal cliffs in the Campi Flegrei volcanic area. Episodic cliff failures can displace huge masses of rock that induce sudden and localized cliff recessions, even if Terrestrial Laser Scanner monitoring activities show that small-scale failures, between  $10^{-2}$  m<sup>3</sup> and 1 m<sup>3</sup>, are more frequent than larger collapses. Findings gained by the multi-temporal monitoring of landslides demonstrated that after the main failure, landslide scars can be affected by further collapses, as well as deposits eventually formed at the cliff toe can be rapidly eroded by the sea wave action and by rainfall-induced surface runoff. Measured short-term retreat rates range from 0.001 to 0.025 m/yr during 2013-2016, while mid-term rates vary between 0.17 to 1.2 m/yr. Geostructural maps and analysis of the tuff coastal cliffs with Terrestrial Laser Scanner surveys and processing show accuracy, precision and resolution that are adequate and consistent for the scope of geomechanical analysis of rock failures. The used geomatic techniques have resulted suitable for monitoring activities.

## **The Marine Geology surveys of the Taranto seas (Northern Ionian Sea): natural resources and anthropogenic impacts**

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*Keywords:* marine geology, geophysics, Ionian sea.

Coastal areas have a significant social and economic value linked to human activities. Despite their undoubted naturalistic value, the transitional and shallow marine environments are strongly impacted by different types of pollutants produced in continental areas and transported at sea by different physical agents (rivers, wind, aquifers, etc.). In particular, marine sediments become the final destination for many types of pollutants, such as heavy metals, various types of PCBs, plastic materials, which are now ubiquitous in coastal areas. In addition, anthropogenic impacts develop directly on the shallow seafloor through a series of activities (intensive fishing and trawling, laying cables and pipelines, foundations of maritime works and wind turbines, etc.) continuously modifying the physical and biological matrices of marine environments. As known, the so-called Taranto Seas (Mar Piccolo and Mar Grande basins) are strongly impacted by a series of industrial activities, shipyards and bases of the Italian Navy, and intensive practices of aquaculture and mussel farming. At the same time, the Taranto Seas show a great variety of underwater landscapes often characterized by great biodiversity and ecological peculiarities linked to the complex interaction between low hydrodynamics and the presence of underwater karstic springs.

We present the results of extensive marine geophysics surveys in the context of numerous research projects both aimed at the environmental characterization of the Taranto Seas and the modern mapping of the seafloor (CARG project). The data collected allow to trace the complex interactions between physical-biological environmental processes and anthropogenic activities, confirming the role of the Taranto Seas as a natural laboratory to test methods of monitoring and intervention for the resolution of environmental issues.

## **Grain shape evaluation by elliptic Fourier and principal component analyses: Application to fluvial sands and its relationship with transportation distance**

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Keywords: EF-PCA, REF1, SEF.

The shape of clastic grains possesses an important information regarding the hydrodynamic transportation and depositional environments. Therefore, many studies have been pursued to quantify the shape of clastic grains. For example, longest, medium, and shortest axes (three axes) of grains can be used to describe the overall shape of grains, such as elongation to roundness parameter, however, these three axes cannot determine the surface smoothness of the grains. The reverse is also true, measurements of the surface smoothness cannot be extended to describe the overall shape of grains. In this contribution, we aim introduce a method to simultaneously quantify the overall shape, as well as the surface smoothness of grains, i.e., elliptic Fourier-Principal component analysis (EF-PCA; Suzuki et al., 2015).

The elliptic Fourier analysis can encode the shape of grains into sinusoidal waves of different frequencies (100 Fourier wave series in this study). Principal component analysis was further conducted using the variance-covariance and correlation matrices of the Fourier descriptors. The use of the former matrix has an effect to maximize the contribution of high amplitude Fourier waves, and thus extracted index reflects the overall shape of grains (REF1). Contrary, the use of latter matrix amplifies the fine Fourier waves, and hence an index regarding the surface roughness (SEF) can be produced.

REF1-SEF indices can distinct and predict grains derived from glacial, fluvial, foreshore and aeolian environments. Furthermore, textural maturity measured by REF1-SEF indices correlates with the physical energy operated. Therefore, it can be expected that fluvial sands mature as downstream distance increases. In this regard, the present contribution aims to investigate the change in shape of fluvial sand in relation with transportation distance.

Fluvial sand samples were collected from six fluvial systems located in Japan as well as, the Red River in Vietnam and the Yangtze River in China. These rivers encompass wide variety of fluvial systems, for example, world's most steep river (The Joganji River) to flat rivers (The Red and Yangtze Rivers), or straight rivers (The Shinano River) to meandering rivers (The Red and Ishikari Rivers). From each river system, 5 to 15 sand samples were collected along the downstream direction.

The REF1 (grain roundness) shows strong positive correlation with distance, indicating an increase in roundness with downstream distance, regardless of the river system. The SEF (grain smoothness) also demonstrates positive correlation with distance, reflecting the deeper abrasion as farther transportation. The SEF values, however, converge into 10 at a transportation distance of 100 to 300 km. This may indicate that the extent of abrasion in fluvial system has its limitation.

In conclusion, the flow distance of fluvial system can well be predicted from grain shape parameters REF1 and SEF.

Suzuki K., Fujiwara H. & Ohta T. (2015) - The evaluation of macroscopic and microscopic textures of sand grains using elliptic Fourier and principal component analysis: Implications for the discrimination of sedimentary environments. *Sedimentology*, 62, 1184-1197.

**Study of the active gravitational phenomena along the provincial road n°18 - Project for the functional recovery of the unstable areas between Km 2+500 and Km 10+700, along the “Panoramic road of southern Sarrabus”**

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*Keywords:* landslide hazard, hydrogeological risk, safety safeguard.

On 14, 15 and 16 November 2021 a “Mediterranean cyclone” hit the Sardinia Region with particular intensity in the south-eastern area due to the prevailing winds from the south-east (Vento di Scirocco). Particular negative repercussions have manifested themselves on the road heritage of the Province of Southern Sardinia, causing particular damage in the areas of Sarrabus, Gerrei and Parteolla, in the municipalities of Villasimius, Castiadas, Muravera, Villaputzu, San Nicolo Gerrei, San Basilio, Ballao, Escalaplano, in correspondence of the provincial roads n° 19, 20, 22, 24, 25, 26, 27, 28, 120 and the “ex SS125”.

On 18 November 2021, with council resolution No. 127 of 11.18.2021, the provincial administration proclaimed the state of natural disaster. Particular problems from gravitational phenomena were encountered along the coastal road n°18, for which, in order to be able to safeguard public safety, it was necessary to proceed with the issue of the executive order n° 15 of 17.11.2021 aimed at the interdiction of traffic at Km 22+700 and between Km 2+500 and Km 10+700. The main reasons that led to the interdiction of traffic were linked to the occurrence of numerous landslides along stretches with halfway up profiles, due to collapses, subsidence of the road pavement and of works of art, widespread washout phenomena, muddy outflows and accumulation of materials on the road platform, landslides and detachment of granite blocks on outcrops of stranded lithologies facing the road.

The geological framework of the area identifies lithologies to be ascribed to granodiorites and inequigranular monzogranites forming part of the intrusive complex of the Sardinian Hercynian Base, i.e. of the so-called plutonic complex (Upper Carboniferous - Permian) into which the Filonian Complex (Upper Carboniferous - Permian) which in the area identifies granite porphyries and microgranite masses with subordinate aplitic and pegmatitic veins.

The studies and detailed examinations carried out by the Road Service of the Province of Southern Sardinia have made it possible to plan interventions aimed at recovering the original functionality of the places in the short term. In the first place, provincial road No.18 was restored and the section was made safe. Subsequently, following the execution of visual monitoring lasting a few months along the section closed to traffic, a careful analysis of the road section followed and an evaluation, as well as planning, of the interventions to be carried out in the medium term for the reduction of the hydrogeological hazard parameters of the intervention area.

To this end, an inclined aerophotogrammetric survey and a punctual survey of the main areas that have been subject to instability were carried out, with the identification of 17 main critical sub-areas. The inspections carried out along the stretch of route under study made it possible to identify a zoning of the “typical interventions” on a map basis, evaluated on the basis of the cost/benefit ratio, as shown below:

- areas where it is not possible to reduce the steepness of the slopes, for which it will be possible to create a geocomposite system of double twist wire mesh combined with the mechanical strength of the wire ropes.
- areas where retaining walls will have to be erected with partial displacement of the road axis.
- areas where have to be placed in adherence, in order to oppose and block old and new phenomena of collapse.
- areas where new containment walls will be positioned, with the simultaneous installation of passive rockfall barriers.

The estimate of the resources required has already been carried out with the definition and study of a technical and economic feasibility project, which can possibly be divided into functional lots.



## Quantifying Quaternary spatio-temporal uplift variations in the Central Apennine from linear inversion of the drainage system

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*Keywords:* central Apennine, tectonic geomorphology, river linear inversion.

The study of uplift variations in time and space can provide significant insights to understand the processes driving the topographic evolution of mountain belts. The Apennine chain is one of the more recent mountain belts of the Mediterranean region, and records a strong Quaternary uplift phase, particularly in the central sector, which is responsible for the present-day topography. In regions where tectonics is the main process driving landscape evolution, drainage systems can record temporal and spatial variations in uplift rates. In particular, for detachment-limited systems in simple settings (e.g., no significant drainage-area variations over the investigated time, drainage directions mostly perpendicular to regional structures), river profiles can be inverted to reconstruct rock-uplift histories. Here, we report results from linear river-profile inversion of 27 catchments spanning the length of the eastern flank of the Central Apennine belt, constrained by short-term incision and catchment-averaged erosion rates from cosmogenic-nuclide data. Our results suggest a spatio-temporal variable uplift event that started around 2.5-3 Ma, younger than the last compressional phase and coeval with the onset of extensional tectonics. Moreover, the uplift pulse migrated southward over time at a rate of ca. 96 mm/yr, progressively increasing in magnitude and reaching the most rapid rates (about 2-2.5 mm/yr) in the region of the highest Apennine massifs (Gran Sasso and Maiella). These results are consistent with previous studies on Apennine paleoelevations, and also with numerical models and field evidence from other regions of fast uplift pulses and uplift migration related to slab break-off. In this scenario, we provide not only new constraints on estimates of Quaternary uplift rates in the central Apennines, but also new insights supporting the break-off of the Adria slab under the Central Apennine and its possible southward propagation over time.

## Geophysical monitoring of the salt wedge in the Po di Goro river (Italy)

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Keywords: salt wedge, intrusion, geophysical.

Climate change causes global sea levels to rise and the model projections indicate a large increase of the sea level. Moreover, on a river, the rainfall deficit produces a decrease of the river flow rate and the saltwater contamination of the coastal zone in terms of intrusion and penetration in the delta system increases. The seawater intrudes in the form of a wedge along the bottom, this phenomenon, from a theoretical point of view, could be hydraulically modelled but numerical models can partly quantify these influences, but it is difficult to accurately predict the salt intrusion length. Therefore, the geophysical approach could give large contributes on the monitoring (Kiflai et al., 2022).

The Po river is the biggest river in Italy and its delta is developed out of the Adriatic Sea. The Po river was affected by a dynamic advancement, which is quite simple in terms of geomorphology and kind of sediments (from sand to silt and clay). In recent decades, however, the saline wedge has assumed increasingly worrying proportions, with a progressive intrusion of water bodies to the hinterland and the 2022 was the worst one when the saline wedge in the Po Delta area intrudes several kilometres inside the delta. From a hydraulic point of view, the Ferrara territory has a flat topography and some part of it on eastern part is below the mean sea level, with value also -3.5 m a.s.l. In most of the aquifer, the water table is below water level and it is maintained by the land reclamation pumping machines that need to drain a territory that would otherwise be flooded. The research activities defined two aims: the observation of the saltwater penetration affecting the surrounding land close the Po di Goro river and the monitoring of the saline wedge. The Po di Goro river is around 50kms long and the geological and geomorphological characteristics highlight buried coastal dunes (with sand) and buried lagoon (clay and silt) deposits. Two geophysical methods were used in these activities: Frequency Domain Electromagnetic (FDEM) and electrical resistivity tomography (ERT). The FDEM method was used to detect the saline wedge in the river and the Electrical Resistivity Tomography was applied to monitor the hydrodynamic interaction between the river and the subsoil around the riverbanks. The indirect data were correlated with a “moving boat” approach with a multilevel EC probe. The ERT sections highlighted how the salty water in the river contaminated the surrounding subsoil. The FDEM data sets defined the hydrodynamic of the saltwater wedge in the river detecting the salty plume front. These results highlight the great potential of the proposed geophysical approach to monitor the saline intrusion in delta system.

Kiflai M.E., Whitman D., Price R.M., Frankovich T.A. & Madden C.J. (2022) - Geophysical Characterization in the Shallow Water Estuarine Lakes of the Southern Everglades, Florida. *Appl. Sci.*, 12, 1154. <https://doi.org/10.3390/app12031154>.

## Integration of ERT and GPR prospecting for coastal areas characterization

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*Keywords:* geoelectrical method, ground penetrating radar, coastal areas.

Nowadays geophysical methods are widely applied in the subsoil multiscale and multipurpose characterization. Their sensitivity to physical properties variations and their impact from low to null on the places where they are applied allow their extensive use also in fragile environments such as the coastal areas. In this framework, electromagnetic geophysical methods are among the most commonly used due to the fact that water and salty water have a relevant influence on the electric and electromagnetic signal propagation within the subsoil.

Geoelectric method (ERT) is the most applied geophysical methodology in coastal areas for identification of seawater intrusion effects, for monitoring the seawater interface, for retrieving the structure and geometry of coastal aquifer systems (Costall et al., 2018). Ground penetrating radar (GPR) is less effective in saline scenarios for well-known radar attenuation phenomena, but it can provide the most high-resolution information for the characterization of the shallower areas close to the sea. Its usefulness is proven for the characterization of coastal dunes, for identifying the sea water-ground water interface, to image ground water surfaces of shallow aquifers in coastal area (Bristow et al., 2000; Ribolini et al., 2021).

From an operative perspective, coastal areas, intended as the onshore and offshore areas close to the coast lines, are challenging places for the application of geophysical methods due to their being highly dynamical and fragile systems and also because they are constituted by two totally different operational conditions: land onshore and sea offshore. At present time, the relatively few surveys aimed to characterize the coastal areas are usually performed by joint together land and marine surveys. This practice, whereas of simple applications, has a relevant limit. The boundary area between the sea and the land, the area close to the shore, remains poorly or not investigated neither by the land survey nor by the marine one.

In this study we present some case studies where geophysical methods have been successfully applied in characterizing coastal environments and the dynamics here taking places. We will show how the combined use ERT and GPR can provide information on the seawater intrusion, on the internal dune structure and on the sediment thickness above the bedrock.

Bristow C.S., Bailey S.D & Lancaster N. (2000) -The sedimentary structure of linear sand dunes. *Nature*, 406, 56-59.  
<https://doi.org/10.1038/35017536>.

Costall A., Harris B. & Pigois J.P. (2018) - Electrical Resistivity Imaging and the Saline Water Interface in HighQuality Coastal Aquifers, *Surv. Geophys.*, 39, 753-816.

Ribolini A., Bertoni D., Bini M. & Sarti G. (2021) - Ground-Penetrating Radar Prospections to Image the Inner Structure of Coastal Dunes at Sites Characterized by Erosion and Accretion (Northern Tuscany, Italy). *Appl. Sci.*, 1(23), 11260.  
<https://doi.org/10.3390/app112311260>.

## **Application of an integrated hydrogeological and geophysical approach for monitoring the effects of climate change on the main aquifer of the lower Val di Magra (SP)**

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*Keywords:* Magra, groundwater, geophysics.

The objective of the research is applying geophysical and hydrogeological techniques to investigate the effects of climate change on groundwater resource availability and quality. In particular, seismic noise cross-correlation techniques will be applied as an innovative method for monitoring groundwater levels and their changes over time.

The research area is the lower Val Magra alluvial plain, in the Ligurian region (Italy), between the Municipality of S. Stefano Magra and the Tirrenian seacoast. It is an intensely urbanised area, with widespread industries that are potential sources of contaminants.

The main aquifer of the Val Magra is qualitatively and quantitatively vulnerable to the effects of climate change. It is an unconfined aquifer in coarse alluvial deposits, characterized by high permeability. The water table is generally very close to ground level (3-7 m in depth). The aquifer is closely connected to the Magra river and continuously exchanges between the surface water and groundwater exist. Furthermore, near the seacoast, the aquifer is influenced by interaction with seawater. In this area, periods of drought favor marine intrusion phenomenon, which occurs through the rising upstream of salt-water along the Magra river. Seawater intrusion is the main responsible of the deterioration of the groundwater quality in this lower part of the Val Magra.

An integrated approach of hydrogeological survey methods and geophysical techniques will be used to achieve the objective of the research:

The traditional hydrogeological used methods are: continuous piezometric level measurements of groundwater (wells), electrical conductivity measurements of groundwater (wells) and surface water (river Magra) and isotopic analyses (Oxygen and Deuterium).

The geophysical techniques used are: 2-D geoelectrical surveys (SEV), active and passive geoseismic surveys (1-D and 2-D) and seismic noise interferometry (SNI).

Groundwater storage is estimated by monitoring the piezometric surface changes over time. The groundwater surface is interpolated from direct groundwater head measurements (wells and river) and indirect measurements from geoseismic and geoelectric surveys. Isotopic measurements of water samples are used as tracers to evaluate the groundwater-surface water exchanges. The data confirm that the main source of recharge of the aquifer is the River Magra.

Groundwater quality is evaluated by the monitoring of the physics and chemical parameters of groundwater and surface water. Geoelectrical surveys and water electrical conductivity measurements allow to investigate underground the presence of the salt wedge and to define the extent of the marine intrusion phenomenon. Preliminary water electrical conductivity result highlights that, during the strong drought period in the summer 2022, the marine intrusion reached the Romito groundwater well field by rising upstream for 7 km along the Magra river from the coastline.

## Satellite multispectral images analysis to develop a rock classification method

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*Keywords:* satellite, multispectral, classification.

The non-access areas are a very problematic issue in Geological survey, that cause lack of data providing low quality results. The first step of the study is the analysis of the 13 bands (1,2,3,4,5,6,7,8,8A,9,11,12) of the Sentinel project multispectral images, in order to create a recognizable reflectance footprint of every outcropping lithology, in eastern Sicily. The second step start with a machine learning training by the ESRI ArcGIS software with the aim of separate every lithological outcrop pictured in the orthophotos from the vegetation, soil and anthropic objects. The main problem is the different resolutions of the orthophotos and the multispectral images (0.25m and 30m, respectively). Consequently we create a fishnet (Grid) 30m x 30m, corresponding to a pixel of the multispectral images, and we extrapolate, for each cell, the number of pixels representing each category (e.g. vegetation) utilizing the categorized orthophoto. Finally, using the Microsoft Excel software, we extrapolate only the reflectance footprint referred exclusively to the lithological outcrops in every cell for the 13 bands. Mediating the data, we will obtain a reflectance range for every recognizable lithologies in outcrop.

In order to validate the elaborated data will be necessary compare the reflectance footprint elaborated with our methodology with the values measured in the field by an optical spectrometer. The main goal of the study, after the acquisition of thousands of field data for every lithology is the mapping of the outcropping terranes of an area using only satellite images. Another item is to recognize a variation of reflectance in the fault rocks outcropping along the main regional tectonic lineaments.

## **The topographic signature of active tectonics: insights from the central Apennines (Italy) and the Peruvian Andes (South America)**

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*Keywords:* river long profile, transformed river long profile, swath profile.

The large diffusion of GIS software and Matlab scripts in recent years, coupled with the online availability of DTM and Lidar data, had driven a jump in tectonic geomorphology studies, allowing the diffuse modelling of the Earth surface and the recognition of both detail- and large-scale tectonic perturbation. These analyses are addressed at the definition of some metrics related both to topography and river network, which include elevation map and its derivative (maximum, medium, minimum and relief maps), swath profiles, river long profiles, transformed (x) long profile and slope/area analysis (that allows the concavity and the normalized steepness index,  $K_{sn}$ , to be derived). Such analysis may be performed in different morphotectonic and climate settings, and their results provide information about both the large-scale distribution of vertical motions (i.e., surface uplift) and local perturbation due to active tectonic structures.

In this paper, the above-described approach has been adopted in two of the most active orogen on Earth, i.e., the central Apennines in Italy and the Peruvian Andes in South America. Topography and river network features in the Umbria-Marche sector of the central Apennines point to a south-ward increase in surface uplift. This trend is suggested by an increase in both the mean and the minimum elevation, which is coupled with the diffuse presence of large knickzone and with high to very high values of the  $K_{sn}$  index. The area affected by enhanced surface uplift correspond with the locus of moderate to strong historical earthquakes that includes the recent 2016-2017 Amatrice-Visso-Norcia seismic sequence. The sudden truncation of the area experiencing recent surface uplift towards the north may be related to the occurrence of some NE-SW trending transversal structures that seems to play a major role in the compartmentalization of the chain.

Topography and river network features have been investigated also in a sector of the Peruvian Andes, i.e., the Bongarà district, that hosts three mixed sulfide - nonsulfide Zn- Pb ore deposits. Here, overall data point to a NE-ward increases in surface uplift that is testified by the sharp increase in maximum, mean and minimum elevation, and the decrease in local relief that are coupled with the large diffusion of knickpoints and knickzone and with a jump in the mean  $K_{sn}$  values. Data about the timing of mineralization are consistent with this uneven distribution of vertical motions, as the higher surface uplift towards the NE, in terms of time and/or rate, has driven the almost complete alteration of primary sulfides and the development of nonsulfide mineralization.



**S16.**

**Georesources and Sustainability: from cultural heritage  
promotion to waste exploitation**

*CONVENERS AND CHAIRPERSONS*

*Sossio Fabio Graziano (Università degli Studi di Napoli Federico II)*

*Rossana Bellopede (Politecnico di Torino)*

*Nicola Careddu (Università degli Studi di Cagliari)*

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## Investigating sustainable processing strategies for recycling granite quarry waste in Sardinia's quarrying industry: a case study of the Buddusò quarry in Northern Sardinia

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*Keywords:* recycling quarry waste, granite, Sardinia.

Starting from the 1970s and within less than twenty years, the Sardinia region, thanks to the different types of granite characterizing the island, became the absolute leader in Italy and second in Europe (after Spain) in the production of ornamental granite. However, since 2010, due to increased competition from other countries, financial crises, and the COVID-19 pandemic, the granite industry sector in Italy has suffered a significant decline in terms of revenue and consequently production (ISTAT, 2023). This has generated serious problems for businesses, resulting in the loss of jobs. Moreover, the extensive production of granite in Sardinia has left a considerable amount of waste associated with the extraction of granite blocks. In fact, due to the high quality standards required by the market for ornamental stones, a notable quantity of extracted material is discarded due to the presence of aesthetic defects (Rana et al., 2016). Over the years, this has led to the creation of several granite waste landfills that generate problems both from an environmental and landscape point of view. The current indications of the European Union are pushing strongly towards reuse and recycling, both to address environmental issues and to deal with the serious problem of the supply of Critical Raw Materials - CRM such as Rare Earth Elements or feldspar minerals, due to the strong dependence of the EU on China and Turkey (European Commission, 2023).

This study focuses on a granite quarry located in the municipality of Buddusò, in the extractive district of northern Sardinia, which has been active for over 40 years. Several landfills have been created in this quarry over the years, hosting over 1.5 million tons of granite waste, resulting in a strong land consumption and landscape degradation. The purpose of this work is to investigate possible solutions for the reuse and recycling of such waste (for example, in the context of the ceramic industry) through the use of processing methods based on physical processes and avoiding the use of chemical substances with resulting environmental issues.

The reuse and recycling of quarry waste would bring benefits both from an environmental and landscape point of view, as well as economic. Indeed, considering the extremely high quantity of granite quarry waste present throughout the Sardinia region, finding a processing methodology and a potential market could contribute to the revival of this economic sector.

European Commission (2023) - Proposal for a regulation of the European Parliament and of the Council establishing a framework for ensuring secure and sustainable supply of critical raw materials and amending Regulations (EU) 168/2013, (EU) 2018/858, 2018/1724 and (EU) 2019/1020.

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## Screening tests on potential recovery of strategic and critical raw materials from mining waste facilities in Italy

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*Keywords:* mining waste, critical raw materials, recovery.

European Union has recently developed policies aimed at the increase of production of Strategic (SRMs) and Critical Raw Materials (CRMs) within its borders. These new regulations are designed to promote the recovery of significant amounts of materials from existing mining operations throughout the continent while contributing towards achieving the ambitious objectives of the European Green Deal and attaining Climate Neutrality. The ultimate goal of this action is to ensure a sustainable and secure supply of crucial raw materials for the European Industry by leveraging internal primary and secondary sources. According to the Italian registry of abandoned mining waste storage sites updated by ISPRA in 2022 (ISPRA, 2022), there are 562 abandoned mining sites in the Italian territory resulting from ceased activities in the last 100 years. In many cases, valuable minerals nowadays reported as SRMs or CRMs, are available or present in these areas. The importance of having a multi-step approach to the definition of sampling and characterization strategies for waste facilities recovery has been underlined in previous works (Dino et al., 2018; Nwalia et al., 2021). In this work, we present a novel approach to implementing a screening methodology suitable for background definition, sampling, characterization, mapping, treatment and recovery of valuable minerals from existing mining wastes in Italy. The procedure is proposed in order to achieve an efficient and reproducible method aimed at the potential recovery of valuable minerals according to theoretical and experimental data. In the first phase, the target site is individuated according to relevant information from official or governmental databases, scientific literature and industrial documents. In addition, already available topographic data can be considered to better confine the area of investigation. The collection of representative waste samples is planned by GIS tools according to standard procedures. The planning is designed for individuating accessible areas for operators and sampling representative portions of the target areas. Main mineralogical and chemical features are characterized using analytical multi-modal methodologies. Consequently, lab-scale mineral processing tests are performed in order to assay the technical potential recovery of target minerals dispersed in the waste material collected. The evaluation of tests is performed by calculating the final products' grade and separation yield of the proposed processing flow sheet. Data collected from laboratory testing are implemented in the GIS model in order to define the detailed mapping phase. A portable XRF mapping campaign and UAV-driven hyperspectral photogrammetry surveys are realized for the digital modelization of waste facilities. As a result, data obtained from remote sensing are matched with the ones coming from preliminary screening. The final model is drawn underlining the concentration of target elements and minerals highlighting the areas having a greater recovery potential. The development of this multi-modal and data-driven procedure for screening mining waste facilities' recovery potential will hopefully deliver a reliable tool for the recovery of SRM and CRM in Italy.

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## **The importance of surface porosity assessment to prevent and to protect ornamental stones from decay**

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*Keywords:* open porosity characterization, artificial ageing, image analysis.

The porosity assessment is strictly connected to the decay state of a stone. The amount of the percentage of void in volume have been strictly relate with stone durability since the end 19<sup>th</sup> century (Winkler, 1985) and, nowadays, the CE marking foresees the assessment of open porosity evaluation on the whole volume of the specimen (EN 1936, 2006) . The relationship between the percentage of porosity and the artificial decay performed in the laboratory, makes it possible to predict the durability of the ornamental stone in relation to the main external factors that influence the decrease in mechanical resistance (freeze-thaw, thermal shock, resistance to salt crystallization). Furthermore, the ability to predict the depth of decay can also provide information on the protection technique to be applied. For in situ analyzes the contact sponge technique can be used (UNI 11432, 2011) but this does not provide clear indications about the depth of decay.

From previous research, some marbles, after aging from thermal shock, are more affected by the increase in porosity with respect to freeze-thaw cycles and above all in the surface portions. For this reason, the evaluation of open porosity on thin sections of artificially aged marble suitably impregnated with dye can provide interesting information.

This research, using the result obtained on different kind of marble on dyed section , gives methodologies and correlation concerning the detection of porosity in the first superficial portion of specimen both in natural condition and artificial aged. The thin sections have been cut in different portion of the specimens parallel to the exposed surface and perpendicular to exposed surface.

Combining the proper cutting and dyed method to the image analysis, reliable information to the depth of the decay can be obtained. The results of two different Carrara marble will be presented and discussed enhancing the importance of this technique mainly in relation to the planning of proper protection treatments (consolidation).

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## **Zeolite synthesis and steam: preliminary data using coal fly ash as raw material**

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*Keywords:* coal fly ash, steam, zeolite.

Zeolites are natural and synthetic phases with a structure characterized by a frame-work of  $\text{SiO}_4$ - $\text{AlO}_4(\text{PO}_4)$  tetrahedra controlling the unique properties of these minerals (e.g. adsorption, catalytic activity, cation-exchange capacity). Literature data have documented the synthesis of zeolite using a wide range of sources, including many types of waste. Among these, coal fly ash (CFA) has largely used to form zeolite (Belviso, 2018). CFA is the combustion product obtained from burning coal in thermoelectric power plants and its increasing production has forced to find new ways to reduce the amount to be deposited on in landfill.

In our previous paper, vapor-phase crystallization method (VPC) was applied to form zeolite starting from natural bauxites (Belviso et al., 2022). Based on these previous successfully results, other tests were performed using a waste as raw material according to the 'circular economy' strategy also promoting the application of an eco-friendly method that eliminates the problems of liquid waste production. In detail, VPC method was used to form sodalite from coal fly ash. During the experiments, raw material was contacted only with steam from distilled water heated at 45, 60 and 90°C.

The data show that thanks to the steam action, thus without using liquid water, it is possible to transform a waste material (coal fly ash) into useful product (zeolite). The preliminary results indicated that VPC treatment controls the zeolite synthesis through an intermediate mechanism between solid-state transformation and hydrothermal synthesis (Dimitrov et al., 2011). The presence of water as liquid solution at 90°C, as a consequence of vapor saturation conditions, is confirmed by the presence of cancrinite. The growth of cancrinite, in fact, takes place from solution and not as result of solid-phase transformation.

Compared to other conventional methods for zeolite synthesis, the steam assisted process results in less liquid waste production.

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## Reuse of by-products coming from blasting of unstable rock blocks

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*Keywords:* by products, blasting, solid waste.

The improvement of safety conditions of unstable rock slopes can be achieved through the use of explosives, for the removal of unstable rock blocks. This technique is often applied because, most of time, drill and blast operations, where they can be used, are cheaper and faster than other techniques and require less subsequent maintenance interventions.

When the activity is performed in an area that can be reached by vehicles (quarry area, slope above a road, etc.) it is possible to recover the blasted material.

Depending on the size of the unstable element to be removed, this kind of operations often lead to the production of large quantities of blasted rocks, which most often ends up at landfill or is marginally reused in unqualified manner (construction of temporary tracks, filling voids left by extractive activity, etc.).

Reusing blasted rocks can offer several benefits: more sustainable engineering practices, economic, environmental and social benefits; in particular, this way of operating can preserve natural resources and prevent the production of unwanted waste. As a rule, on-site and nearby-site reuse is preferred to meet sustainable goals. Specific cases where blasted material has been adopted for both slope protection and final rehabilitation works, in a quarry area, can be mentioned.

Unfortunately, due to unclear legislation, lack of technical data and extreme variability of the materials produced (for instance quantity, size and physical properties), the reuse of blasted material is not common: It can be estimated that only 15-20% of these materials are currently reused properly.

To improve this practice, the type of reuse must be a design goal since the beginning of the planning phase.

According to the quality of the rock mass and the type of blasting, different by-products can be obtained, i.e. armour stones to be applied in hydraulic engineering works, gabion stones, drainage stones and crusher run as a mix of different types of aggregates, that can be employed as paver layer on road construction.

When ornamental stone quarries are involved, hard rock fragments are obtained for high mechanical performances.

The main purpose of blasting demolition of unstable rock elements, as mentioned, is to improve the safety conditions of the site, depending on local features, as well as by the safety of the workers, that can force the blasting scheme geometry and firing and impose important limitations on the operating techniques.

Two case studies will be presented, both in the northern Italy; they show how the blast design can be arranged to obtain different fragmentation and greater quantities of a specific by-product, according to the local needs and specific reuse.



## Critical raw materials supply: potentialities and challenges to exploit REE from granites' and gneisses' extractive waste facilities

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*Keywords:* extractive waste, feldspars, REE.

The growing demand for raw materials requires the optimization of extractive processes and innovative approaches, such as recovery of quarrying and processing waste. Waste materials from gneisses and granites (ranging from blocks up to residual sludge) used as dimension stones were characterized for chemistry, mineralogy, and texture. The investigated sites cover Piedmont Region, facing quarry waste facilities present in the two most important dimension stone quarry areas of the Region: Luserna Stone and Verbano Cusio Ossola (VCO) quarrying areas. In particular, the research focuses on granites (White Montorfano and Pink Baveno, VCO area) (Dino et al., 2020) and gneisses (Serizzi and Beole from VCO area and Luserna Stone) (Cavallo & Dino, 2022). Further to this, a short overview on REE associated to silicatic rocks will be presented, introducing some data about Monte Bracco quarrying area (in which ore deposits linked to quartzite and kaolinised gneisses can be recognised) (Dino et al., 2021).

In general, both for granites and gneisses, quartz and feldspars (plagioclase and K-feldspar) are the most abundant minerals, followed by micas (biotite and minor muscovite) and traces of chlorite and epidote (allanite) in gneisses and monazite in granites. Thanks to a proper treatment activity (grinding, screening and magnetic separation, which guarantees the removal of micas), these materials, present in past extractive waste facilities and in extractive waste coming from exploitation and working activities, could be used to produce quartz and feldspars for the industrial minerals sector (e.g. ceramics). The most critical issues connected to the exploitation of quartz/feldspars' concentrates is related often to the small grain size of the original rocks and to the relative abundance of mica in some commercial varieties (especially as for gneiss varieties). The presence of allanite in gneisses and of monazite in granites could open new possibilities for the recovery of REE (critical raw materials) during the treatment phase:

- quartz and feldspar concentrates for ceramic and glass industries
- magnetic concentrated to exploit REE.

After the first phase, connected to “waste” characterisation, the following activities will be linked to processing of the richest samples to exploit (at Laboratory level) REE, and to economic issues.

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## **Mining waste and tailings: examples of recovery and use for a sustainable approach to the management of extractive operations**

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*Keywords:* sustainable mining, EW recovery, circular economy.

Mining activities have produced and produce large amounts of extractive waste (EW) and tailings.

In recent years, the circular economic model has replaced the linear approach (based on “take-use-and-throw”): from this perspective even waste and extractive residues acquire importance through sustainable use and recovery.

Sustainable EW recovery consists of an approach that takes into account the positive impacts from a technological, economic, social and environmental perspective.

The recovery and use of EW takes place thanks to the development of new technologies, new professional figures with skills and abilities related to the sustainability of different activities and a marked reduction of the ecological footprint.

The use and recovery of EW occurs through the application and development of BAT (Best Available Techniques), a set of innovative protocols related to the exploitation of waste (sustainable and environmentally friendly). These new protocols aim at the technological and process improvement of operations and the production of renewed, high-performance green materials.

Mining waste and tailings, if suitably characterized, can be used to improve and make sustainable the works connected to the management of mining activities. Qualitative-quantitative characterization of EW is fundamental not only to define the areas of application but also to assess the extent of environmental impacts (e.g. dust, AMD, etc.) in the various matrices (water, air soils) and the risk to human health and the environment.

The typology of waste and mining tailings (physical, geochemical, petrographical and mineralogical characteristics), the morphological characteristics of deposits and the geological, geomorphological and logistical context of the site are crucial in defining application areas.

In this study, new technologies for the investigation and treatment of EW are presented as well as some examples of sustainable utilization of tailings and mining waste (e.g. waste for mining backfills, landfill waste/scrap recovered for RM/CRM mining, use of limestone tailings to reduce acid drainage and production of artificial substrates for environmental rehabilitation, etc.).

Positive impacts on the economic, environmental and technological/social level are also analysed.

The combination of all these actions, together with the adoption of appropriate financial instruments and energy saving, contribute to the transition of mining activities into “sustainable mining”.

## **Characterization of Chianocco Marble employed for Palazzo Madama façade in Turin (North-West Italy)**

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*Keywords:* ornamental stone, ancient marble, multidisciplinary approach.

The study of ancient marbles plays an important role in the interpretation of historical and archaeological sites and gives interesting information about building materials used in ancient times (Gambino et al., 2018) and their trade routes. This work focuses on Chianocco Marble that represents one of the most important ancient white marbles for cultural heritage exploited in the Piedmont region (North-West Italy) and employed for several historical building in Torino (NW Italy).

In particular, our attention was focused on the façade of Palazzo Madama, one of the most important historical monuments in Torino and a UNESCO World Heritage site, which has been recently the subject of archaeometric studies aimed at its next restoration. A detailed geo-architectural relief and minero-petrographic and isotopic studies were carried out comparing quarry samples coming from the historic sites of exploitation with selected fragments detached from the façade. The main results may be summarized as follows:

- the variety of ornamental stone used and their checked distribution on the façade were defined distinguishing the original stone materials from the ones used during historical restorations;
- the originally used material, the Chianocco Marble, is still the most abundant and the one which shows the greatest degradation;
- the minero-petrographic study of the Chianocco Marble and the comparison with the same material cropping out in the historical quarries shows that some features observed on Palazzo Madama façade such as a vacuolar structure and local reddening, usually absent in ornamental marbles, are primary features of the rock itself and are not due to degradation in an urban context. They are conversely related to the very complex geological evolution of the rock which started in the Triassic age as deposition of a carbonate sediment, evolved through Alpine metamorphism and deformation into a carbonate breccia, and finished with exposure at the surface where dissolution by meteoric waters generated the vacuolar structure. Only gypsum crystals grown in voids and the application of mortars in natural voids, enhancing the physical degradation of the stone, are due to pollution and human interventions.

This research highlights the importance of geological studies in conservation issues in cultural heritage by defining the characteristics of stone materials, and the reasons for their degradation (Lazzarini, 2004). In particular, this is true for local heritage stones which can be studied not only on the historical buildings but also in the provenance areas.

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## **Preliminary results on the characterization of zeolitized tuffs mining waste from Sorano Formation (Tuscany - Italy) for high-value technological applications**

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*Keywords:* zeolite, Sorano, Vulcini.

The Sorano Yellow Tuff is a pyroclastic formation of the Vulcini Volcanic District (Tuscany, Italy) and was widely exploited, mainly in the building sector, to produce dimension stones. This formation derives from syn- and post-depositional minerogenetic processes that lead to the formation of significant amount of zeolites (i.e., chabazite and phillipsite) (Cappelletti et al., 1999). The large amount of waste material deriving from this activity may represent an interesting resource to be used in different high-value technological applications such as, for example, lightweight aggregate production (de Gennaro et al., 2009), pozzolanic additive in cement production (Montesano et al., 2022), pharmaceutical carrier (Mercurio et al., 2018).

In order to evaluate the potential use of the Sorano Yellow Tuff for the abovementioned applications, a mineralogical and technological characterization of representative geological samples collected from Piandirena (Piandirena Zeolite Toscana) and Campimaglia (Campimaglia s.r.l.) quarries has been carried out by means of X-ray powder diffraction (XRPD) and fluorescence (XRF), polarized light microscopy (PLM), scanning electron microscopy and energy dispersive X-ray spectrometry (SEM/EDS), mercury intrusion porosimetry (MIP), simultaneous thermal analyses (STA), and Fourier Transform infrared spectroscopy (FTIR). Cation exchange capacity (CEC) and external one (ECEC) were also experimentally determined according to literature (Mercurio et al., 2018).

Zeolites in Sorano Yellow Tuff mainly consist of chabazite (ca. 56 wt.%), minor phillipsite (ca. 2 wt.%) and traces of analcime, as also confirmed by SEM/EDS. Low-ordered and amorphous phases range from 18 to 26 wt.%, whereas calcite is between 1 to 3 wt.%. PLM allowed to detect pyroxene, biotite, and feldspars as main phenocrysts whereas MIP analyses provided an open porosity of 43-39% and an average pore diameter of 156.9 nm and 199.6 nm for Campimaglia and Piandirena samples, respectively. CEC is ca. 2.0 mEq/g for Piandirena and ca. 2.3 mEq/g for Campimaglia. ECEC is ca. 0.06 mEq/g for both samples.

The examined geological materials demonstrate a good performance in the production of lightweight aggregates, showing proper physical and mechanical characteristics. At the same time, the Fratini test (for the evaluation of pozzolanic activity) made possible to plan future developments concerning the technical aspects related to the use of such additives, by evaluating mechanical resistance of the hardened blended cements during the hydration reactions. Lastly, surface charge reversion of the zeolites, confirmed by means of  $\zeta$ -potential measurements and obtained after sorption of cationic surfactant (i.e., cetylpyridinium chloride), allowed the uptake of non-steroidal anti-inflammatory drugs encouraging future developments in the technological characterization of this georesource for drug delivery and/or removal of emerging contaminants from wastewaters.

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## Sustaining heritage architecture with Basalt: exploring geomechanical and thermal properties

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*Keywords:* geomechanics, architecture, thermal properties.

The mining of basalt rocks in the vicinity of Lubań (Poland) has a rich industrial history dating back to 1905. However, the use of this local stone for constructing larger architectural objects, such as defensive walls and towers, can be traced back as early as the 14<sup>th</sup> century, highlighting the rock material's significance as a cultural heritage of the city.

Geomechanical studies have shed light on the valuable properties of the material and its natural features, which are important in architecture and construction (Pinińska, 1996). In conjunction with thermal testing, the material's historical utility and potential for future investments can be evaluated, not only in construction but also in the prospect of storing thermal energy (Mangold & Deschaintre, 2015).

For this purpose, comprehensive geomechanical studies of the Lubań basalts were carried out, analyzing their physical, acoustic (Yang et al., 2019), strength-deformation and thermal parameters (conductivity and heat capacity) in various temperature and water conditions. These tests reproduce the geoenvironment in which stone architectural structures are currently located in and illustrate the behavior of the rock material in conditions of road infrastructure, as well as the conditions in borehole heat exchangers.

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## The HerSTONES project: a step forward for the heritage stones recognition

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*Keywords:* scientific achievements, stone preservation, geoscientists.

HerSTONES (HERITAGE STONES RECOGNITION: A STEP FORWARD) moves the step from the already funded IGCP-637. In particular, the project Heritage stone designation funded in 2014 by IUGS-IGCP (Pereira, 2021) had the goal of firmly establishing the first international standard for building and ornamental stones via extensive documentation of those stones that have been significant in human culture with the following yearly general scientific achievements, facilitating the participation of young researchers in meetings and projects with research laboratories (which work on heritage stone characterisation and preservation using innovative instruments and techniques) and experienced stone conservation geoscientists. From 2016, 32 Heritage Stone designation have been reached (Ehling, 2023).

HerSTONES really started in 2021 with the workshop held in Turin in October where researchers had the opportunity to share results and research methods during workshop and conference, young and female researchers had the possibility to attend to scientific workshop and to publish their results in international journals. The partners involved with their coordinators are: Italy (Paola Marini), Italy (Giovanna A. Dino), Brazil (Nuria Castro), India (Gurmeet Kaur), Argentina (Leonor M. Trucco), Portugal (Jose Delgado), Colombia (Javier Becerra), Mozambique (Sandra R. Siteo).

The goal of the HerSTONES project are in compliance with the following SDGs: 11 Sustainable cities and communities, 10 Reduce inequalities, 17 Partnership for the goals. The monitoring and prevention of stone in Heritage sites and monuments is surely a contribution to make our city and communities sustainable.

Till now several activities have been carried out as financing the participation to 5 scientific meetings on heritage stones to 86 scientists (32 male) of 10 countries, where 31 under 35 years of age, 34 coming from developing countries. The project produced 26 publications covering a wide range of journals and online articles in both English and Portuguese.

The next important appointment will be in India from 1<sup>st</sup> to 6<sup>th</sup> of December 2023 with the III Workshop-cum-Seminar on natural stones and conservation of cultural heritage.

Ehling A. (2023) - IUGS Heritage Stone Designation – First Experiences. EGU General Assembly 2023, Vienna, Austria, 24-28 Apr 2023. EGU23-16123, <https://doi.org/10.5194/egusphere-egu23-16123>.

Pereira D. (2021) - Final report of IGCP-637: a Project Linking Researchers and Heritage Stones from around the World. Episodes, 44, 75-80. <https://doi.org/10.18814/epiiugs/2020/020086>.



## From waste to valuable resources: exploitation of mineral waste in environmental application

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*Keywords:* mineral waste, circular economy, technosols.

Mineral wastes coming from extractive industry and demolition activities (Construction and Demolition Waste – CDW), including rock and soil from excavations (RSE), represent the second and the first sources of waste production at the EU level (26.6% and 35.9% respectively). Although some of these waste products can cause environmental and economic problems if not adequately managed and disposed, they represent an alternative resource for civil, building, infrastructure and, focus of the present research, environmental applications.

This study introduces the state of the art of the research and applications of products arising from mineral waste, with a focus on new potential applications of fine fractions for artificial substrate production. The agronomic characteristics of the produced mixes were tested to evaluate their use and the environmental criticalities for land rehabilitation. The results showed that, when mixed with organic materials, the overall quality and fertility of the mineral waste fine fraction was improved, and that this mixture was not phytotoxic. This indicates that when properly managed and treated the mineral waste fine fraction could be effectively employed for land rehabilitation. In general, fine mineral waste fractions are valuable alternative materials for environmental applications. Sustainable and circular management of mineral waste contributes to guaranteeing raw materials supply, contemporary reducing environmental (including CO<sub>2</sub> production) impacts associated with waste management and landfilling. The potential decrement of environmental impacts and CO<sub>2</sub> production will contribute to enhancing the NET-zero greenhouse gas emissions EU strategy.

The production of technosol, mixing different minerals (extractive waste, CDW, RSE, topsoil) with organic compounds (shredded green materials, mature compost, bio-fertilizers) is in line with the circular economy paradigm. These materials represent the first source of wastes (in mass) in Europe and innovative processes for their efficient reutilization are needed. This research addressed the main problems connected with their management, focusing on some experimental processes, such as the production of artificial substrates (Dino et al., 2015), as a sustainable alternative to contrast the land consumption. However, the updating of the current legislation and the inclusion of these new products for public works (Green Procurement) is regarded as fundamental to the effective application of novel technologies.

Dino G.A., Passarella I. & Ajmone Marsan F. (2015) - Quarry rehabilitation employing treated residual sludge from dimension stone working plant. *Environ. Earth Sci.*, 73, 7157-7164. <https://doi.org/10.1007/s12665-014-3895-0>.

## The potential of eggshells to capture rare earth elements from waste waters

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*Keywords:* rare earth elements, circular economy, acidic mine drainage.

The European Union recently passed the European Critical Raw Materials Act (March 2023) which encourages the local production, processing, and recycling of critical elements. Among them are the rare earth elements (REE) which are indispensable to the green energy transition, one of the leading strategies to keep global warming as low as possible (Zhou et al., 2017). Acid mine drainage from sulfide and coal mines can contain up to 10,000s µg.L<sup>-1</sup> of REE (Jyothi et al., 2020) and thus have the potential to provide a sustainable and local source of REE.

REEs have an affinity for carbonates. Our group has previously demonstrated the crystallization pathways from calcite to rare earth hydroxycarbonates at low hydrothermal temperatures (Szucs et al., 2022). With AMD, carbonates can both neutralize the acidity and potentially capture and partition light and heavy rare earth elements.

In this study, we investigate the potential of biogenic carbonates, notably hen eggshells. Biogenic carbonates have a more complex chemistry, porosity and structure than inorganic carbonates, which could lead to increased sorption and/or partitioning (e.g., light vs heavy) capacity. We tested commercial eggshells at various experimental conditions (10-7,000 ppm La-Nd-Dy, 30-205°C, 3 hours to 3 months). The resulting products were characterized by 1) powder XRD and Rietveld refinement for quantitative phase identification; 2) laser ablation inductively coupled mass spectrometry for mapping out the diffusion patterns of REE in the not yet dissolved calcite; 3) SEM secondary electron imaging to characterize mineral habitats and 4) SEM-EDS with REE standards for quantitative elemental mapping of the rare earth carbonates.

We observe that REE preferentially diffuse along the eggshell internal discontinuities before crystallization occurs on the outer surface of the grains. Dissolution (of calcite)-recrystallization (of rare earth carbonate) occur along two replacement fronts progressing from both the external and internal surfaces of the eggshells. The crystallization pathway is temperature-dependent: calcite > lanthanite > kozoite > hydroxylbastnäsite. Spherulitic growth is prevalent at lower temperatures while prismatic rare earth carbonates are produced at higher temperature. Partial partitioning of La, Nd and Dy is observed at two spatial scales: 1) at the small scale of individual rare earth carbonate grains, where zoning create variation of +/- 10% of La and Dy; and 2) at the larger scale of the eggshell grains, where we observe a preferential uptake of Nd on the outer edges and of La in the internal part. The results points towards hen eggshells as potentially sustainable and effective REE sorbents that can both capture and partition light vs heavy REE.

Jyothi R.K., Thenepalli T., Ahn J.W., Parhi P.K., Chung K.W. & Lee J.-Y. (2020) - Review of rare earth elements recovery from secondary resources for clean energy technologies: Grand opportunities to create wealth from waste. *J Clean. Prod.*, 276, 1-26. <https://doi.org/10.1016/j.jclepro.2020.122048>.

Szucs A.M., Maddin M., Brien D., Guyett P.C. & Rodriguez-Blanco J.D. (2022) - Targeted crystallization of rare earth carbonate polymorphs at hydrothermal conditions via mineral replacement reactions. *Global Chall.*, 7(2), 220008. <https://doi.org/10.1002/gch2.202200085>.

Zhou B., Li Z. & Chen C. (2017) - Global potential of rare earth resources and rare earth demand from clean technologies. *Minerals*, 7(11), 1-14. <https://doi.org/10.3390/min7110203>.

## Sustainable management of resources in Small-Scale Mining

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*Keywords:* small scale mining, artisanal mining, underground gold exploitation.

Integrating small-scale mining into an active and sustainable system of mineral resource exploitation is a major challenge facing the industry today. Small-Scale Mining (SSM) comprises mining activities with low production rates, capital expenditure, and revenues. Artisanal Mining (AM) is just a subset of SSM, characterized by rudimentary mechanization, inefficient recovery, unsafe working conditions, and labor exploitation, which defies the principles of sustainability.

A distinction must be made between artisanal mines and artisanal processing plants. Most of the environmental damage attributed to artisanal mining originates from treatment facilities, due to the employment of hazardous chemicals, such as mercury and cyanide. As a result, the mine itself represents a low source of large-scale environmental hazards. Hazards associated with the environment are related to water, air, land system, and waste. Basic indicators must include the destination of outflow water, whilst any suspicion of acid drainage should also be checked, as should the diffusion of dust, smoke, and fumes outside the mine. Waste disposal is always neglected by artisanal miners; evidence of rock fall hazard and acid drainage from the waste material must therefore be investigated, especially if directed towards the third-party property. The lack of methodology creates the highest levels of uncertainty, hence a lack of credibility and a negative image for investors. A vicious circle is automatically triggered, which is a quite common situation among SSM operators.

Sustainable mining requires cost-efficient practices. To achieve favorable conditions for investment, a novel approach to the management of mineral resources must be found.

A methodology is proposed using some performance indicators; it considers that SSM is characterized by quick installation, rapid payback, and high flexibility, and uses these aspects as keystones. The methodology was applied to an actual underground gold mining operation in Ecuador and proved that the reserves required for a small-scale operation are much less than those required for large-scale mining when both businesses own the same level of feasibility.

## 12 stones for 12 months: the project for the promotion of the stones of Bergamo

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*Keywords:* dimension stones, promotion, local stones, mark.

In 2003, the Chamber of Commerce of Bergamo created the “Pietre Originale di Bergamo” collective mark to promote the stones quarried in the Bergamo area, which are geologically and genetically unique.

The Chamber of Commerce of Bergamo, as part of its mission to support the competitiveness of the area, offers concrete services to the companies of the province and, in this regard, also carries out promotional activities in support of the “Pietre originali della bergamasca” collective mark, its operators and the entire industry chain.

In order to increase the knowledge and visibility of the brand and to increase the awareness of the brand throughout Bergamo, it was decided to create a broad, massive and capillary communication path.

The creation of the 2023 calendar offers the opportunity to reach the greatest number of people in the county and, more importantly, to increase knowledge of the brand among citizens and professionals in the field.

To carry out this territorial marketing activity in support of the brand in question, it is considered effective to use the L’Eco di Bergamo channel, given its large user/subscriber/reader catchment area, by producing the 2023 calendar dedicated to the twelve stones of the “Pietre originali della bergamasca” mark.

The project consists of:

- printing 40,000 copies of the calendar;
- A communication plan to be carried out by means of:
  - The publication of 12 web articles on [Eppen.it](http://Eppen.it) with a related organic social campaign on Eppen’s channels. Eppen is the new portal dedicated to culture and leisure in Bergamo and its province. A detailed calendar of events in the fields of art, cinema, music, theatre, sport, outdoor activities, food & wine, family, festivals and fairs. And a web magazine with in-depth articles, interviews, mini-guides, photo galleries and videos on a daily basis. Total daily web unique users: 12.500 (Eppen) + 240.000 (L’Eco di Bergamo);
  - The publication of 12 articles in the local daily newspaper “L’Eco di Bergamo”. Total daily readers: 360.000 (paper), 240.000 (web, unique users);
  - An ADV organic social campaign in the newspaper and Eppen websites with monthly advertising spaces. L’Eco di Bergamo: 170.000 FB followers, 70.000 IG followers; Eppen: 20.000 FB followers, 4.000 IG followers;
  - The publication of 4 articles in ARK magazine. Ark is a quarterly magazine that describes the most significant landscapes and architecture of Lombardy in the 20th century and today. Ark is dedicated to Bergamo and its province, but also to Lombardy, whose exceptional works it illustrates, loved by those who care as much about places as they do about research and design culture. Ark is a multidisciplinary magazine in which scholars, including architects, sociologists, anthropologists, photographers and historians, discuss and analyse a specific theme from different angles. Ark talks about architecture, materials and furniture, photography and landscapes, natural or man-made, through the experiential gaze of a participating observer. The magazine is distributed to most designers in Lombardy (5.000 copies);
- guided lithological itineraries to discover the geology of the land and the built environment (estimated participants: 500).

Through all these actions, this project aims to a very inclusive and wide-spread communication and promotion of the values, history, characteristics, identity, and heritage of local dimension stones.

## From nature to nature. Vegetable fibers replace cement

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*Keywords:* stone paving, circular economy, grouting mortar, re-used vegetable fibers.

Designers, citizens and administrators have been paying more and more attention to the quality of landscape and urban open spaces design, also following the pandemic and related lockdowns. This new sensitivity adds further awareness to the issues of sustainability, circular economy and, for outdoor paving, of de-paving.

In the context of the European provisions aimed to sustainability in the construction and redevelopment sector, including the European Green Deal, Green Public Procurement and Bringing nature back into our lives, the availability of highly sustainable products is increasingly becoming one of the key-requirements either for new construction, refurbishing and conservation of historical buildings and archaeological sites.

Plant fibres are a renewable and environmentally friendly resource, especially as they are often available as recycled waste from other production processes. They are being investigated in some countries as they could also be an interesting, much cheaper alternative to cement.

Consequently, much research has been carried out to characterise the performance of cement or lime-based mortars reinforced with plant fibres. These are often mortars for structural use.

Coconut, sisal, jute, hibiscus cannabinus, eucalyptus grandis pulp, mallow, ramie raffia, pineapple leaf, kenaf raffia, sansevieria leaf, abaca leaf, vakka, date, bamboo, palm, banana, hemp, linen, cotton and sugar cane fibres are among the natural fibres used for this purpose.

With a view to formulating a pre-mixed mortar for grouting architectural paving, therefore not for structural purposes, but with very limited emissions, it was decided to proceed along a path little travelled in literature.

This involved eliminating hydraulic binders, i.e. lime and cement, and combining the mineral raw materials with vegetable fibres of various types, favouring those from recycled sources.

About 20 different formulations have therefore been developed, characterised and evaluated, both from a technical performance point of view and from a physical application point of view. Workability and ease of use on site depend on this.

The formulation named MAPESTONE GR-ECO, a combination of GREEN and ECO, proved to be the best combination of performance and workability. It consists of mineral aggregates (about 85-88%, with an average particle size of about 2 mm)(about 10%) and the remaining 3-4% of recycled cellulose plant fibres with an average particle size of about 500 microns and apple fibres from apple juice production with an average particle size of less than 50 microns, which act as a thickener, thanks to the pectin, and as a binder.

Thanks to the research and selection of materials recovered from other industrial processes, a premixed mortar free from cement and lime and based on mineral aggregates and re-used vegetable fibers was developed, to be used as grouting for pedestrian and low traffic architectural paving.

Durability tests (weathering cycles) and environmental profile have been performed with successful results. Test results show that the vegetable fiber mortar is weathering resistant and that, compared to a traditional cement grout, its CO<sub>2</sub> emissions are reduced by 95%.

## Residual sludge from Carrara marble exploitation: characterization, challenges and potentialities

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*Keywords:* ornamental stone, waste reducing, sustainability.

In Italy, in 2011, the total turnover of the production chain linked to the extractive activities (quarries, processing, shops, etc.) represents about €40 billion (almost 2% of the Italian Gross Domestic Product). Furthermore, the exploitation of Italian ornamental stones during 2012 shows an increase in exports of 9.8% compared to 2011 and a decrease in imports of -6% (Dino et al., 2017). The modernization of excavation methodologies and planned management of quarries and associated landfills, however, have not completely solved the problem concerning the management and disposal of waste. Among the most emblematic cases in the Italian panorama is the Carrara marble quarry basin, which is represented by a hundred quarries that cultivate different types of marble and waste production about 80 Mm<sup>3</sup> of waste present in the old quarry landfills (“ravaneti”) and 3 Mm<sup>3</sup>/year of waste from actual mining activities (like sawdust sludge, known as “marmettola”), with only 0.5 Mm<sup>3</sup>/y of EW is exploited for secondary raw materials production (Vagnon et al., 2020). The economic difficulties faced by the Italian stone sector, closely linked to the increasing presence on national and international markets of products and producers from countries such as China, India and Brazil, means that, in order to envisage a recovery in the sector, it is necessary to consider the integral use of the extracted resource, trying to value most of those wastes, which currently represents only a liability item on the companies’ annual financial report.

The present research aims to increase knowledge about the exploitation potential of the fine marble sludges produced in the Carrara quarry basin. The work was divided into two phases: an initial sampling of the materials of interest (produced both in the quarry and in the processing plants), followed by analytical work, both geotechnical (grain-size, Atterberg tests), and mineralogical (XRD). In parallel, specific leaching-tests, in accordance with Italian legislation, were conducted on the marble powders, to evaluate their characteristics and possible contamination. The obtained results have provided further useful indications and shown promising data regarding the waste produced by the sawing and processing of stone stones in the Carrara area (MS), such as evident size homogeneity (silt), with very few clay particles, the non-plasticity of the materials, the predominantly carbonate mineralogical composition (>90%) and the absence, in principle, of potentially polluting substances. These characteristics could prove to be favorable for a possible reuse of the materials, in line with the circular economy approach.

Dino G.A., Chiappino C., Rossetti P., Franchi A. & Baccioli G. (2017) - Extractive waste management: A new territorial and industrial approach in Carrara quarry basin. Italian Journal of Engineering Geology and Environment. <https://doi.org/10.4408/IJEGE.2017-02.S-05>.

Vagnon F., Dino G.A., Umili G., Cardu M. & Ferrero A. (2020) - New developments for sustainable exploitation of ornamental stone in Carrara basin. Sustainability, 12, 9374. <https://doi.org/10.20944/preprints202010.0642.v1>.



## Multi-scale analysis on soil improved by alkali activated fly ashes

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*Keywords:* soil improvement, alkali activated fly ashes, multi-scale analysis.

The development of soil treatment techniques using alkali-activated binders is a relevant issue since the increasing interest into the use of new and environmentally friendly binders as an alternative solution for geotechnical engineering applications, such as soil improvement.

Alkali activated binders are formed by alkaline activation of an aluminosilicate source, containing precursor materials like fly ash, silica fume, steel sludge, which chemically react with an alkaline solution (i.e. sodium hydroxide, sodium silicate) forming a three-dimensional aluminosilicate gel with cementitious properties (Duxon et al., 2007; Provis & van Deventer, 2014). Recycling of waste materials such as by-product from industrial process to synthesize a new binder favors a closed loop of material use, which minimizes the generation of waste and reduces the costs of production. Alkali activated binders represent a viable sustainable alternative to the use of ordinary binders for soil improvement (Vitale et al., 2017a; Vitale et al., 2017b).

In the present study, an insight into the mechanical improvement induced by alkali-activated binders based on the activation of two different type of fly ashes on a clayey soil has been presented. An experimental multiscale analysis on chemo-physical evolution of the systems and its influence on microstructural features of treated soil has been developed highlighting the link between alkaline activation processes and macroscopic evolution of soil properties. Mechanical tests have been performed and interpreted taking into account the chemo-physical evolution of alkali activated fly ashes. Effects of binder content and curing time have been also considered. Addition of alkali-activated binders increases shear strength of the treated samples since the very short term. A reduction of compressibility and an increase of yield stress of treated samples have been also detected, whose extent depends on the curing time and on the binder content. Macroscopic behaviour of treated soil has been linked to the experimental evidences at microscale. Mineralogical and fabric changes induced by alkali-activated binders have been monitored over time by means of X ray diffraction (XRD), thermogravimetric analysis, <sup>29</sup>Si NMR spectroscopy and Mercury Intrusion Porosimetry (MIP). Test results showed a high reactivity of alkali activated fly ashes as alumino-silicate source promoting precipitation of new mineralogical phase forming chains and networks with cementitious properties, responsible of the mechanical improvement of the treated soil. The efficiency of treatment has been also highlighted by comparing the mechanical performance induced by alkali-activated binder with the one promoted by ordinary Portland cement.

Duxon P., Fernández-Jiménez A., Provis J.L., Lukey G.C., Palomo A. & van Deventer J.S.J (2007) - Geopolymer Technology: The Current State of the Art. *J. Mater. Sci.* 42, 9, 2917-2933.

Provis J.L. & van Deventer J.S.J (2014) - Alkali Activated Materials. Volume 13: RILEM State of the Art Reports. Springer Netherlands.

Vitale E., Coudert E., Deneele D., Paris M. & Russo G. (2017a) - Multiscale analysis on a kaolin improved by an alkali-activated binder. Proceedings of the 2<sup>nd</sup> Symposium on Coupled Phenomena in Environmental Geotechnics (CPEG2), Leeds, UK.

Vitale E., Russo G., Dell'Agli G., Ferone C. & Bartolomeo C. (2017b) - Mechanical behaviour of soil improved by alkali activated binders. *Environments*, 4, 80. <https://doi.org/10.3390/environments4040080>.

**S17.**

**From waste to resource: the contribution of mineralogy  
to past and present waste management**

*CONVENERS AND CHAIRPERSONS*

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## **Testing the new Hypercolorimetric Multispectral Imaging method to understand pigment technology in ancient ceramics: the Graffita ware from Moliterno Castle (Basilicata region, southern Italy) case study**

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*Keywords:* multispectral imaging, archaeometry, medieval ceramics.

Diagnostics applied to Cultural Heritage has developed exponentially over the years. Among the most important portable, non-invasive, and non-destructive diagnostic analyses there are multispectral surveys. The new multispectral imaging system, named Hypercolorimetric Multispectral Imaging (HMI), developed by Profilocolore (Laureti et al., 2019; Colantonio et al., 2021), is a non-invasive, rapid, and diagnostic technique that allows in-situ accurate and reproducible spectral reflectance measurements (between 300 nm and 1000 nm) to obtain seven monochromatic very high-resolution images. HMI analysis is based on the simultaneous exploitation of the UVA to NIR bands and can characterize surfaces in a more detailed way than using the standard colorimetry. The main feature of the system includes speed of execution, speed of calibration, radiometric and colorimetric accuracy, great wealth of analysis functions, and integration with other analysis tools and technologies. HMI is applicable in any context and on any type of artifact. In fact, the instrumentation, easily transportable and equipped with batteries that make it energy self-sufficient, allows data acquisition in any operating condition. The results obtained in a short time and with ease provide a vast amount of scientific information and measurements, in a precise and repeatable manner over time.

To date, the technology has never been applied in ancient ceramic studies. To further exploit the great potentials of HMI, its application in understanding pigment technology in medieval ceramics was tested. An innovative integrated analysis that combines HMI with Micro X-ray fluorescence, micro-RAMAN spectroscopy, and X-ray diffraction (PDXRD e  $\mu$ -XRD) data is proposed for the identification of the compositional characteristics of glazes and decorations in the Graffita ware from Moliterno Castle (Basilicata region, southern Italy) attested at the 14<sup>th</sup> and 15<sup>th</sup> centuries (with the Courtesy of the Superintendence of Basilicata) (Annunziata, 2022; Annunziata et al., 2022). The technique of graffito ware has a remote eastern origin; transmitted from China to Persia in the 9<sup>th</sup>-10<sup>th</sup> centuries, it then moved from there to the Mesopotamian and Syrian areas, and finally to the Byzantine empire. Glazed Graffita ware is generally characterized by a production process consisting of distinct stages: engobing, scratching, first firing, coloring, glazing, and second firing. Indeed, we strongly believe that such a complete piece of information is strongly needed to be used as an alluring source of information on technological know-how, production areas, and commercial relations as well as on commissioning and export/import, economic level, and social habits. Achieving this information involves a very complex job which, to be performed, requires the crossing investigation between classification, purely technological aspects, and diagnostic items: the analysis of pigments, both in ceramic glazes and/or decorations implies indeed a great complexity.

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## Understanding the effect of iron in porcelain stoneware tiles: can red clays represent a viable alternative raw material?

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*Keywords:* ceramic, local raw materials, Rietveld method.

The largest industrial district of the Italian tile production is located in the Sassuolo area where, starting from 90's, the conversion of production into porcelain stoneware induced a shift from local resources to imported raw materials. In Italy, before 2022, a third of ball clays (40% of the employed raw materials) was imported from Donetsk basin, in Ukraine. The recent geopolitical upheaval poses serious questions on the supply chains for the ceramic production, stressing how the supply on alternative chain is strategic and vital for the ceramic sector.

In the current geopolitical scenario a partial return to local resources, alongside favoring the tendency toward a circular economy, can represent an option to reduce the import reliance.

Regarding the characterization of raw material deposits located near Sassuolo district, the literature data were mainly obtained by qualitative mineralogical analysis coupled with chemical data, which provide a semi-quantitative mineralogical analysis, while accurate quantitative phase analysis and detailed testing are missing.

In this work, we present the full characterization of two red clays deriving from quarries located near the Sassuolo ceramic district. These red clays are iron-rich (~7% Fe<sub>2</sub>O<sub>3</sub>), thus compounding well-known issues in the ceramic tiles production. The features of these samples were compared with those of a German ball clay containing rather high levels of iron (~3% Fe<sub>2</sub>O<sub>3</sub>). The employed analytical techniques are X-ray diffraction with Rietveld analysis, X-ray fluorescence, and thermogravimetric analyses. In this project, we tested the effects of a partial substitution of Ukrainian ball clay body (used as benchmark) with the most suitable Italian red clay and the German ball clay into a standard batch for porcelain stoneware. The obtained bodies were fully characterized from milling to firing. The amount of the novel raw materials added to the batches were carefully chosen to evaluate the effect of the iron on the technological properties of the semifinished and finished products.

Results demonstrated that the substitution of the classic Ukrainian ball clays with the Italian and German clays do not introduce any bottleneck in the ceramic production. The addition of the German ball clay resulted in a slight increase of the sintering temperature (compared to the benchmark), possibly related to the higher quartz content of this raw material. Conversely, the addition of Italian red clay induced a reduction in the firing temperature (compared to the benchmark), possibly related to the higher content of iron as well as of feldspars. The most significant variations are in the color of the tiles, which results darker (compared to the benchmark) in all the tested bodies, for the presence of iron.

## White steel slags as alkaline activator for hydraulic binders with heavy metal adsorption capabilities

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*Keywords:* white steel slags, hydraulic binders, metal adsorption capabilities.

Alkali-activated materials (AAMs) are generally known as low-CO<sub>2</sub> binders alternative to Portland cement in construction (Provis, 2014). AAMs also constitute an important tool in promoting circular economy, since they offer the possibility to convert many inorganic wastes into useful products (Mehta & Siddique, 2016). Many different aluminosilicates can be used as precursors for the preparation of AAMs, one group of highly reactive materials being ground and granulated blast furnace slag (GGBS). Although per se blast furnace slag is a byproduct of pig iron production, GGBS is an engineered material with controlled composition and structure, highly demanded by the construction industry because of its reactivity. Several alkaline activators may be used in combination with GGBS: alkaline silicates, sodium carbonate or sulphate and calcium aluminates. Calcium aluminates represent an interesting group of activators, resulting in peculiar properties of for the hardened AAMs. The hydration products of these AAMs are constituted mainly by ettringite, AFm and C-(A)-S-H, that are well-known for their capability to effectively adsorb heavy metals (Liu Y. et al., 2022). Ladle white steel slag, a byproduct of Al-killed steel production, can be effectively used as a source of calcium aluminates for GGBS activation. Contrary to GGBS, white steel slag to date has no useful application and it is entirely landfilled.

This study explores the use AAM from GGBD activated with ladle white steel slags as adsorbers for the treatments of heavy metals contaminated waters (Latorrata et al., 2021). The adsorbing material is prepared by granulation, on a granulating plate where water is slowly added to the AAM powder blended with 50% monodispersed quartz sand, to obtain granules with high porosity and water permeability. The structure of the granules suggests that the formation occurs through a surface-layering mechanism. The compressive strength of the mortar at 7 days of curing, measured on 15x15x60 mm<sup>3</sup> prisms, is 4.8±1.0 MPa. The contacting between the granules and the liquid is performed in batch mode, in a stirred tank where the granules are supported by a plastic wired mesh, with a liquid/solid volumetric ratio of 8. The granules have been used for treatment of two discharge waters from galvanic treatment, one from Zn deposition and the other from Cr deposition, and of a surface water rich in As. In all cases the final metal concentration is below the limits for discharge in surface waters (D.L. 152/06 attachment 5), decreasing from 94000 to 0.033 mg/l Zn, from 12 to 0.075 Cr and from 6.4 to 0.15 As.

As a conclusion AAMs manufactured from metallurgical byproducts, blast furnace slag and ladle white steel slag, have been proven effective in heavy metal capture from discharge water and from contaminated surface waters, opening the way to valorization of industrial byproducts in safeguarding the environment.

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Mehta A. & Siddique R. (2016) - An overview of geopolymers derived from industrial by-products. *Constr. Build. Mater.*, 127, 183-198.

Provis J.L. (2014) - Introduction and scope. In: Provis J.L. & Van Deventer J.S.J. (eds.). *Alkali activated materials, state-of-the-art report*, RILEM TC 224-AAM. Springer, Dordrech, 1-9.

## Zeolite synthesis from natural bauxite by low-temperature vapor phase treatment

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Keywords: bauxite, zeolite A, vapor-phase crystallization method.

Bauxites are aluminum deposits formed as results of aluminosilicates rocks weathering under warm, humid, tropical-to-subtropical climate conditions. The chemical and mineralogical composition, mainly characterized by the presence of boehmite and kaolinite, makes these rocks as natural sources of Si and Al and therefore as inexpensive raw materials for the zeolite synthesis. Several patents and literature data have in fact documented the zeolite formation by mixtures of bauxite and kaolinite or waste (e.g. rice husk) (Zhu et al., 2011; Zhang et al., 2020). Many more papers have documented zeolite synthesis from waste bauxite products (red mud or bauxite tailings) (Belviso et al., 2018).

In this work, three samples of bauxite were used as natural raw material for the zeolite formation by a green process based on vapor-phase crystallization (VPC) method without the addition of pure chemical components or other sources but only exploiting the chemical composition of the natural raw materials. In detail, the synthesis was carried out using a water bath with deionized water heated at 35, 45, 60 or 90°C. During the process, NaOH pre-fused bauxites were contacted only with vapor from the liquid.

The results display that zeolite formed in all the samples. The data indicate that the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio, the competitive presence of geopolymers vs glass in amorphous materials and the general lower amount of water molecules, control the synthesis of zeolite with LTA topology during VPC at low temperature (35 and 45°C). The larger amount of water by vapor crystallization treatment at higher temperature (60 and 90°C) determines, instead, the formation of more stable sodalite with typical well-defined rose-like. The zeolite crystallization mechanism at lower temperature takes place essentially through a solid-state transformation process of geopolymers into well-defined crystals whereas the processes at higher temperatures can be approximate to a hydrothermal process improving geopolymers transformation. This is in accordance with literature (Dimitrov et al., 2011) describing VPC method as an intermediate mechanism between solid-state transformation and hydrothermal synthesis.

Besides the mechanisms determining the type of zeolite crystallization, the results shown in our experiments indicate that the vapor phase crystallization process represents a green and economic method to form zeolite reducing the amount of water and, most important think, generating no liquid waste generally produced by conventional hydrothermal method.

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- Zhang Q., You W., Ma Y. & Wang S. (2020) - Rice husk assisted like-dry-gel synthesis of FeSAPO-44 molecular sieve from natural bauxite. *J. Solid State Chem.*, 291, 121662.
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## **Fireclay-ceramics industry: technological properties and mineralogy by tuning slip composition and raw materials (waste included) particle size distribution**

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*Keywords:* ceramic waste, ceramic reactions, technological properties.

In the sanitary-ware field, Fireclay (FC) technology represents an alternative to the more common Vitreous China (VC) due to its peculiarities that made it an excellent candidate to design large pieces like sinks and shower trays (Kingerly et al., 1976).

FC slip is made of a plastic component plus filler, typically chamotte, whose cost and supplying chain are problematic. Moreover, FC/VC industrial wastes (named FC and VC pitcher) are becoming large in volumes with related waste management criticities.

For a more sustainable production, the FC body behavior as a function of chamotte and both VC/FC pitchers is investigated. In particular, two different chamotte and VC pitcher particle size distributions (i.e. 250 and 75  $\mu\text{m}$ ) are considered as well as the partial replacement of chamotte with FC pitcher and nepheline.

Both technological (water absorption, shrinkage and thermal expansion) and mineralogical analyses (XRPD-QPA and SEM) are performed for a better comprehension of the occurring phase reactions.

The reduction of VC pitcher and chamotte particle size increases the greification and the body's  $\alpha_L$  linear thermal expansion coefficient, respectively. Nepheline is a very powerful action to decrease the water absorption as it promotes glass at the expense of the other crystalline phases (especially cristobalite), with consequent  $\alpha_L$  reduction. FC pitcher can partially replace chamotte, being a source of cristobalite upon firing, thus providing a way to increase the body's  $\alpha_L$ .

These results show that ceramic wastes represent a resource that is worth to introduce in the FC production, either for a conservative porous body or for a new ceramic, more compact and less expansive.

Kingerly W.D., Bowen H.K. & Uhlmann D.R. (1976) - Introduction to Ceramics, Wiley.

## **Investigation of iron-based pigments using infrared spectroscopy and chemometrics as guidance in a multi-analytical approach: the case of Røros (Norway)**

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*Keywords:* ochres, FTIR spectroscopy, PCA.

Iron oxides and hydroxides-based pigments have been extensively used for artistic purposes throughout the ages and all over the world. Ochres are iron-rich natural deposits with colors ranging from bright red, to yellow, to brown. In this work, a series of 16 iron-based dry pigments, both commercial and natural ochres, have been investigated with the multiple aims of characterizing the materials and evaluating the validity of the proposed methodological approach. In detail, the natural materials come from the Røros district in Norway, where they were widely applied for painting the wooden houses' facades and interiors. They belong to a UNESCO World Heritage site, from whose conservation intervention the analyzed pigments were taken.

A multi-analytical approach was employed, but special emphasis was given to infrared spectroscopy in multiple spectral ranges and configurations (attenuated total reflectance mid and far infrared: ATR-MIR and ATR-FIR, and diffuse reflectance infrared Fourier transform spectroscopy: DRIFTS). A multivariate statistical analysis such as principal components analysis (PCA) was applied to interpret the infrared data and was useful to understand the data resulting from the other techniques, too.

This combined approach of infrared spectroscopy and chemometrics proved pivotal in the distinction of groups of samples on the basis of their molecular composition. The comparison with the results of the other analyses (colorimetry, X-ray fluorescence (XRF), X-ray diffraction (XRD) and Raman spectroscopy) confirmed that IR and statistical results could be used as a guide to obtain a thorough and consistent description of the samples. Furthermore, the results are particularly important in the framework of the conservation works of Røros houses, starting to build a database of the ochre pigments used in the past in this area.

## Understanding the pigment technology of the matt painted pottery from the north-Lucanian district: the SandDMAN project

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*Keywords:* pigment technology, matt painted, north-Lucanian district.

By having a new approach to the study of the matt painted pottery decorations - which is based on the consideration that this ceramic represents both an instrument of cultural identity conservation and a tool for dissemination of cultural messages among the indigenous communities of southern Italy - the SandDMAN project involves the interaction of data and results obtained from the analysis of archaeological, archaeometric, anthropological, ethnographical, and semiotic aspects. The matt painted pottery productions from the north-Lucanian district present differences in their ceramic styles but are connected by substantial cultural similarities. The analysed potteries come from the archeological site of Potenza, Baragiano, Ruvo del Monte, Oppido Lucano, Serra di Vaglio and Ripacandida sites and several potsherds were selected to understand the pottery productions and to depict the workshops. In the present study, technological aspects will be drawn from the analysis of black, red, and brown pigments carried out using micro-RAMAN spectroscopy (micro-RAMAN) and powder X Ray Diffraction (PWXRD).

The brown pigmented surfaces of the pottery contain amorphous carbon (black carbon), hematite, magnetite, titanium oxides (anatase or rutile) and calcite. The amorphous carbon shows a characteristic peak at 1397 cm<sup>-1</sup> (D-band of black carbon), characteristic peaks at 1319 cm<sup>-1</sup> (this peak could also be attributed to hematite) and 1567 cm<sup>-1</sup> (G-band of black carbon) for sample. The lack of a Raman band at 960 cm<sup>-1</sup>, related to phosphates from charred bones indicated that the carbon used is derived originally from charred plant material (Goodall et al., 2009). Hematite and magnetite reveal their presence from Raman spectroscopy and XRD.

The red pigment contains amorphous carbon, as indicated from several peaks in the 2000-800 cm<sup>-1</sup> region. The desirable red colour of the pottery slips could be obtained by firing an iron-rich clay in an oxidizing atmosphere, which could cause the oxidation of iron (Striova et al., 2006). The higher intensity of the 297-299 cm<sup>-1</sup> Raman band of hematite and its intense XRD peak on sample from Baragiano could be due to the use of a more crystalline phase of hematite when comparing to hematite from all other potsherds from other sites (Goodall et al., 2009). Under reducing conditions hematite is converted to magnetite between 650°C and 900°C and magnetite would remain stable and produce a black pigment (Goodall et al., 2009). The fact that magnetite is not always evident on all the brown surfaces of the studied potsherds might be due to the high fluorescence background observed, which tends to mask the magnetite bands (Goodall et al., 2009). In summary, the presence or absence of magnetite on the brown and red coloured surfaces of the potsherds does not necessarily suggest different raw material used for pigments, but rather a single component (ochre/hematite) applied to coat the pots and different sintering temperatures and/or kiln atmospheres used to achieve the final colour (Colomban et al., 2004; Smith & Clark, 2004), and therefore allow to hypothesize different workshops in matt painted production.

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Goodall R.A., Hall J., Viel R. & Fredericks P.M. (2009) - A spectroscopic investigation of pigment and ceramic samples from Copán, Honduras. *Archaeometry*, 51, 95-109.

Smith G.D. & Clark R.J.H. (2004) - Raman microscopy in archaeological science. *J. Archaeol. Sci.*, 31, 1137-1160.

Striova J., Lofrumento C., Zoppi A. & Castellucci E.M. (2006) - Prehistoric Anasazi ceramics studied by micro-Raman spectroscopy. *J. Raman Spectrosc.*, 37, 1139-1145.

## Recycling detoxified cement asbestos in cement mortar and concrete

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*Keywords:* asbestos containing materials, cement and concrete, recycling.

Asbestos containing materials (ACMs), although no longer produced, are still abundant in buildings and in the environment and represents a health hazard. Their disposal requires a smarter solution than currently adopted landfilling, and aligned with current policy of circular economy, i.e. detoxification and reuse. With this premise, we explored the production of cement mortar and concrete by adding ACM thermally treated at 1100°C with two different methods: (1) in standard oxidizing conditions (Vergani et al., 2022), henceforth “R” for its reddish colour, and (2) with an innovative, energy sustainable patent (Marian et al., 2021), henceforth “G” for its greenish colour.

The recycling of ACM in the production of cement mortars was explored adding respectively 4 and 7 wt.% of thermally treated ACM in a pre-mixed mortar used in traditional plasters. We determined compressive and flexural strength on both R and G samples after hardening time of up to 90 days and performed durability tests on R samples along a time span of 25 weeks, during which the test samples were subjected to wetting-drying cycles and temperature (20-80°C) cycles.

Our results reveal that the addition 4-7 wt.% of thermally treated ACM to the pre-mixed mortar does not affect neither the most important technical properties of the mixture (such as thixotropy, viscosity, water demand), nor compressive and flexural strength after hardening, which are preserved also after repeated temperature and wetting/drying cycles for 25 weeks.

We also added 20 wt.% of thermally treated ACM to a concrete mixture (quartz sand + CEM I 52.5 R). The mechanical properties were evaluated after a hardening time of 24h at 85°C (quick test) and after a hardening time of 28 days in saturated water conditions at room temperature. Samples at 85°C show flexural strength properties extremely similar to those of standard concrete (-3% and -9% for R and G, respectively), while compressive strength properties show a decrease of -36% e -40%, respectively. Samples at room temperature show an increase of flexural strength properties of ~20% in both R and G, while compressive strength properties show a decrease of -23% e -44%, respectively.

Overall, these data seem to indicate that the addition of deactivated cement asbestos to mortar for plaster application with loads within 7 wt.% is very promising, whereas loads as high as 20 wt.% in concrete mixtures increase the flexural strength of the product but decreases the compressive strength. Moreover, R seems to perform better than G.

Marian N.M., Giorgetti G., Magrini C., Capitani G.C., Galimberti L., Cavallo A, Salvini R, Vanneschi C. & Viti C. (2021) - From hazardous asbestos containing wastes (ACW) to new secondary raw material through a new sustainable inertization process: a multimethodological mineralogical study. *J. Hazard Mater.*, 413, 125419. <https://doi.org/10.1016/j.jhazmat.2021.125419>.

Vergani F., Galimberti L., Marian N.M., Giorgetti G., Viti C. & Capitani G.C. (2021) - Thermal decomposition of cement-asbestos at 1100°C: how much “safe” is “safe”? *J. Mater. Cycles Waste*, 24, 297-310. <https://doi.org/10.1007/s10163-021-01320-6>.

## Tuning syntetic minerals for recovering raw materials from WEEEs

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Keywords: urban mining, critical metals, recovery.

Europe is among the greatest buyers and users of mineral resources and raw materials in the world and the rare presence of mines and quarries makes the region strongly dependent from importations (especially from China). Moreover, more than 50% of WEEE is directly delivered into landfills, even if most of these wastes could be recycled and tons of precious metals and REE recovered, decreasing the environmental risks and the need of importations.

This approach is also advised by the 2030 Agenda for Sustainable Development, a document adopted by all United Nations Member States in 2015 to guarantee prosperity and peace for people and the planet, especially in the imminent future.

This document includes 17 Sustainable Development Goals, and few of them are strictly environmental. In this paper, it is also estimated that recovering of raw materials from waste could lead to a reduction of gas emission of 415 Mt and could create about 860,000 new jobs by the end 2023 (Beasley & Georgeson, 2014).

Our research group is focused mainly on the recovery of precious metals and REE from the WEEEs: the final goal is the reuse of recovered elements to close the recover cycle.

This work is funded by MITE project and supervised by prof. Gabriele Giuli.

This work focuses on planning and implementation of a method to manage the WEEEs, as eco-friendly as possible, from collection to recovery. The work mainly consists of two steps, both occurring after a selection of the waste and its pre-treatment with ball mill to decrease the size. The first phase is the choice and optimization of selective hydrometallurgical leachings to extract metals from the WEEEs.

The second process is a crystallochemical recovery, based on the use of synthetic minerals as LDH (Layered Double Hydroxide). This phase is particularly innovative because generally the elements are extracted from the leachate solutions by electrochemistry, that is an efficient method, but it is also energetically expensive and use large amounts of polluting reagents (e.g cyanides). The crystallochemical recovery seems to be more eco-friendly, using both a lower amount of energy and of reactants.

Moreover, the extraction method here proposed allows to reuse the synthetized minerals to multiple scopes, for example as electrodes in batteries.

Preliminary results show that the selective leaching pathway proposed by (Oh et al., 2003) in three consecutive different extraction seems to be the most promising process. It is our goal to improve this process and then used LDH to catch metals from the leachate solutions, searching for a structure that can be easily re-employed.

Beasley J. & Georgeson R. (2014) - Advancing Resource Efficiency in Europe. European Enviromental Bureau.

Oh C.J., Lee S.O., Yang H.S., Ha T.J. & Kim M.J. (2003) - Selective Leaching of Valuable Metals from Waste Printed Circuit Boards. *J. Air Waste Manage.*, 53(7), 897-902. <https://doi.org/10.1080/10473289.2003.10466230>.

## Raman spectra of feldspars from critical environments

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Keywords: inertisation, anorthite, Raman spectroscopy.

Waste inertization by high temperature reactions is a widespread technique, having its most notable application in the incineration of municipal wastes. The concept is very simple, transforming low temperature phases containing potentially toxic elements in high temperature ones, crystalline or glassy, where the critical element is caged and less prone to leaching. In the high temperature inertization, high temperature phases commonly found in nature are formed, like anorthite, pyroxenes or melilite. Often these phases contain potentially toxic elements (PTE), present in traces in natural environment. This is observed in anorthitic feldspars with 1:1 Al/Si ratio.

Anorthite is a phase commonly found during the high temperature inertization of PTE enriched wastes, but the Pb analogue of anorthite, Pb-feldspar, also forms commonly after stabilization (Ma et al., 2020). Ba and Sr-feldspars are found in high value ceramics, obtained after stabilization of industrial wastes in ceramics, and Sr-feldspars show strong technologic applications (Xue et al., 2020).

High temperature feldspars with anorthite structure can be easily overlooked, when they are interspersed in a matrix, and when in low amount could be revealed just by SEM-EDS. Analysis based by micro-Raman provide a reliable alternative for their identification, but, as yet, Raman spectra for these feldspar phases were not available.

Here the Raman spectra of natural and synthetic anorthite ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ ), Sr-feldspar ( $\text{SrAl}_2\text{Si}_2\text{O}_8$ ), Pb-feldspar ( $\text{PbAl}_2\text{Si}_2\text{O}_8$ ), celsian ( $\text{BaAl}_2\text{Si}_2\text{O}_8$ ) and Ca-Sr feldspar solid solutions are reported. Compositional related phase transitions strongly affect the aspect of the Raman spectra, which changes from the P-1 structure of natural anorthite, to the mottled P-1 of synthetic anorthite and Ca-Sr feldspar solid solutions up to about 50% in anorthite, and to the I-1 and I2/c structures of Sr-richer feldspars and celsian.

In Pb-feldspar the peak intensities are markedly different from celsian and Sr-feldspar, in spite of sharing the same I2/c symmetry. In Pb-feldspar the strongest peaks are a doublet between 80 and 100  $\text{cm}^{-1}$ , which strongly overtakes the intensity of the peak at 503  $\text{cm}^{-1}$ , which is generally the most intense in feldspars. We interpret this as an effect of the different polarizability of Pb with its lone pair respect to Ca, Sr and Ba in alkali-earth feldspars.

Ma W., Meng F., Qiu D. & Tang Y. (2020) - Co-stabilization of Pb/Cu/Zn by beneficial utilization of sewage sludge incineration ash: Effects of heavy metal type and content. *Resour. Conserv. Recy.*, 156, 104671. <https://doi.org/10.1016/j.resconrec.2019.104671>.

Xue J., Song, M., Noh H.M., Park S.H., Choi B.C., Kim J.H. & Du P. (2020) - Achieving non-contact optical thermometer via inherently  $\text{Eu}^{2+}/\text{Eu}^{3+}$ -activated  $\text{SrAl}_2\text{Si}_2\text{O}_8$  phosphors prepared in air. *J. Alloys Compd.*, 843, 155858. <https://doi.org/10.1016/j.jallcom.2020.155858>.



## High-temperature stabilization of bottom ashes (BA) from Municipal Solid Waste Incinerator: composition of residuals and leachates

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Keywords: bottom ashes, high temperature, stabilization.

One of the most challenging points in waste management is the recycling of the ashes produced by incinerators of municipal and special wastes. This is particularly critical for the enormous mass-produced, in Italy up to one million tons of ashes, from 5.3 millions tons of incinerated wastes. Any project of reuse or recycling of the ashes from incinerators faces two kinds of problems: 1) the high reactivity of bottom ashes that may release potentially toxic elements, and 2) the unwanted reaction of a non-stabilized material that may hinder possible reuse. Several methods of stabilization were discussed, among which inactivation by high temperature is of paramount importance (Ardit et al., 2022). At high temperatures, we expect the formation of ceramic like phases, which stabilize the Potentially Toxic Elements (PTE). However, in relation to the large amount of sample to be processed and energetic constraints, a compromise between the time and temperature has to be done to obtain stabilization in the least time and temperature. Also, it is important to verify the effect of different grain sizes in relation to the higher reactivity and content in PTE of smaller grain sizes.

In this work, we investigated a set of samples with different grain sizes from the bottom ashes of the Parma Waste to Energy (WtE) plant. We have tested three grain size class samples: 0.062-0.2, 0.3-0.5, and 1-2 mm. They were previously powdered to avoid the size surface effect and heated for 24 hours at 200, 400, 600, 800, and 1000°C.

In a previous report (De Matteis et al., 2022) the mineralogy of the obtained phases through ex-situ and in-situ X-ray diffraction, the changes in weight due to different heating, the higher decrease in weight for the smaller grain size, and the differences between ex-situ runs and in-situ thermo-gravimetric weight loss were discussed. Here we report the preliminary results of the XRF analysis of the residuals and the ICP-MS/ chromatographic analysis of the leachates, after leaching tests following the procedures codified in EN-12457-2 (Andreola et al., 2019)

XRF analysis of the after-heating shows only minor changes in major elements, but a strong decrease, as expected, in LOI. However, about 2% LOI is still present after heating at 1000°C. Only Pb and Br show a significant decrease after heating at 600°C. In leachates, we find a higher release in sulfates, Cr, Li, and Mo at T higher than 600°C, and a strong decrease in Cl, likely in relation to the volatilization of chlorides.

The results indicate that stabilization was not achieved in these conditions. Further investigation at higher temperature is foreseen, together with SEM-EDS analysis.

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Ardit M., Zanelli C., Conte S., Molinari C., Cruciani G. & Dondi M. (2022) - Ceramisation of hazardous elements: Benefits and pitfalls of the inertization through silicate ceramics. *J. Hazard. Mater.*, 423, 1-17

De Matteis C., Toller S. & Tribaudino M. (2022) - In situ and ex situ Bottom Ashes (BA) from Municipal Solid Waste Incinerator (MSWI) heating: mineralogical application for solid waste stabilization. *Congresso SGI-SIMP Torino 2022*, book of abstracts, 436.

## **Vegetal biomass ashes as a potential resource for sustainable production of mineral fertiliser: characterisation and feasibility study**

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*Keywords:* fertilizer, circular economy, minerals.

Over the past few decades, the fertilizer industry has primarily relied on non-renewable resources for plant nutrition. Minerals of commercial interest such as phosphorite and potassium salts are removed from natural deposits causing significant environmental and economic costs (Van den Berg et al., 2016). Consequently, there is an urgent need to adopt sustainable methodologies that preserve these fundamental non-renewable environmental resources while simultaneously supplying agricultural soils with the necessary nutrients for healthy plants growth. Recent studies suggest that vegetal biomass ashes i.e. the inorganic residue produced during the incineration of biomass for electricity production, have the potential to serve as a valuable source of essential plant nutrients thanks to their high concentration of potassium (K), phosphorus (P), magnesium (Mg), and calcium (Ca). Additionally, these ashes can be an effective soil amendment due to the presence of basic cations in the form of oxides, hydroxides, and carbonates (Vassilev et al., 2013, Zhai et al., 2021). In this perspective, this study aims to investigate the potential from a mineralogical and chemical point of view, of vegetal biomass ashes in order to recover elements and minerals useful for the growth of plants and, at the same time, to reduce the landfills disposal in accordance with the Circular Economy principles. In this study, eight samples of vegetal biomass ashes, consisting of four fly ashes and four bottom ashes from different cogeneration plants producing electricity through the combustion of agroforestry residues, were characterised from the chemical and mineralogical point of view to evaluate their potential as resource for sustainable production of mineral fertiliser. Results show high physical and chemical variability in both fly and bottom ashes from different agroforestry residues investigated. This variability is related to factors such as, the type of incinerator, the combustion temperature, and the type of ash (fly or bottom). However, results indicate a potential as a valuable fertilizer due to the occurrence in all samples investigated of high proportions of  $K_2O$ ,  $CaO$ ,  $MgO$  and relevant soluble mineral phases, especially in fly ash. Furthermore, investigations show the occurrence of basic cations in the form of oxides, hydroxides, and carbonates, which could be an excellent amendment to deal with soil acidity and compensate for the loss of nutrients.

Van den Berg M., Neumann K., van Vuuren D.P., Bouwman A.F., Kram T. & Bakkes J. (2016) - Exploring resource efficiency for energy, land and phosphorus use: Implications for resource scarcity and the global environment. *Glob. Environ. Change*, 36, 21- 34. <https://doi.org/10.1016/j.gloenvcha.2015.09.016>.

Vassilev S.V., Baxter D., Andersen L.K. & Vassileva C.G. (2013) - An overview of the composition and application of biomass ash. Part 1. Phase-mineral and chemical composition and classification. *Fuel*, 105, 40-76. <https://doi.org/10.1016/j.fuel.2012.09.041>.

Zhai J., Burke I.T. & Stewart D.I. (2021) - Beneficial management of biomass combustion ashes. *Renew. Sustain. Energy Rev.*, 151, 111555. <https://doi.org/10.1016/j.rser.2021.111555>.

## From Libiola's natural woodwardite to the energy storage systems: a journey through the Layered Doubled Hydroxides (LDHs)

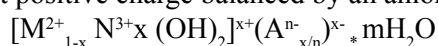
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*Keywords:* waste treatment, energy storage, LDH.

Layered doubled hydroxides (LDHs) belong to the hydrotalcite supergroup, their crystal structure is composed of brucite-type layers in which a trivalent cation partially substitutes a divalent cation, generating a net positive charge balanced by an anionic species in the interlayer giving the general formula:



Where M and N are respectively a divalent and a trivalent cation, A is an anion with n charge, x is the molar ratio N/(M+N) and m is a value between 1 and 4.

The interlayer is very flexible and could host different compounds both anions, cations and not charged ones; furthermore the wide range of possible combination of M,N and A lead to a lot of different applications for those class of compounds.

This work reports the results obtained starting from the synthesis of the analogue of the natural woodwardite (AlCu-SO<sub>4</sub> LDH and its affinity for rare earths elements (Consani et al., 2018). Moreover a number of synthetic LDHs have been properly planned and synthesised for the adsorption of dangerous pollutants such as Cr(VI) (Cardinale et al., 2020) and electrochemical purposes, to be applicable as active materials in metal ions batteries (Li et al., 2021).

Cardinale A.M., Carbone C., Consani S., Fortunato M. & Parodi N. (2020) - Layered double hydroxides for remediation of industrial wastewater from a Galvanic plant. *Crystals*, 10(6). <https://doi.org/10.3390/cryst10060443>.

Consani S., Balić-Žunić T., Cardinale A.M., Sgroi W., Giuli G. & Carbone C. (2018) - A novel synthesis routine for woodwardite and its affinity towards light (La, Ce, Nd) and heavy (Gd and Y) rare earth elements. *Materials*, 11(1). <https://doi.org/10.3390/ma11010130>.

Li X., Fortunato M., Cardinale A.M., Sarapulova A., Njel C. & Dsoke S. (2021) - Electrochemical study on nickel aluminum layered double hydroxides as high-performance electrode material for lithium-ion batteries based on sodium alginate binder. *J. Solid State Electr.*, 26, 49-61. <https://doi.org/10.1007/s10008-021-05011-y>.

## **Eco-technological solutions for resource supply from secondary sources**

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*Keywords:* bioleaching, anthropogenic materials, remediation.

The lecture will introduce recent advancements and method developments for the treatment of anthropogenic matrices, providing sustainable solutions to improve their related value chain. Starting from diversified sources of supply exhibiting hidden metal value, comparable to natural ores, chemical concentrations and mineralogical phases will be evaluated in the light of microbe-mineral interactions to plan biorecovery and bioremediation for a waste-tailored hybrid treatment, emphasizing the role of geosciences in the circular economy and the amelioration of industrial ecosystems. Industrial slag (Gomes et al., 2018), Municipal Solid Waste Incineration residues (Funari et al., 2023), and car catalytic converters are three use cases that will be discussed to ascertain geochemical and mineralogical characteristics, thus eco-technological effectiveness of new treatment solutions.

Funari V., Toller S., Vitale L., Santos R. & Gomes H. (2023) - Urban mining of municipal solid waste incineration (MSWI) residues with emphasis on bioleaching technologies: a critical review. *Environ. Sci. Pollut. R.*, 30(21), 59128-59150. <https://doi.org/10.1007/s11356-023-26790-z>.

Gomes H.I., Funari V., Mayes W.M., Rogerson M. & Prior T.J. (2018) - Recovery of Al, Cr and V from steel slag by bioleaching: Batch and column experiments. *J. Environ. Manage.*, 222, 30-36. <https://doi.org/10.1016/j.jenvman.2018.05.056>.

## Competitive adsorption of 4-hydroxybenzaldehyde (p-HBA) and toluene (TOL) by Y and ZSM-5 high-silica zeolites

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Keywords: high-silica zeolite, 4-hydroxybenzaldehyde, toluene.

Natural organic matter (NOM) is a complex mixture of organic molecules that can affect water treatment and remediation processes. It can interact with metals or other synthetic organic molecules and transport them through the treatment system. Additionally, treating waters containing NOM with chlorination processes produces harmful disinfection by-products (DBPs). Halogenated DBPs can be toxic even at low concentration levels. Nonhalogenated aromatic compounds were identified as new intermediate DBPs in chlorination, and they behave as intermediates for halogenated aromatic DBPs formation. Removal of nonhalogenated aromatic DBPs from water can significantly decrease the concentration of halogenated DBPs in treated water (Jiang et al., 2020). It is important to explore suitable adsorbent materials and to assess the capability of adsorbents to remove these substances from water in chlorination treatment to reduce halogenated DBPs, and to understand the selectivity of adsorbent material towards dissolved organic molecules and anthropogenic contaminants (Braschi et al., 2016; Chi et al., 2022). The present study examined the adsorption of 4-hydroxybenzaldehyde (p-HBA) and toluene (TOL) by two different high-silica zeolite materials (HSZs).

Y and ZSM-5 zeolites, differ from each other in structure and opening windows of the framework, and the comparison of their adsorption properties was performed to evaluate the importance of the competitive interference of water with pore size. The p-HBA target compound, was selected as one of the nonhalogenated DBPs, and the adsorption of p-HBA in the absence and presence TOL was compared to assess the selectivity of HSZs by batch adsorption test, and p-HBA/TOL concentrations were determined by High Performance Liquid Chromatography using Waters HPLC system (Waters Associates, Milford, Mass) equipped with a binary pump and a DAD UV-Vis detector. The bare and loaded zeolites structural investigation was carried out by X-ray powder diffraction on Bruker AXS D8 Advance diffractometer equipped with Si(Li) solid state detector (Sol-X) and full profile Rietveld refinements. Thermogravimetric (TG) and differential thermal analysis (DTA) of zeolite samples before and after p-HBA/TOL adsorption were performed in air using an STA 409 PC LUXX®-Netzsch operating at 10°C min<sup>-1</sup> heating rate from room temperature (RT) to 900°C. In the absence of TOL, both zeolites exhibit a high saturation capacity for p-HBA; however, as the concentration of TOL rises in solution, the zeolites saturation capacities for p-HBA rapidly decrease. Thermal and XRD investigations further support the higher affinity for TOL in p-HBA-TOL binary mixtures. The localization of the molecules within the zeolite offers information on the host-guest and guest-guest potential interactions between p-HBA, TOL, water, and the zeolite framework. Additionally, the DTA curves for the p-HBA-TOL binary mixtures exhibit behavior that is identical to that of the TOL-ZSM-5 and TOL-Y samples, demonstrating the selected zeolites preferential adsorption of TOL over p-HBA.

Braschi I., Martucci A., Blasioli S., Mzini L.L., Ciavatta C. & Cossi M. (2016) - Effect of humic monomers on the adsorption of sulfamethoxazole sulfonamide antibiotic into a high silica zeolite Y: An interdisciplinary study. *Chemosphere*, 155, 444-452.

Chi X., Zeng L., Du Y., Huang J., Kang Y., Luo J. & Zhang Q. (2022) - Adsorption of levofloxacin on natural zeolite: effects of ammonia nitrogen and humic acid. *Water Sci. Technol.*, 85(10), 2928-2944.

Jiang J., Han J. & Zhang X. (2020) - Nonhalogenated Aromatic DBPs in Drinking Water Chlorination: A Gap between NOM and Halogenated Aromatic DBPs. *Environ. Sci. Technol.*, 54(3), 1646-1656.

## A multi-analytical investigation for the characterization of the vergaut pigment in polychrome wooden statues from Liguria, Italy

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Keywords: orpiment, indigo, ultramarine blue.

We report the results of a multi-analytical investigation for the characterization of the vergaut pigment in polychrome wooden statues (XV-XVII centuries) from Liguria, Italy. According to the definition of the Conservation and Art Materials Encyclopedia Online (CAMEO, Conservation & Art Materials Encyclopedia Online, [https://cameo.mfa.org/wiki/Main\\_Page](https://cameo.mfa.org/wiki/Main_Page). Accessed on May 2023), vergaut is a green pigment used as an alternative to verdigris by medieval painters mostly for illuminated manuscripts. Vergaut is reported as a composite pigment prepared by mixing orpiment and indigo, but a variety of alternative recipes has been described in literature (e.g., orpiment and ultramarine blue, yellow ochre and indigo, orpiment and woad, lapis lazuli and orpiment, azurite and lead tin yellow).

The green pigments of four polychrome wooden crucifixes from Imperia, Savona, and Genova Provinces and the wooden statue of San Pantaleo from Zoagli (Genova) have been analyzed by means of Field Portable X-ray Fluorescence (FP-EDXRF), Scanning Electron Microscopy and Microanalysis (SEM-EDS), and  $\mu$ -Raman spectroscopy. The results allowed to recognize the vergaut pigment in three of the five analyzed statues, whereas in the remaining works the green parts are composed by cupriferos pigments. In two of the three cases, the vergaut was found to consist of a mixture of orpiment and indigo, whereas in the third case the presence of ultramarine blue was detected in addition to indigo.

The presence of the orpiment in the vergaut pigments raises the question about the origin of this arsenic sulphide. It is in fact known that both the natural phase and the synthetic equivalent were used in the production of this pigment. Natural orpiment is mostly found in low temperature hydrothermal veins, hot springs, and fumaroles but also as an alteration product of realgar and other arsenic minerals. As this type of deposit is not present in Liguria, it is likely that the mineral pigment came from other Italian geological contexts (e.g., Tuscany, Campania, Lombardy). Concerning the possibility of the use of synthetic arsenic sulfides, several manuscripts mention the use of "artificial orpiment" since the fifteenth century, even though the first precise reference related to a sublimation process for arsenic sulfides is dated to the second half of the eighteenth century (Delbey et al., 2019 and references therein). Based on the current results, it must be emphasized that we cannot be completely sure of the origin of the orpiment, i.e., whether the natural phase or the synthetic equivalent was used.

Finally, the discovery of the use of vergaut in wooden painting is of particular importance because, to the best of our knowledge, any historical documents mention the use of vergaut in media other than paper or parchment. The use of *vergaut* in wooden media, as for the illuminated manuscripts, may be due either to the need to obtain different shades of green by varying the proportions of yellow and blue pigments, and/or for protective purposes, given the effective antimicrobial activity of arsenic compounds.

Delbey T., Holck J.P., Jørgensen B., Alvis A., Smith V.H., Kavich G.M., Harmon K.A., Dorch B.F. & Rasmussen K.L. (2019) - Poisonous books: analyses of four sixteenth and seventeenth century book bindings covered with arsenic rich green paint. *Herit. Sci.*, 7:91. <https://doi.org/10.1186/s40494-019-0334-2>.



## Hollandites and pyrochlores for heavy-metal removal from contaminated water

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Keywords: heavy-metal incorporation, ionic exchange, crystallography.

Heavy-metal water pollution is a serious threat for human health and one of the most debated environmental issues. The high mobility and persistence of heavy metals, combined with their high level of toxicity, makes it very difficult, but critical, to find technical solutions for their removal from contaminated aqueous matrices. The aim of this study is to investigate the ability of pyrochlore-like and hollandite-like compounds to incorporate and remove heavy-metals like Tl and Pb via ionic exchange from contaminated waters. The structures of pyrochlore and hollandite consist of rigid octahedral frameworks defining tunnel-shape cavities in which a wide range of cations can be hosted and exchanged. Over the past years, due to their ionic exchange properties, such structures have been synthesized in a wide range of chemical compositions in order to use them as catalysts (e.g., Jitta et al., 2015), materials for battery applications (e.g., Oh et al., 2012) and radwaste disposal (Mu et al., 2015). Powders of  $K_2Ta_2O_6$  (microlite structure; space group Fd-3m) and  $KMn_8O_{16}$  (cryptomelane structure; space group I4/m) were produced via hydrothermal synthesis, characterised by means of PXRD and used for imbibition experiments in concentrated solutions of Tl [1M of Tl(CHO<sub>2</sub>)] and Pb [1M of Pb(NO<sub>3</sub>)<sub>2</sub>]. Rietveld refinements conducted on PXRD data collected on both treated and untreated  $K_2Ta_2O_6$  samples revealed variations of the unit-cell parameters (from  $a = 10.624 \text{ \AA}$  for untreated pyrochlore to  $a = 10.637 \text{ \AA}$  for Tl-treated microlite and  $a = 10.545 \text{ \AA}$  for Pb-treated microlite) and tunnel sites electron density (14 e<sup>-</sup> for untreated sample; 51 e<sup>-</sup> for the Tl-treated sample and 36 e<sup>-</sup> for the Pb-treated sample). The increase of the cell parameter is consistent with the substitution of K<sup>+</sup> with the slightly larger cation Tl<sup>+</sup>, while the decrease with the entry of the smaller cation Pb<sup>2+</sup>. Similarly, the increasing of the tunnel sites electron density is indicative of the exchange of K with the heavier Tl and Pb cations. XAS measurements collected on Pb- and Tl-treated samples confirm that a K ↔ Tl/Pb ion exchange has been obtained; EXAFS preliminary results on the Tl-treated sample are compatible with Tl being hosted in a distorted, highly coordinated site suggesting that most of it is incorporated inside the tunnels. EDS preliminary analysis on treated  $KMn_8O_{16}$  powders confirmed the incorporation of considerable amounts of Tl and Pb. Variations of the unit cell parameters (from  $a = 9.848 \text{ \AA}$ ;  $c = 2.857 \text{ \AA}$  for  $KMn_8O_{16}$  to  $a = 9.896 \text{ \AA}$ ;  $c = 2.865 \text{ \AA}$  and  $a = 9.835 \text{ \AA}$ ;  $c = 2.856 \text{ \AA}$  for Tl- and Pb-treated  $KMn_8O_{16}$ ) are again indicative of an ionic exchange substitution. Further investigations are ongoing.

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## Hydrothermally dewatered sewage sludge as a substitute of clay for the production of ceramics

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*Keywords:* hydrothermal treatments, ceramics, sewage sludge.

The production of large quantities of sewage sludge (s.s.) by wastewater treatment plants represents a continuous and pressing environmental problem. Sewage sludge is classified as waste and must be managed according to European Directive 2008/98/EC, which prioritizes reuse and recycling over landfill disposal. A valuable solution that is proving to be effective on wet organic waste is the hydrothermal treatment, which is able to largely reduce s.s. volume, recover water and raw materials. With this goal in mind, a hydrothermal plant capable of continuous treatment of s.s. was built as part of the EU LIFE FREEDOM project (LIFE19/ENV/IT/000165).

The hydrothermal process generates a solid side stream called HTD cake. The main aim of this research is to investigate the possibility of using this HTD cake as a substitute for clay for the production of ceramics.

The materials, the cake and the Fe-rich alluvial clay (Cascina Gropello pit, Valenza, AL), were characterized to define their chemical composition, the contained crystalline phases, and the general microstructure, through X-ray diffraction (XRD), X-ray fluorescence (XRF) and scanning electron microscopy (SEM). The HTD cake was used as a substitute for the clay at variable percentages of 10 wt%, 30 wt%, and 50 wt%, and subsequently mixed with the clay itself to form the ceramic body. The mixture was added with water at the ratio of 1:1, stirred homogeneously, then slipped into molds, aged, and let dry in an open atmosphere for 2 days. The obtained raw ceramics were fired in an industrial brick kiln with a slow firing ramp, for about 45 hours including reaching the maximum temperature and cooling down to room temperature.

The predominant crystalline phases in the obtained ceramics are quartz, albite-feldspars, micas (muscovite and biotite), hematite, and phases resulting from the introduction of HTD cake, in particular Ca phosphate phases. In all the samples, from that with the lowest addition of cake to those with the highest amount, it is possible to observe fractured and zoned alkali feldspars, with an albite-like core and a K-feldspar-like rim indicating a progressive replacement of Na by K, available from the clay matrix. In addition, from a textural point of view, a marked primary porosity is observed probably due to the degradation of the organic matter contained in the cake, and a secondary porosity due to the mica degradation with the temperature.

The ceramics obtained, including those with the highest percentage of added cake, have good chemical and physical characteristics, comparable even with reference standards. To conclude, the feasibility test demonstrated that it is possible to use a large quantity of HTD cake as a substitute for a primary raw material. In this way, it is possible to release the pressure on natural resources and use waste material as secondary raw material in a circular economy perspective, in complete accordance with European legislation and directives.

## **Archaeometry and contemporary archaeology: the case of POW camp 65 (Altamura, Southern Italy)**

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*Keywords:* archaeometry, contemporary archaeology, mortars.

The site commonly known as PG65, located near the town of Altamura (Bari), was, covering 31 hectares, the largest concentration camp for prisoners in fascist Italy during World War II. After the armistice in 1943, it became a training camp for Yugoslav partisans and, in the 1950s, a collection center for refugees. In later years, plans to convert it into barracks were halted, and it became a military exercise site, before being almost completely razed to the ground in the late 1980s.

The short history of the site is complex, however, and so is its materiality. Since 2021, archaeological investigations conducted by the Universities of Bari and Foggia have begun to search for material traces of the transformations associated with the various phases. The signs are difficult to read, with tiny stratigraphy remaining, and must be sought in the transformations of the few walls and floors that survived destruction.

Mineralogical and petrographic analyses will be fundamental in understanding the chronological succession between very closely spaced phases, which were moreover made with materials unusual in archaeological research and therefore not very comparable with already known realities.

The research design was oriented to check the complex building stratigraphy through the petrographical (POM, SEM-EDS) and mineralogical (XRPD) analysis of mortars.

35 samples were taken in two kitchens: one made in 1942 and abandoned after a few months and another, of which a renovation a few years later (1955) is known.

The particular military building context raises questions too about the binder and aggregate procurement during and after World War II, as well as provides evidence of lime and cementitious binders technology in the mid-20<sup>th</sup> century.

## **The contemporary art paradox: to conserve asbestos**

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*Keywords:* eternit, painting.

When you approach the world of Contemporary Art, seen from the perspective of a conservator, you feel like Alice in Wonderland, everything is upside down, but at the same time everything is in the right place. There are no conventional rules, nor traditionally codified practices. We have to face artists who have an unconventional and sometimes unconscious relationship with the materials they choose to represent, whose composition or characteristics are often unknown. This research, carried out under the FOP programme, deals with a series of artworks containing a particular and unusual material in the Cultural Heritage field, that is asbestos, more precisely Eternit. In 1982, Luicciana, a small village in Tuscany of circa 100 inhabitants and more or less 100 buildings, managed to renew itself by transforming the town into an extraordinary Museum of Contemporary Art en plein air. Traveling around the village, it is possible to come across wall paintings, ceramic creations, marble sculptures and multi-material objects, artworks created by national artists, exponents of the Florence and Prato avant-garde in the 60s and 70s, and international names such as Sebastian Matta. It is an extremely varied collection, both in terms of art techniques and materials selected. In order to safeguard this cultural heritage which presents many critical issues, due also to the outdoor setting, the municipality, in 2017, asked for the support of CONI'arte APS and YOCOCU APS, to plan appropriate conservation treatments. My research is part of this large project but it is focused on artworks which contain Eternit, used as a support for paintings. Dealing with cultural heritage objects that contain carcinogenic material requires deep reflection, not because they are less dangerous than a fiber cement roof, but because they are the creative expression of human nature, they represent identities in terms of culture and they are a unique and non-renewable resource. It is therefore necessary to preserve these artworks and it would mean safeguarding the constituent materials, as well as the support of the artwork itself in its entirety. This concept guided the research in order to focus on a very clear goal to safeguard the artworks and at the same time the health of those who, by chance or by passion, will be able to enjoy it. Because there is no standardized conservation procedure in this regard, I have made a plan based on the possibility of decline procedures applied to manage materials containing asbestos from the current legislation (Decreto Ministeriale del 6 settembre 1994, Normative e metodologie tecniche di applicazione dell'articolo 6, comma 3 dell'art.12, comma 2, della legge 27 marzo del 1992, n. 257, relativa alla cessazione dell'impiego dell'amianto), that unfortunately concerns exclusively the construction field and the industrial sector. Furthermore, the comparison among analogous art cases constitutes an important method of reflection and starting point for formulating a shareable conservation approach. All these research materials have been essential for planning a functional conservation strategy in order to protect the works, minimize the risk and guarantee a safe visit in Luicciana.

## Optimization lithium recovery from LiFePO<sub>4</sub> batteries based on agri-food wastes through experimental design

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*Keywords:* urban mining, lithium recovery, electronic wastes.

Lithium recovery from batteries is becoming increasingly important due to the growing demand for lithium as a critical material in the production of rechargeable batteries used in electric vehicles and consumer electronics. (Mahandra & Ghahreman, 2021).

Recycling lithium from spent batteries not only conserves the limited resources of lithium but also helps reducing the environmental impact associated with mining and refining the metal. In addition, lithium recovery from batteries can also help reduce the cost of production of new batteries and improve their sustainability. (Pražanová et al., 2022).

The best process to recover lithium from LiFePO<sub>4</sub> can be done through the hydrometallurgical process that involves the dissolution of the battery material in an aqueous solution, followed by separation and purification of the lithium. This process can be more environmentally friendly than the pyrometallurgical process and is often used for recycling batteries on a larger scale. (Forte et al., 2021).

The aim of this work is developing and optimising a cost-effective and sustainable hydrometallurgical process using tartaric acid in order to recover lithium from LiFePO<sub>4</sub> pouch cells. Tartaric acid is an eco-friendly weak organic acid that occurs naturally in many fruits (grapes, bananas, tamarinds, citrus, ecc.) and can be recovered from various natural by-products, mostly from winery ones. (Kontogiannopoulos et al., 2016) It is an effective leaching agent for metal extraction because of its ability to complex with metal ions and it is also a perfect substitute for common strong inorganic acids (H<sub>2</sub>SO<sub>4</sub>, HCl, HNO<sub>3</sub>) and strong basis (NaOH, NH<sub>4</sub>OH).

In other words, using agri-food wastes it is possible to process another waste, the industrial one, to recover and reintegrate precious metals for an efficient circular economy.

A representative batch of pouch cells was considered to ensure that the project outcome was representative, including the possibility of exporting it to a pilot and/or industrial process. So, LiFePO<sub>4</sub> pouch cells were characterized by X-ray Diffraction (XRD) to determine the mineralogical composition and the degree of crystallinity; by Scanning Electron Microscopy (SEM) and by an elementary analysis; by inductively coupled plasma (ICP-OES). For the recovery process were considered a series of independent variables: solid to liquid ratio (g/L), reaction times (min), temperature (°C), acid concentrations (mol/L) and H<sub>2</sub>O<sub>2</sub> concentration (vol%). An experimental design (DOE) was carried out in order to determine the optimal conditions for an efficient metal recovery and to maximize profits.

Forte F., Pietrantonio M., Pucciarmati S., Puzone M. & Fontana D. (2021) - Lithium iron phosphate batteries recycling: An assessment of current status. *Crit. Rev. Env. Sci. Tech.*, 51(19), 2232-2259. <https://doi.org/10.1080/10643389.2020.1776053>.

Kontogiannopoulos K.N., Patsios S.I. & Karabelas A.J. (2016) - Tartaric acid recovery from winery lees using cation exchange resin: Optimization by Response Surface Methodology. *Sep. Purif. Technol.*, 165, 32-41. <https://doi.org/10.1016/j.seppur.2016.03.040>.

Mahandra H. & Ghahreman A. (2021) - A sustainable process for selective recovery of lithium as lithium phosphate from spent LiFePO<sub>4</sub> batteries. *Resour. Conserv. Recycl.*, 175, 105883. <https://doi.org/10.1016/j.resconrec.2021.105883>.

Pražanová A., Knap V. & Stroe D.-I. (2022) - Literature Review, Recycling of Lithium-Ion Batteries from Electric Vehicles, Part II: Environmental and Economic Perspective. *Energies*, 15, 7356. <https://doi.org/10.3390/en15197356>.

## Recycling of thermally deactivated cement asbestos material in the production of mineral wool fibers

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*Keywords:* rock wool, secondary raw material, ACM.

Asbestos-containing material (ACM) still represents an emergency in Italy because of the related health problems. Based on the present dedicated legislation, ACM must be managed through several different operations such as: i) confinement, ii) encapsulation and iii) removal and consequent disposal in controlled landfills. A more attractive alternative to these non-ideal solutions, safer and sustainable, is the transformation of the ACM through thermal, thermo-chemical or thermo-mechanical methods into a non-hazardous secondary raw material.

Asbestos is an excellent thermal and electrical insulator; it is fire-resistant and can improve significantly the mechanical properties of various materials (e.g., cement) when used as filler. For this reasons, during mostly of the 20<sup>th</sup> century, it was commonly used across the world as a building material. After the asbestos ban in 1990s, a large number of efforts has been played to develop new materials with similar properties. One of these materials is the so-called rock-wool. Rock wool is an inorganic fibrous substance produced by fiberization on cooling of a molten glass, usually obtained from silicate rocks and slags. Rock wool is frequently used for acoustic insulation, fire protection, cement reinforcement, pipe insulation, and even as synthetic soil for growing plants.

This contribution deals with rock wool production, using thermally deactivated ACM as a secondary raw material mostly consisting of non-hazardous Ca-Mg-rich silicates and glass (Vergani et al., 2022).

Two different tests were carried out using different percentages of the thermally treated ACM: 63.2% ACM + 36.8% basalt sand and 77.4% ACM + 22.6% quartz sand. The produced rock wool fibers were characterized by the means of XRF, DSC, XRPD, and SEM-EDS analyses, as well as by mechanical tests.

ACM, basalt and quartz mix well in the furnace, creating a homogenous melt that can be poured and fiberized at reasonable temperatures (1500°C). The obtained fibers are also characterized by chemical compositions quite similar to the normal rock wool range that conforms to biosolubility standards. Moreover, Young's modulus estimated according to Rocherulle et al. (1989) are totally comparable with those of the typical rock wool.

These results show that deactivated cement asbestos materials can be successfully re-used in rock wool production.

Rocherulle J., Ecolivet C., Poulian M., Verdier P. & Laurent Y. (1989) - Elastic moduli of oxynitride glasses: Extension of Makishima and Mackenzie's theory. *J. Non-cryst. Solids*, 108, 187-193.

Vergani F., Galimberti L., Marian N.M., Viti C. & Capitani G.C. (2022) - Thermal decomposition of cement-asbestos at 1100°C: how much "safe" is "safe"? *J. Mater. Cycles Waste Manag.*, 24, 297-310. <https://doi.org/10.1007/s10163-021-01320-6>.



**S18.**

**Geomaterials: characterization, industrial uses and environmentally friendly innovative applications**

*CONVENERS AND CHAIRPERSONS*

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## **The mineralogical composition of granitoids from the Igoudrane region of Jbel Saghro in Morocco's eastern anti-atlas**

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*Keywords:* mineralogy, Igoudrane, thin sections.

The purpose of this study is to determine the mineralogical composition of Precambrian granitoids present in the Moroccan Anti-Atlas, particularly the Igoudrane area. The latter is characterized by Ediacaran plutonic magmatic rocks made mostly of quartz, plagioclases, and alkali feldspars. The macroscopic description and thin-section petrographic investigations show that granites, granodiorites, syenites, diorites, and monzonites predominate. Granites are mostly composed of quartz, alkali feldspars, plagioclases, and altered biotite. Granodiorite with amphibole is defined by its significant amphibole concentration, the presence of biotite, and plagioclase that has been extensively transformed into sericite. Furthermore, there are traces of quartz, potassium feldspar, and chlorite as well, with zircon and apatite as accessory minerals. Syenites have an identical composition to granites, except they contain less quartz, altered alkali feldspar (orthose), microcline, chloritized biotite, and altered amphiboles. Moreover, the diorites consist mainly of altered pyroxene and amphibole, quartz, alkali feldspars, biotite, and muscovite. Monzonites are composed of almost equal amounts of alkali feldspars and plagioclases, pyroxene, biotite, and chlorite, with less quartz. The granitoids of the Igoudrane region went through deep alteration, either superficial or hydrothermal, including argilization (alteration of plagioclases), which is more common in the Igoudrane area; disappearance of pre-existing minerals; silicification of fractured zones (secondary quartz); chloritization caused by ferromagnesian mineral decomposition (alteration of minerals such as pyroxenes, amphiboles, and biotite); and oxidation (hematite, goethite, and chabazite). Concerning hydrothermal alteration, it should be noted that the nature of the mineral assemblages is controlled by several important factors: the lithological character of the host rocks, the permeability of the stones, both the temperature and pressure conditions of the entire system, and the fluid constitution.

## Pressure-mediated adsorption in 6-membered ring zeolites with EAB topology

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Keywords: zeolites, high-pressure, synchrotron X-ray diffraction.

The intrusion of molecules or solvated ions into the nano-cavities of microporous materials, such as zeolites, through P-induced intrusion, has opened new opportunities for promoting mass transfer from fluids to molecules incorporated in framework structure. Understanding this phenomenon in natural or synthetic zeolites could expand their utilization, tailor new functional materials or improving catalytic abilities in industrial processes. In this study, we synthesized EAB samples using the Aiello-Barrer protocol (Aiello & Barrer, 1970) and treated them to obtain the Na- and K-form. The high-pressure behaviour of the Na- and K- EAB zeolites has been then investigated using in-situ single-crystal and powder synchrotron X-ray diffraction, with a diamond anvil cell, at the ID15B beamline of ESRF in Grenoble, France. Additionally, high-pressure experiments were performed also on bellbergite (ideally  $(K,Ba,Sr)_2Sr_2Ca_2(Ca,Na)_4[Al_3Si_3O_{12}]_6 \cdot 30H_2O$ ), the natural analogue of EAB zeolite. Distilled water, methanol, and the non-penetrating silicone oil were used as hydrostatic pressure-transmitting fluids. The results of this research allowed to understand the role played by the pre-existing extra-framework population in the adsorption of penetrating pressure fluids, and lead to a qualitative assessment of the fluid adsorption, by comparing the compressibility of these microporous crystal structures compressed in different P-transmitting media. Additionally, relevant high-pressure deformation mechanisms were described.

Aiello R. & Barrer R.M. (1970) - Hydrothermal Chemistry of Silicates. Part XIV, Zeolite Crystallization in presence of Mixed Bases. J. Chem. Soc. A: Inorganic, Physical, 1470-1475.

## Perlitic volcanic rocks for the production of high permeability lime plaster mortars

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*Keywords:* Chapelle test, hydraulic mortar, physico-mechanical tests.

Perlites are volcanic rocks mainly consisting of glass with intermediate to acid composition (dacite to rhyolite) and characterized by a network of cracking with spheroidal to ellipsoidal surfaces (perlitic structure). Perlitisation is genetically linked to a three-dimensional strain field, due to the contraction that the rock mass undergoes following very rapid cooling. Statistical analysis of line densities reveals a direct relation between the sublinear and the perlitic (rounded) fractures, highlighting that the rounded cracks originate near primary sublinear cracks and then their formation proceeds to the center of the beads. Perlite can expand up to 20 times its original volume when subjected to high temperatures, due to the release of water bound within the glassy matrix. The rock is finely ground and then heated at 900-1000°C so that each original grain expands, becoming a whitish, highly vesiculated (with high porosity), low-density material. Its main use is in the building industry, where it is used as a thermal insulator in the cavities of perimetral walls, roofing, or waterproof bottoms, or mixed with water and hydraulic lime to lighten subfloors and screeds in intermediate floors.

A new possible use, as a pozzolanic material, is tested here. The compositional and microstructural characteristics of some selected perlite facies outcropping at Monte Sparau (Monte Arci, central Sardinia, Italy) were studied to understand if it is able to provide hydraulic properties to common quicklime-based mortars. The aim is to obtain a low-cost, water-resistant, highly permeable, and sustainable binder having mechanical strength similar to that of hydraulic lime.

Laboratory tests using the Chapelle method indicate a good reactivity of such pozzolans with hydrated lime. The results of the physical-mechanical tests carried out on mortar specimens show good mechanical resistance (PLT test, uniaxial compression and indirect traction) starting as early as 1 month of aging and gradually improving after two years. The compressive strengths after 1 month (from 3.7 to 5.9 kg/cm<sup>2</sup>), are then further increased after 2 months (from 2.6 to 8 kg/cm<sup>2</sup>), up to 18-20 kg/cm<sup>2</sup> after 2 years. The porosity, initially around 44-61% in the samples with the highest pozzolana concentration, it undergoes a reduction over time up to values of 40.4% in two months, and a further reduction 2 years after packaging. Moreover, the specimens preserve high values of vapor permeability increasing over time, ranging for a specimen thickness of 10 mm at 20°C from 100-220 to 170-320 g/m<sup>2</sup>×24h after 1 and 2 months respectively, suggesting that the plasters can be used in moisture-bearing rooms where humidity dissipation is required. These characteristics, together with good water-repellent properties of mortar specimens, indicate the excellent qualities of these perlites to be used as a pozzolanic additive in the production of construction plasters for both indoors and outdoors.

## Producing high-performing foundry sands from ophiolite chromitites: an arduous challenge?

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*Keywords:* chromite, foundry sands, ophiolites.

Chromite foundry sands are employed in the industry to form molds for high demanding casting of metal and steel (e.g., automotive casting, filler in steel production...). They have high melting point (2090°C), low thermal expansion and neutral chemical behavior, making them difficult to replace for high performing materials casting. Chrome sand is also used in the production of magnesite chrome refractory bricks providing resistance to abrasion and high temperature.

Because the sintering behavior of chromite sand influences the casting process, the quality parameters of the sands are quite strict. The main parameters are: i) fineness index (FI), depending on the grain size distribution, ii) SiO<sub>2</sub> content and iii) Acid Demand (AD), which measures the reactivity of the sand with binding resins.

Chromite foundry sands in the EU market mainly come from South Africa ore deposits. For this reason, the present study aims to evaluate ophiolite chromite deposits in the European territory as possible new sources for the foundry industry (Bussolesi et al., 2020).

For the study, four chromite sands from different enrichment plants were evaluated and confronted with two different South African products. The four sands are from Neyriz (Iran), Vourinos (Greece), Kalimash and Balleja (Albania).

The grain size distribution shows that all the sands fit into the Fineness Index range (between 40 and 75), making them suitable candidates. The SiO<sub>2</sub> content, which should normally lie below 2 wt%, is below 1.4 wt% for the South African samples, below 2.0 wt% for Neyriz, 3.5 wt% for Balleja, 7.0 wt% for Vourinos and 10 wt% for Kalimash.

The high SiO<sub>2</sub> content is directly connected to the AD, a titration method used as a proxy for sand-resin reaction potential, and calculated at pH 3, 4 and 5 for all the sands. South Africa samples have AD values below 10 (the upper limit for foundry sands). Ophiolite chromite samples show much higher values: 21 for Neyriz, 40 for Vourinos, 30 for Balleja and 31 for Kalimash.

The high values for Vourinos and Kalimash can be easily correlated to the high SiO<sub>2</sub> content in the sands, indicating a bad separation efficiency in the enrichment plants, but Neyriz and Balleja AD values cannot be explained through their high SiO<sub>2</sub> content.

Further analyses revealed that the silicate mineralogy strongly influences the AD values. Pyroxene, the main silicate mineral within the South Africa sands, is the lowest reactive, while serpentine, widespread in ophiolite contexts, is highly reactive with the binding resins. Intermediate results are to be attributed to olivine, which shows higher reactivity than pyroxene but much lower than serpentine.

The use of ophiolite chromitites for foundry purposes is limited to serpentine-poor (e.g., unaltered) deposits, and only after careful studies of the enrichment processes, in order to increase the separation efficiency of the plant and lower the SiO<sub>2</sub> content in the final chromite concentrate.

Bussolesi M., Grieco G., Eslami A. & Cavallo A. (2020) - Ophiolite chromite deposits as a new source for the production of refractory chromite sands. *Sustainability*, 12, 7096. <https://doi.org/10.3390/su12177096>.

## Valorization of Granite waste materials for the sequestration of carbon dioxide via mechanochemical activation

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*Keywords:* granite wastes, carbon dioxide.

In order to mitigate the ever-increasing CO<sub>2</sub> concentration in the atmosphere, cheap materials and sustainable approaches, part of the carbon capture utilization strategies (CCU) are required (Voldsund et al., 2016; Farina et al., 2022). In this context, the present work focuses on the investigation of the weathering reaction, activated by mechanical processing, of granite waste materials when exposed to carbon dioxide and water (Oliva et al., 2003). For the first time by our knowledge, vigorous carbon sequestration via solids products (carbonates) has been achieved with orders of magnitude larger than conventional thermally activated processes. The potential of these new routes for the sequestration of carbon dioxide exploiting waste minerals and some of the related challenges, are also briefly discussed.

Farina V., Simula M. D., Taras A., Cappai L., Tahar Sougrati M., Mulas G., Garroni S., Enzo S. & Stievano L. (2022) - Unveiling redox mechanism at the iron centers in the mechanochemically activated conversion of CO<sub>2</sub> in the presence of olivine. *J. Mater. Sci.*, 57, 10017-10027. <https://doi.org/10.1007/s10853-022-06962-x>.

Oliva P., Viers J. & Dupré B. (2003) - Chemical weathering in granitic environments. *Chem. Geol.*, 202(3-4), 225-256. <https://doi.org/10.1016/j.chemgeo.2002.08.001>.

Voldsund M., Jordal K. & Anantharaman R. (2016) - Hydrogen production with CO<sub>2</sub> capture. *Int. J. Hydrogen Energ.*, 41(9), 4969-4992. <https://doi.org/10.1016/j.ijhydene.2016.01.009>.



## Pressure-driven phase transitions in hydrated borates

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Keywords: borates, geomaterials, X-ray crystallography.

Hydrated borates (e.g., colemanite, ulexite, kernite and borax) are the most common ore minerals of boron, an important geochemical marker, in pegmatitic and granitic systems, for petrogenetic processes and a strategic element in a series of technological applications. Hydrated borates, which have been listed as critical raw materials by the EU (European Commission, 2017), could be used as aggregate in neutron-shielding Sorel or Portland concretes, enhancing the adsorption towards thermal neutrons. In hydrated borates, the main structural units are  $B\phi_x$  units (tetrahedra and planar trigonal group where  $\phi$  is an anion,  $O^{2-}$  or  $OH^-$ ), connected in such a way to form clusters of polyions connected to alkaline/Earth alkaline (mainly  $Na^+$ ,  $K^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ) polyhedra. In these structures,  $H_2O$  molecules and  $OH^-$  form a complex and pervasive hydrogen-bond network, often enhancing the connection between the polyions clusters and the cations-polyhedrons, therefore playing a paramount role in the stability of the crystalline edifice (Comboni et al., 2021; Pagliaro et al., 2021). The aim of this contribution is to analyze and provide insides on the high-pressure behavior and structure evolution of several hydrate borate minerals, unveiling the phase transition driving deformation mechanisms that lead to the formation of their high-pressure polymorphs. A common pattern, that could be used to predict the high-pressure phase stability of this class of minerals, has been detected.

Comboni D., Poreba T., Pagliaro F., Battiston T., Lotti P., Gatta G.D., Garbarino G. & Hanfland M. (2021) - Crystal structure of the high-P polymorph of  $Ca_2B_6O_6(OH)_{10} \cdot 2(H_2O)$  (meyerhofferite). *Acta Crystallogr. A*, 6, 940-945.  
European Commission (2017) - Study on the review of the list of critical raw materials. <https://doi.org/10.2873/876644>.  
Pagliaro F., Lotti P., Battiston T., Comboni D., Gatta G.D., Cámara F., Milani S., Merlini M., Glazyrin K. & Liermann H. (2021) - Thermal and compressional behavior of the natural borate kurnakovite,  $MgB_3O_3(OH)_5 \cdot 5H_2O$ . *Constr. Build. Mater.*, 266, 121094.

## High-pressure phase transition and crystal structure evolution of inderite, $\text{MgB}_3\text{O}_3(\text{OH})_5 \cdot 5\text{H}_2\text{O}$

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*Keywords:* borates, geomaterials, X-ray crystallography.

Inderite, ideally  $[\text{MgB}_3\text{O}_3(\text{OH})_5 \cdot 5\text{H}_2\text{O}]$ , is a light ( $1.80 \text{ g/cm}^3$ ) Na-free hydrated borate, discovered in the Inder deposit (Kazakhstan), which could be efficiently employed in radiation-shielding concretes due to its relatively high  $\text{B}_2\text{O}_3$  content ( $\sim 37 \text{ wt}\%$ ). The crystal structure of inderite is made by  $[\text{B}_3\text{O}_3(\text{OH})_5]^{2-}$  polyions, organized in 3-membered rings of 2  $\text{B}\phi_4$  tetrahedra and one  $\text{B}\phi_3$  unit (where  $\phi$  is an anion;  $\text{O}^{2-}$  or  $\text{OH}^-$ ). Prior to any utilization, is advisable to correctly characterized the thermodynamic parameters of any aggregate, if used in neutron-shielding concretes, where temperature can increase due to the interactions with the highly energetic neutron beam. Overall, phase transitions occurring at different pressures (and temperatures) were discovered in all the hydrous borates investigated so far (e.g., Comboni et al., 2021; Pagliaro et al., 2021), suggesting that the high-pressure stability of hydrated borates having polyions organized in isolated units (e.g., inderite) is directly correlated with the total  $\text{H}_2\text{O}$  content of the mineral itself. Inderite is the ideal case-scenario to validate this model and here we report the results of this study that leads to: 1) track the isothermal compressional path, based on the experimental P-V data, 2) derive the elastic parameters, currently unavailable in the literature; 3) investigate the phase-stability field of inderite at high-pressure; 4) describe the high-pressure structural re-arrangement of inderite at the atomic scale.

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## Claystone deposits in the middle Jurassic of central Sardinia: a reappraisal

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Keywords: claystones, Middle Jurassic, quarry.

In the Middle Jurassic succession of Central Sardinia are significant ore deposits of kaolinitic clays that were extensively exploited in open quarries during the last century (Marini et al., 1991). Presently the extractive activity is still ongoing only in the Funtana Piroi area (Escalaplano). The ores are usually located in the intermediate part of the Bajocian-Bathonian Genna Selole Formation (Dieni et al., 1983; Costamagna, 2015). This latter is a continental to transitional unit at the most 80 m thick and passing upwards to the marine dolostones of the Dorgali Formation. The Genna Selole Formation usually rests unconformably over the weathered Variscan metamorphic basement and is built by three lithofacies: a lower one made up of quartzose rudites and arenites, an intermediate one made up of fine sandstones, siltstones, and claystones, and an upper one of alternations of sandstones, carbonaceous clays, and carbonates. This latter lithofacies represents the transition to the marine environment. The clay ores are located in the intermediate lithofacies of the Genna Selole Formation, formerly known as “Sarcidano Claystones”: it is characterized by a repeated sequence of illitic-kaolinitic clayey horizons interbedded with minor levels of pyritic-carbonaceous clays and scattered siltitic-arenaceous beds. The clay formation is featured by the following crystalline phases: kaolinite, open illite, quartz, and subordinate mixed phyllosilicates layer and traces of feldspars (k-feldspars and plagioclase), dolomite, pyrite and smectite. The origin of these minerals is connected to the supergenic alteration of the metalavas and the metavolcanoclastic units of the Variscan metamorphic basement (kaolinization of feldspars and replacement of chlorite with illite). This alteration process probably developed during intermittent emersion times occurring along the Permian-Triassic period. The clayey minerals thus formed accumulated in the Jurassic deltaic-lagoon basins of the borders of the Middle Jurassic Barbagia structural high (Costamagna, 2016) in central Sardinia. The productive lithological unit crops out right below the ledges of the “Tacchi” area, where several carbonate highplains form plateau covering the ore and preserving it from erosion. The sedimentary basin that is the object of exploration and exploitation is roughly ellipsoidal and has been estimated to be about 35 to 40 km long and 20 km wide. New surveys and analyses are now in progress to evaluate the mining potential of the remaining deposits. Samples have been collected along the old quarry faces and the exposed sections were scrutinized. The results expected, if positive in quantity and quality, could prove the possibility of a wide-scale reprise of the mining activity.

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## Geological and mineralogical investigation of the S'Aliderru bentonite deposit

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Keywords: Sardinia, bentonite.

Bentonites are a group of rocks formed essentially by smectites, mainly belonging to the Montmorillonite - Beidellite series. Bentonites derive from the alteration of volcanic and/or sedimentary rocks, with a prevalent siliceous-vitreous component, by aqueous fluids that operate at temperatures between 90°C and 120°C. During the alteration, chemical elements are remobilized and the composition and structure of the minerals are modified. The resulting mineral assemblage depends on the nature of the protolith and the composition of the altering fluids (Cuadros et. al., 1999). Bentonites have a wide range of properties (CEC, thixotropy, swelling, viscosity, water absorption) which make them a very important industrial mineral, which are periodically tested also by the EU for the possible inclusion in the list of critical raw materials. The aim of the present study is to investigate the genesis of the S'Aliderru deposit, located in north-western Sardinia (Italy), which represent one of the largest bentonite deposits of the Mediterranean area. The bentonite formed at the expense of arc-related Cenozoic tuff and ignimbrites products. From fieldwork, distinct bentonite horizons were identified, belonging to multiple pyroclastic flows that were progressively emplaced in a pull apart basin hosted in the Mesozoic carbonate basement. The occurrence of travertine bodies and conglomerate and sand lenses hosted in the pyroclastic sequence suggest that the deposition and alteration took place in a marine-transitional environment. Mineralogical and petrographic analyses on several samples collected in the S'Aliderru deposit allowed to classify the bentonites into four classes and to discriminate the featuring minerals of the other lithologies. Petrographic analyses confirmed that the alteration of the volcanic glass into clay minerals occurred in a marine environment, but the presence of barite as well as of other phases suggests that low-temperature hydrothermal fluids also contributed to determine several peculiar features of this deposit.

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## Fluoride removal from water by Layered Double Hydroxides (LDHs)

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*Keywords:* layered double hydroxides, sorption processes, defluoridation.

LDHs are natural and synthetic minerals with general stoichiometry  $M^{2+}_{1-x}M^{3+}_x(OH)_2(A^{n-})_{x/n} \cdot mH_2O$ , where  $M^{2+}$  and  $M^{3+}$  are bivalent ( $Mg^{2+}$ ,  $Zn^{2+}$ ,  $Ca^{2+}$ , etc...) and trivalent ( $Al^{3+}$ ,  $Fe^{3+}$ , etc...) cations, respectively, and  $A^{n-}$  are anions ( $CO_3^{2-}$ ,  $SO_4^{2-}$ ,  $Cl^-$ ). The LDHs structure consists of octahedral brucite-like sheets positively charged as a consequence of the partial substitution of bivalent metals with trivalent ones, alternating with negative interlayers containing anions and variable quantity of water (Dore & Frau, 2019 and references therein). Thanks to their structure LDHs are able to remove contaminants from solutions. As an instance, both natural and synthetic LDHs can remove dissolved anions ( $F^-$ ,  $Sb(OH)_6^-$ ,  $HAsO_4^{2-}$ , etc.) through the anion exchange or by rehydration after calcination (Ardau et al., 2013; Dore & Frau, 2019 and references therein). Moreover, also cations (Pb, Zn, etc.) can be removed by adsorption on surface or coprecipitation (Frau et al., 2020 and reference therein). Another advantage of LDHs is the possibility to be re-used for several cycles after regeneration.

Fluorine is an essential element with positive effect on human health, however, the consumption of high concentration of fluoride (for long time) represents serious health hazard (e.g., dental and skeletal fluorosis, neurological disorder etc.). The regular consumption of water with fluoride concentration above the limit set by the World Health Organization ( $F = 1.5$  mg/L; World Health Organization, 2011) is a current concern affecting about 200 million people worldwide.

In the framework of the Horizon2020 FLOWERED project (de-FLuoridation technologies for imprOving quality of WatEr and agRo-animal products along the East African Rift Valley in the context of aDaption to climate change), LDHs with different compositions have been synthesized, with a coprecipitation method at constant pH, to assess the LDHs fluoride removal capacity from solutions. For this purpose, calcined and uncalcined LDHs were used to carry out sorption experiments in batch mode and column tests. Waters with different chemical compositions have been used to assess the competition effect of coexistent anions in solution.

Results show that LDHs, especially calcined ones, effectively remove fluoride from solution, up to 43 mg of fluoride per g of sorbent, and encourage further investigation. Carbonate species, especially  $CO_3^{2-}$ , significantly decrease the LDHs fluoride removal capacity. Next study will be addressed to assess the most suitable experimental conditions (solid-liquid ratio, flux of solution in column tests, etc.) in order to obtain the best LDHs fluoride removal capacity.

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## **Study of a Quaternary fluvial-estuarine deposit at the mouth of the Tensift River, Souiria Laqdim, Morocco**

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*Keywords:* sedimentary rocks, clay minerals, X-ray diffraction.

This research was conducted on a Quaternary fluvial-estuarine deposit near the mouth of Tensift in the Souiria region, which is part of the coastal meseta and is located 30 kilometers south of the Moroccan city of Safi on the Moroccan Atlantic coast.

Physicochemical and mineralogical analyses were performed on samples collected along a stratigraphic log, including X-ray diffraction, calcimetry, and a petrographic study of thin sections, with the goal of determining the variation in mineral, clay, and carbonate percentages along the log.

The log is composed of flowing layers from the bottom to the top: top marl, marly sandstone, alternating sandstone and conglomerate, laminated sandstone, and lastly massive sandstone.

The percentage of calcium carbonate increases from the base to the layer of alternation between sandstone and conglomerate, where there is a slight decrease.

X-ray diffraction revealed the existence of clayey, non-clayey, and carbonated minerals such as smectite, kaolinite, vermiculite, illite, diopside, anorthite, aragonite, dolomite, and finally calcite. Some of these minerals are evidence of a calm coastal environment and hot and arid paleoclimate.

Petrographic analysis of thin sections revealed the presence of quartz, biotite, altered volcanic debris, iron oxide, and bioclasts, particularly algae, indicating a shallow environment, gastropods, and ostracods.



## Furfural (C<sub>5</sub>H<sub>4</sub>O<sub>2</sub>) encapsulation and release by ZSM-5 zeolite for sustainable treatment in agriculture

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Keywords: zeolite, furfural, ZSM-5.

Widespread application of synthetic nematicide on the crops aimed to fight nematode parasite could be a threat to human health and overall environmental quality. Most of synthetic nematicides have been withdrawn from the market, due to their toxicity. This had led to looking for a non-chemical alternative which must be equally effective and eco-friendly, derived from natural materials, aiming to reduce synthetic pesticide input. Recently, has been proved that an aldehyde, namely furfural (C<sub>5</sub>H<sub>4</sub>O<sub>2</sub>) is an efficient nematicide, thus representing a good candidate to prevent and treat plant and vegetation parasite and disease in agriculture (Kabbour & Luque, 2020). This organic compound derived from a variety of agricultural products including corn, oats, wheat, bran, and sawdust could limit and contrast the use of synthetic and environmental persistent pesticides. The present work aims to report the encapsulate furfural molecules into microporous alumina-silicate matrices (ZSM-5 zeolite) to obtain a controlled release nematocidal biomaterial as a final target. The selected adsorbent is cheap and available on the market, it's commercial as-synthesized hydrophobic ZSM-5 zeolite (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 500) in ammonium form from Zeolyst International. Our interest was focused on the study of type and strength of the host-guest interactions which take place between the zeolite (with the highest adsorption and best release performance) and aldehydes, in order to explain the mechanisms which control the adsorption and the desorption. X-ray powders patterns were collected before and after adsorption on a Bruker D8 Advance diffractometer equipped with SOL-X detector. Thermal analyses (TG and DTA) were performed in air up to 900°C at 10°C/min. This combined study allowed us to: I) programme the maximum adsorption capacity of hydrophobic ZSM-5 zeolite against molecules of furfural; II) localise the furfural molecules in the zeolite channel system; III) probe the interactions between the adsorbate and the zeolite framework; IV) evaluate the release of the encapsulated molecules in gas phase. Results obtained indicate ZSM-5 as an interesting material for nematode pest management. ZSM-5 may help improving environmental protection while minimizing pesticide consumption and implement agricultural treatment effectiveness.

Project funded under the National Recovery and Resilience Plan (NRRP), Mission 04 Component 2 Investment 1.5 – NextGenerationEU, Call for tender n. 3277 dated 30/12/2021, Award Number: 0001052 dated 23/06/2022.

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## **Alkali-silica reaction in commercial high-strength concrete: role of mineral aggregate fraction on fracture mechanisms**

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*Keywords:* alkali-silica reaction, X-ray microtomography, image analysis.

Alkali Silica Reaction (ASR) is one of the most deleterious pathologies of concrete which impairs its durability with relevant economic and social impact. The damage is detected in form of extensive cracking and expansion in presence of secondary reaction products. Despite the large body of literature on the subject, some crucial open questions related to the triggering mechanisms, its evolution and impact on material performance still remain.

The process is described as the reaction of the alkaline pore solution of the concrete with the silica present in the mineral fraction which is added as aggregate. A product, commonly described as ASR gel, which possesses different degrees of crystallinity, is produced, and the process is accompanied by the generation of stress. This leads to the formation of cracks in the mineral grains and the cement paste, which are eventually filled with the ASR gel.

It is accepted that one critical parameter for the process to develop is the availability of silica, therefore, the reactivity of the mineral respect to the alkaline environment. It is thus apparent that the assessment of the ASR susceptibility of the mineral fraction used as aggregate in concrete is of paramount practical importance. The methods for the assessment of the reactivity of the mineral are based on the measurement of damage, either directly or indirectly (DRI, PDI, SDT, ASTM C1260, ASTM C1293 and many RILEM recommendations, developed in TCs 191, 219 and 258) and many efforts are devoted to their improvement (Mohammadi et al., 2020).

In order to gain insights into the role that the nature of the mineral aggregate fraction plays in determining the extent of the damage and the mechanical behavior, samples of commercial high-strength concrete affected by ASR, exposed to different environmental and life service conditions, have been investigated. This study combined optical microscopy, SEM/EDS, XRD and in-situ X-ray computed microtomography measurements performed under uniaxial compressive strength tests. The latter approach allowed for the investigation of the microstructural properties and to follow the formation and evolution of cracks within the imaged volume. The identification of crack propagation patterns and the volume distribution of the ASR damage, made possible thanks to advanced algorithms for image analysis, were related to the mineralogy of the aggregates in the context of a model for the ASR weakening mechanism. This information is of relevance to implement strategies for the design of concrete and for the improvement of its durability under severe life service conditions, enabling a more reliable prediction of their remaining life service.

Mohammadi A., Ghiasvand E. & Nili M. (2020) - Relation between mechanical properties of concrete and alkali-silica reaction (ASR); a review. *Constr. Build. Mater.*, 258, 119567. <https://doi.org/10.1016/j.conbuildmat.2020.119567>.

## **New conservative treatment based on a functionalized phosphate for silicate rocks: the study-case of the pyroclastic tuffs**

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*Keywords:* chemical treatment, porosity, permeability.

Pyroclastic tuffs generally show a high compositional heterogeneity due to the variable presence of ashes, pumice, cognate fragments, juvenile- and xenoliths, crystal- and rock-clasts. This heterogeneity results in high porosity which can even reach 50% vol. in the poorly welded, pumice-cinerite-rich facies. Such a high porosity implies that pores are likely to be interconnected allowing fluids (i.e., aqueous solutions) circulation from the external environment, and leading to chemical-mineralogical and physical degradation. Considering the great use of pyroclastites as a building/decorative material in historical and contemporary times, due to their excellent workability, the study of possible protection interventions from the attack of atmospheric agents becomes essential. The research on the stone restoration has made great advances in understanding degradation processes and in finding effective chemical and natural products to protect/consolidate the materials, but the main efforts have been focused on purely or partially carbonate stones as marbles, limestones, calcarenites, sandstones (Columbu et al., 2017; Aragoni et al., 2021). Little has been done for silicate rocks which, in general, are less affected by degradation problems. This work intends to advance a specific study to identify innovative and effective products in the protection of pyroclastic rocks. The research started by testing an organophosphate ammonium salt, which was specifically synthesized and characterized by microanalytical and spectroscopic means.

Various techniques and methodologies were used (polarized light microscopy, SEM-EDS, XRD, helium pycnometry, mercury porosimetry, vapor permeability, Point Load Test, colorimetry) with the aim of, (i) defining the composition and microstructure of not-treated natural materials, (ii) understanding the interactions between the lithoid substrate and the inorganic phosphate to reveal the chemical-physical exchange and the possible formation of new bonds that can effectively decrease the water absorption and saturation index without modifying the physical-mechanical characteristics. The laboratory results, determined pre- and post-treatment, show a reduction in water open porosity ( $D$  range = ~10-25%), with a decrease ( $D$  = ~50%) of permeability to the vapor phase. Saturation index shows a decrease between 7% and 21% in the treated samples. Considering the compositional heterogeneity, the mechanical resistance remains substantially unchanged; PLT normalized strength index varies (in the case of welded samples) from 0.8 and 1.33 MPa in not treated specimens and between 0.88 and 1.02 MPa in treated specimens. All treatments results in negligible chromatic variations ( $DE_{CIE} < 3$ ). This last aspect is very important in the application and use of protective products because it respects the physical-mechanical behavior of the stone substrate without altering their intrinsic characteristics.

Aragoni M.C., Giacopetti L., Arca M., Carcangiu G., Columbu S., Gimeno D., Isaia F., Lippolis V., Meloni Navarro Ezquerria A.P., Podda E., Rius J. & Pintus A. (2021) - Ammonium monoethyloxalate (AmEtOx): a new agent for the conservation of carbonate stone substrates. *New J. Chem.*, 45, 5327-5339. <https://doi.org/10.1039/D0NJ06001A>.

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## Bentonite Geopolymers: a possible reuse of burned foundry bonding clays

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*Keywords:* foundry clays, geomaterials, industrial clays.

This work focuses on exploring the potential reuse of foundry bonding clays, specifically bentonite, as a raw material to produce geopolymers. Foundry clays, including bentonite, are extensively used in the casting industry for their excellent binding properties. However, after their service life in the foundry, these clays often become waste materials. This study investigates the feasibility of transforming bentonite bonding clays into geopolymers, which are environmentally friendly alternatives to traditional cement-based materials.

The reuse of bentonite bonding clays offers several advantages, including waste reduction, cost-effectiveness, and the utilization of a readily available resource. The study focuses on evaluating the geopolymerization process, which involves activating the bentonite clays through an alkaline activation process. This process chemically transforms the clay into a solid binder with improved mechanical properties suitable for various construction applications. Laboratory experiments are conducted to investigate the effects of varying solid precursors, such as different types of burned bentonite clays and curing conditions, on the geopolymerization process. Mechanical tests are performed to evaluate the performance of the resulting geopolymers. Additionally, microstructural analysis techniques, such as X-ray diffraction (XRD) and scanning electron microscopy (SEM), are employed to study the mineralogical and morphological characteristics of the geopolymers.

Preliminary results indicate that bentonite bonding clays can be successfully transformed into geopolymers with desirable mechanical properties. The alkaline activation process effectively activates the clay particles, leading to the formation of a solid binder matrix. The compressive and flexural strengths of the geopolymers exhibit promising values, comparable to or even surpassing those of conventional cement-based materials. The microstructural analysis reveals the formation of a dense and homogenous structure within the geopolymers, indicating their potential for durable applications.

The findings of this study suggest that burned bentonite bonding clays can be effectively repurposed as a valuable raw material to produce geopolymers. This alternative utilization offers a sustainable solution for managing and reducing the environmental impact of foundry waste. The use of geopolymers derived from bentonite clays could contribute to the construction industry's efforts to minimize reliance on traditional cement, which is associated with significant carbon emissions.

The results of this study contribute to the body of knowledge regarding the potential reuse of foundry bonding clays and the application of geopolymers in sustainable construction practices. Further research and development are warranted to optimize the geopolymerization process, explore different formulations, and assess long-term durability to ensure the practical implementation of bentonite geopolymers in the construction industry.

## **Poison Block: evidence of As-Sb mineralization waste used as aggregate in Portland Concrete in Matra Mining District (Corse, France)**

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*Keywords:* tailings, building material, reuse.

This work focuses on the investigation of the utilization of As-Sb mineralization waste as aggregate in Portland Cement in the Matra Mining District (Corse). The study aims to provide evidence of the presence of toxic elements and potential environmental hazards associated with the usage of this waste material in cement production.

The Matra Mining District in Corse is known for its rich mineral deposits, including arsenic (As) and antimony (Sb). These elements are often present in various mineralization wastes generated during the mining and extraction processes. During field research conducted in the Matra Mining District, we observed that several structures belonging to mining facilities have been constructed using As-Sb mineralization waste as aggregate in cement production. Considering that approximately 0.8 m<sup>3</sup> of aggregate is required for every 300 kg of cement, it is evident that the practice of utilizing mining waste and by-products can serve as a viable solution to reduce the volume of these waste geomaterials.

This study employed a combination of field surveys and laboratory analyses to assess the extent of As-Sb mineralization waste usage in Portland Cement production within the Matra Mining District. Field surveys were conducted to identify the cement plants that employed this waste material and to collect representative samples for further analysis.

Laboratory analyses involved the characterization of the mineralization waste and its potential release of toxic elements. Techniques such as X-ray fluorescence (XRF) and scanning electron microscopy (SEM) were employed to determine the mineralogical composition and elemental distribution. In future we want to perform a leaching test to evaluate the potential release of toxic elements from the waste material.

The results indicated that several cement plants within the Matra Mining District utilized As-Sb mineralization waste as aggregate in Portland Cement production. The mineralization waste exhibited significant concentrations of As and Sb, with variations depending on the specific waste source.

The implications of these findings highlight the need for careful consideration of the usage of As-Sb mineralization waste in local cement production. Although it offers a promising solution for waste management, its potential impact on the environment and human health should be thoroughly evaluated. Mitigation measures such as appropriate waste treatment and monitoring systems should be implemented to minimize the release of toxic elements and ensure sustainable cement production practices.

This study provides valuable evidence of As-Sb mineralization waste usage in Portland Cement and emphasizes the importance of conducting comprehensive assessments to ensure the safety and environmental sustainability of such practices. The findings contribute to the understanding of the potential risks associated with the incorporation of mining waste into construction materials, enabling stakeholders to make informed decisions regarding waste management strategies in the Matra Mining District and similar regions.

## **EcoCalMix Project (Ecofriendly Mix based on Calabrian clay for tanning applications): the use of local clays for eco-sustainability in the tanning sector**

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*Keywords:* clayey materials, anti-microbial performances, leather industry, sustainability.

The tanning sector and its supply chain, to be competitive in the current market, needs to invest in new technologies to improve processes and product quality while respecting the environment.

In this context, the EcoCalMix Project (Ecofriendly Mix based on Calabrian clay for tanning applications) funded by Calabria Region in the frame of the POR Calabria 2014-2020 (<https://www.ecocalmix.net/>) aims to develop a non-invasive and environmentally sustainable product to be applied during the tanning process starting from innovative formulations based on clay nanoparticles with multifunctional characteristics (anti-microbial, fillers, etc) and low environmental impact.

The research project involved in particular the finishing phase of leather processing. After a preliminary evaluation of the data already present in the literature and an initial selection of materials based on the know-how of the partners, the selected clays, available in the Calabrian territory, have been fully characterized and applied in leather treatments. In particular, granulometric analysis of samples were firstly performed followed by mineralogical analysis on bulk clay samples other than clay speciation. The latter allowed the recognition of clay minerals abundances in the deposit. Moreover, chemical analysis by XRF and ICP-MS were also carried out. The final phase of the project was aimed at optimizing the best solution highlighted during the application tests on selected leather skin types. At the same time, performances in terms of antimicrobial activity were also verified. Dissemination activities and exploitation of results accompanied the development of the entire project together with the necessary planning, management and monitoring activities.

The achieved results allowed the development of a competitive product designed for the tanning sector, having access to a new sustainable market interested in environmental and economic aspects (reduce the economic and ecological costs of transport and distribution due to the availability on the territory and the ease of obtaining clayey raw materials) and at the same time guaranteeing multifunctional properties.

Moreover, the use of these clayey raw materials would result in a significant reduction in the use of organic-based chemical compounds normally employed in some phases of the process (tanning or finishing) with a consequent reduction of their emissions.



## Waste food-packaging plastic as a possible additive modifier in asphalt mixtures

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*Keywords:* waste food-packaging plastic, recycling, sustainable roads.

Plastic waste generation has become one of the main problems worldwide. Particularly, packaging plastics represent the most generated plastic waste by the industrial sector. Regarding food-packaging typically used for products such as juice, water, and milk, the plastic waste is obtained through the maceration process, which allows the separation of aluminum foil, paper, and plastic. Due to this process, paper and aluminum foil can be reused, while plastic must be disposed. The aim of this research study is to reuse the disposed plastic material coming from the maceration processes as additive modifier to produce Polymer Modified Asphalt (PMA) mixtures. The research was carried out in two stages, chemical and mechanical analyses, respectively.

The chemical analysis was performed, firstly, to understand whether the temperature (from 160 to 170°C) used during PMA production is high enough to properly melt the waste plastic or not, and, secondly, to study the chemical composition of the plastic used. To assess these key points, a Differential Scanning Calorimetry (DSC) test was performed to identify the melting points of the plastics in the analysed material. The Fourier-transform infrared (FT-IR) spectroscopy and X-Ray Diffraction (XRD) analysis were performed to assess the type of plastics which compose the reused material. The analysis of the mechanical characteristics was performed by comparing the PMA mixtures, containing two percentages of reused plastic (5% and 10% by the aggregate weight), with two Hot Mix Asphalt (HMA) prepared with 3.5% linear- and -radial Styrene-Butadiene-Styrene (SBS) modified asphalt, using the SuperPave Indirect Tensile Test (IDT) performed at 10°C. The results obtained by XRD and FT-IR spectroscopy confirmed the heterogeneous composition of the analysed plastic, which is mainly composed of Polyethylene (PE), High-Density Polyethylene (HDPE), Low-Density Polyethylene (LDPE), Polypropylene (PP), Polyethylene terephthalate (PET), and Polystyrene (PS). The DSC highlighted that the melting points of the identified type of plastics are all compatible with the temperature required to properly prepare PMAs. The mechanical analysis showed that the mixtures containing 5% of waste plastics behave quite similarly to the ones containing 3.5% linear SBS modified asphalt at the failure stage, and the permanent deformation proneness is improved. The 10% of waste plastics content instead led to improving the bitumen absorption while decreasing PMA workability. In conclusion, when the plastic content increases (10%), PMAs do not achieve the required standard parameters in terms of air void content, leading to an early failure of mixtures.

## Potential and industrial uses of basalt as a georesource in the perspective of a circular economy

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*Keywords:* glass and basalt fibers, performance, fusion.

Basalt is a basic volcanic rock with precise geochemical and petrographic characteristics. However, the term “basalt” is often used to refer to volcanic rocks from ultra-basic (i.e., basanites, undersaturated in silica) to basic (i.e., basalt, andesitic basalt), to basic-intermediate (i.e., basaltic andesite, andesite), sometimes also with transitional to alkaline affinities (e.g., trachybasalt).

Most of the Sardinian basalts belong to the Plio-Pleistocene anorogenic volcanism (typically intraplate), but there are basalts belonging to the Oligo-Miocene orogenic volcanic cycle (38-15 Ma) with calcalkaline affinity. Basalt has been used for millennia as a building or ornamental material in the Nuragic, Punic-Roman, medieval (e.g., Romanesque architecture) phases, demonstrating excellent resistance to chemical-physics decay. In the modern age it has been quarried and exploited on an industrial level, also for other purposes (e.g., in the production of anti-abrasive coatings and tiles molded from the melt, as an aggregate in concrete, for railway and road ballasts, street furniture, etc.). Basalt has also been the object of study and research for its use as a raw material to produce fibers to replace common glass fibers (Dhé, 1923). Several European and American researchers continued with the experimentation in the extrusion of basalt for several industrial application and especially for military and aerospace uses. The chemical-physical characteristics and the lower production costs make basalt suitable for the production by extrusion of continuous filaments of various diameters (9-24  $\mu\text{m}$ ), showing, in some respects, better performances than glass fibers.

The present research aims at studying the potential to produce fibers of basaltic rocks with various geochemical compositions outcropping in the volcanic plateau of central Sardinia, where today they are mainly extracted as building/ornamental materials. The waste produced during basalt extraction have been studied by XRF, XRD, SEM-EDS, TGA-DSC, to assess their potential reuse in the production of fibers. The preliminary results highlight optimal compositional features, responding to the chemical major elements concentration ranges of the common commercial basaltic raw materials. Trials and experimental tests are currently in progress aimed at: i) defining the thermal inertia and the physical-mechanical behavior of basalt at medium-high temperatures of use (up to 700°C); ii) observe the rheoplastic behavior in the proximity of the microstructural softening at high temperatures ( $T > 900^\circ\text{C}$ ); iii) analyze the relationships between the compositional aspects of the different basalt samples and the melting temperatures (close to 1450°C). The final results of the tests, together with other laboratory application tests on the partially and fully processed products, will allow to define the performance characteristics and its effective commercial potential for the production of fibers.

Dhé P. (1923) - Filament composed of basalt. Patent: US 1438428 A, 1921.

## **REDIRECT Project (REDuce REuse Ceramic Tiles): from the circular economy to a sustainable economy**

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*Keywords:* ceramic tiles, sustainability, 4.0 circular business.

The REDIRECT (REDuce REuse Ceramic Tiles) project aims to design, implement and validate a 4.0 Circular Business model both at an operational (manufacturing) and strategic (corporate and business) level. Gruppo Ceramiche Gresmalt (coordinator), Eurit, the University of Modena and Reggio Emilia, the University of Sassari and the University of Calabria have formed a partnership and prepared an industrial research and experimental development project called REDIRECT (REDuce REuse Ceramic Tiles), co-financed by the Italian Ministry of Economic Development (<https://www.redirect.gresmalt.it/>). The project, which was launched in October 2020 with a planned duration of 36 months, was granted a 3-month extension due to the pandemic and will therefore continue until December 2023. Gresmalt and Eurit are important players in the ceramic industry's value chain, the former representing the tile manufacturing industry and the latter the mining industry which supplies raw materials to the ceramic sector. The two companies are working together with the universities on the design, implementation and validation of a new Circular Enterprise 4.0 model that integrates sustainability best practices with the digital transformation of production facilities using Industry 4.0 technologies. For this purpose, the REDIRECT Team has adopted a definition of circular economy that is more suitable for the industrial sector from an organisational perspective, i.e. a set of organisational planning processes for the manufacture and delivery of materials and products with maximum utility for customers through the rational use of available resources.

REDIRECT's approach is therefore an alternative to the process-slowness paradigm which involves manufacturing and consuming less in order to reduce environmental impact while giving ecosystems time to regenerate. The same goal of the classical vision of the circular economy is instead achieved through an operational paradigm that combines the criterion of efficiency, i.e. maintaining the same level of production while using fewer resources (doing the same with less), and productivity, i.e. producing more with the same quantity of resources (doing more with the same).

REDIRECT also plans to use the digital transformation of processes as an enabling factor to switch from the traditional linear business model typical of the mining and ceramic industries to an innovative circular business model in which the two companies' value propositions include the four dimensions of sustainability: environment, society, economy and technology. This multidimensional approach to circularity aims to link up with the pillars of sustainable development in order to transform the ideal narrative of the circular economy into the more concrete context of sustainability, which also involves the use of metrics and evaluation systems for environmental, socioeconomic and technological performance. These include, for example, the rediscovery of raw materials at deposits in Calabria, Tuscany and Sardinia and their experimentation, an outcome that had not been foreseen in the initial research phase two years ago but which, in the light of the current interruption of supplies from Ukraine, could prove extremely beneficial to the Italian ceramic industry.

## **Evaluation of residual tension in enamelled large porcelain stoneware slabs through chemical and mineralogical phase evolution and SEM microstructural analysis**

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*Keywords:* porcelain stoneware, engobes, fusibility.

The technology of porcelain stoneware revolutionized the ceramic sector bringing innovation, not only in the production process, but also in the final product, which became to be employed in for new applications. Today, porcelain stoneware is the best-selling ceramic material in the world. In recent years, with the advent of new technologies and production plants, there has been a huge leap in the range of formats which has led to production of the so called “large slabs”. The development of ceramic products with large dimension induced the redefinition of interior architecture. Large porcelain stoneware ceramic slabs are in fact used as coating for doors, wardrobes, kitchen doors, kitchen and bathroom tops. From the large formats it is then possible to obtain a whole series of smaller formats through the use of different cutting techniques. One above all is that of the “split cut” which consists in engraving the slab coming out of the kiln and breaking it along the groove. The large slabs production, in addition to bringing many advantages, has however to face some issues in the manufacturing steps, especially in relation to the possible stress and tensions that could occur during cooling. It has been observed that excessive tension inside large slabs induces breakage and defects at the moment of split cutting. Hence the need to understand the origin of the stress states inside the large slabs that cause them to break when cut. In particular, it was observed that, keeping the same firing cycle and the same ceramic body, ceramic products made with different types of engobes showed different behaviours when cut. This evidence therefore led to the formulation of a hypothesis according to which the origin of the problem could lie in the chemistry and mineralogy of the engobe used. A series of engobes realized with different formulation has been deeply analysed from chemical and mineralogical point of view before and after firing in order to evidence the phase evolution during the production cycle. The results obtained from XRF and from Rietveld refinement on the pristine and fired samples indicates a rather complex picture in which the origin of the tensions inside the large slabs may be linked to the degree of fusibility of the engobe used. The large slabs were also investigated with SEM and EDS analysis with the aim to observe the microstructure of these materials. These analyses are still in progress and the preliminary results showed the presence of a layer between the engobe and the ceramic glaze well formed in the slab showing excessive tension. These preliminary results highlight complex situation indicating that the excessive tension inside large slabs could arise from diverse factors. In fact, this contribution is part of a wider work aimed at formulating a model considering all the possible variables in order to predict the behaviour of engobes once used in large slabs.

## **S19.**

# **Elemental behaviour for a sustainable future: geochemistry in petrological, environmental and industrial research**

### *CONVENERS AND CHAIRPERSONS*

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## Land use effects on soil characteristics in Fiuggi basin ecosystem

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*Keywords:* chestnut forest, land use, soil quality.

Chestnut forest ecosystems cover an area of about 35,000 hectares in the Lazio Region. Compared to the conventional context, the Fiuggi chestnut forest provides an “unconventional” ecosystem service, produced by the complex interaction “chestnut coppice-litter-soil.” The forest ecosystem has been credited with a direct responsibility for enriching the waters with humic substances with remarkable therapeutic properties.

The Fiuggi basin is and its delicate hydrogeological balance are extremely sensitive to the geological, hydrogeological and ecological characteristics of the area. The particular susceptibility and fragility of the natural system is due to the high variability of vegetation cover types. In this specific case, the complex ecosystem involved contains more than just chestnut forests: the complex ecosystem that lies on the aquifers is characterised by the presence of an extensive wooded area overlying the aquifers, of the conterminous natural grasslands and a meadow managed for recreational activities.

This research aims to study how different land covers and land uses influence the chemical, physical and biochemical properties of the soil. In particular, it studies the effect of different types of cover (natural grassland - chestnut forest - managed grassland) on soil quality in Anticolana Valley ecosystem.

To this end, soil sampling was performed identifying 3 parallel transects and 9 different samples were taken on each transect. Results that will be shown and discussed include: soil physico-chemical characteristics, elemental and isotopic composition of distinct fractions of carbon (and nitrogen) and membrane phospholipid analysis (EL-FAME) to characterize the soil microbial community from the three areas.



## **Describing the environmental impact from Construction and Demolition Waste (CDW) pollutants release through in-deep mineralogical and geochemical analyses**

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*Keywords:* CDW, leaching, ceramic.

Construction and Demolition Waste (CDW) unsorted-waste streams are characterized by a strong heterogeneity which can sometimes lead to contaminant releases above the legal limits for recovery. In the Mediterranean countries, compared to a pure concrete-derived waste stream, the impurities are for the largest part composed of ceramic-based materials. At the same time, soluble sulphate content and heavy metals released seem to be strongly influenced by the amount of clay brick inside CDW (Barbudo et al., 2012). Beside clay bricks, other types of ceramic building materials are usually found, such as perforated clay bricks, roof tiles, gres, sanitary-porcelains, floor tiles, ancient and industrial clay bricks. Furthermore, the presence of residual cement paste enhances the pH values, which has been proved to promote the leaching process (Englesen et al., 2010). In our study we conducted an in-depth chemo-mineralogical characterization by analyzing various CDW from two regions in Italy, namely Emilia Romagna (Ferrara) and Umbria (Perugia). The analysis was carried out using X-ray fluorescence (XRF), inductively coupled plasma mass spectrometry (ICP-MS), and X-ray diffraction (XRD) with Rietveld quantitative phase analysis. In addition, in all samples carbon (C) and sulphur (S) contents and, for the first time, the relative isotopic signature ( $^{13}\text{C}/^{12}\text{C}$ ;  $^{34}\text{S}/^{32}\text{S}$ ), have been measured through elemental-isotopic ratio mass spectrometry (EA-IRMS). Leaching analyses, following UNI-EN 12457-2:2004, have been conducted on pure samples and on materials with 50 wt.% mixed CDW hydrated-cement-paste. The leachate solutions have been analyzed with ICP-MS after 24 hours since the start of the leaching. The concentration of contaminant releases is compared with the legal limits that are going to be introduced in Italy in 2023 (End of Life decree).

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## Soil organic carbon pools in managed temperate forests: two case studies in the Apennine chain of the Emilia-Romagna Region (Northern Italy)

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Keywords: soil, forest, carbon.

Forest soils are an important component of the global C budget as they store most of total organic C contained within the terrestrial ecosystems. Several pedogenetic factors can drive the C stored in forest soils, such as vegetation type and climate. Consequently, changes in these factors may affect soil C pool and significantly impact on global carbon cycling. In the view to monitor the soil organic C (SOC) in forest ecosystems, SuoBo project financed by the Rural Development Programme (RDP) of Emilia-Romagna Region (Italy) aims to assess and preserve the quantity and quality of SOC in mountainous forest ecosystems located on the Apennine chain of the Emilia-Romagna Region. Our specific goal was to explore the quantity of SOC pools in 2020 and 2021 within two managed forests: a mixed forest of Branchicciolo farm (BRA), located at about 225 m above sea level (a.s.l.) and a chestnut forest of Beghelli farm (BEG), located at about 550 m a.s.l. Soil samples were collected at 0-15 cm and 15-30 cm depths. Each sample was analyzed for the elemental contents of the total (TC) and organic (OC) carbon pools and the relative isotopic ratios ( $\delta^{13}\text{C}_{\text{TC}}$ ,  $\delta^{13}\text{C}_{\text{OC}}$ ). According to the results, in one year the BRA soil recorded sharp decrease in TC and OC fractions content and their relative isotopic signatures became less negative. These findings indicated a preferential loss of organic matter few transformed. On the contrary in BEG soil both TC and OC fractions and the related isotopic signatures unchanged. The lowering of OC in BRA occurring in one year might be attributed to several reasons, excluding erosional processes being BRA site located in flat area. Factors affecting organic matter stabilization/mineralization should be instead taking into consideration. The decrease of SOC in BRA from 2020 to 2021 might be due to the different mean air temperatures occurring at the two altitudes, which enhanced in the 2021, as it was recorded as one of the warmest years since then. Specifically, the generally lower mean air temperature that occurs in BEG (14.2°C) compared to BRA (13.8°C) in 2021 reduce SOC mineralization processes by microbial community. In addition, BEG showed a larger amount of clay compared to BRA which further limited SOC mineralization. In fact, in BRA soil samples the ROC, i.e., the most stable C pool with the high turnover decrease from 2020 to 2021, whereas in BEG soil samples, remained stable. Finally, in a view of forest SOC conservation within the global change scenario, the present study highlighted the necessity to act forest practices for SOC preservation especially where the pedo-climatic conditions are less suitable for C stabilization processes.

## Major ions and trace element concentrations in rainwater of Palermo (Sicily, Italy)

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*Keywords:* major ions, trace elements, urban pollution.

The chemical composition of the atmospheric deposition was studied in Palermo City (Sicily, Italy) from January 2015 to January 2016. The research was carried out by collecting rainwater samples at four urban sites and one site in a semi-rural area. For each monitoring site, an average of 23 samples were collected on a fortnightly basis, for a total of 115 samples. pH and Electrical conductivity were between 5.2 and 9.4 (median 6.65) and between 11  $\mu\text{S cm}^{-1}$  and 446  $\mu\text{S cm}^{-1}$  (median 46  $\mu\text{S cm}^{-1}$ ), respectively. Major ions concentrations were measured by IC; total alkalinity, expressed as  $\text{HCO}_3^-$ , was measured by titration; trace element concentrations were measured by ICP-OES and ICP-MS. Concentrations of major ions followed the sequence  $\text{Cl}^- > \text{HCO}_3^- > \text{NO}_3^- > \text{SO}_4^{2-} > \text{F}^- \gg \text{Br}^-$  for anions, and  $\text{Na}^+ > \text{Ca}^{2+} \gg \text{NH}_4^+ > \text{Mg}^{2+} \gg \text{K}^+$  for cations. High loads of  $\text{Na}^+$  (median 0.177 meq  $\text{L}^{-1}$ ),  $\text{Cl}^-$  (median 0.196 meq  $\text{L}^{-1}$ ), and  $\text{Mg}^{2+}$  (median 0.064 meq  $\text{L}^{-1}$ ) reflected the proximity of the urban sampling sites to the sea coastline. On the other hand,  $\text{nss-SO}_4^{2-}$  (median 0.051 meq  $\text{L}^{-1}$ ),  $\text{NO}_3^-$  (median 0.032 meq  $\text{L}^{-1}$ ),  $\text{NH}_4^+$  (median 0.074 meq  $\text{L}^{-1}$ ), and  $\text{F}^-$  (median 0.002 meq  $\text{L}^{-1}$ ) were mainly from anthropogenic sources.  $\text{HCO}_3^-$  (median 0.111 meq  $\text{L}^{-1}$ ),  $\text{Ca}^{2+}$  (median 0.130 meq  $\text{L}^{-1}$ ),  $\text{K}^+$  (median 0.009 meq  $\text{L}^{-1}$ ), and partially  $\text{Mg}^{2+}$  (nss-fraction) had terrigenous origins. For all major ions higher concentrations were recorded at the urban sites rather than at the semi-rural site. The concentrations of trace elements were determined on two different aliquots of the same samples, one filtered and one unfiltered. Elements such as Fe, La, Ce, Al, Pb, and Ti showed higher median concentrations in the unfiltered aliquot than that in the filtered one, highlighting that the filtration process may lead to an underestimation of the deposition values of less water-soluble trace elements. For example, the median concentrations of Fe were 1.8  $\mu\text{g L}^{-1}$  and 17.6  $\mu\text{g L}^{-1}$  in the filtered and in the unfiltered aliquot, respectively, while for Pb they were 0.09  $\mu\text{g L}^{-1}$  and 0.45  $\mu\text{g L}^{-1}$ , so with differences of even an order of magnitude. With a few exceptions, higher concentrations of trace elements were recorded for the Palermo city monitoring sites than for the semi-rural site, especially for Sn, Cu, Ba, Cr, and B. The scientific evidence produced by the present research highlights the multiplicity of sources for both major ions and trace elements in rainwater samples. Some critical issues regarding common methods of analysis of the trace element concentrations of atmospheric deposition were highlighted and examined. Some questions are still open, such as speciation and solubility of trace elements, chemical transformations during their transport, and estimation of soluble versus insoluble fractions. Future studies, currently in progress, will provide additional information regarding the problems highlighted by the present research.

## **Salinity as a regulator of microbial communities and greenhouse gas emissions in temperate coastal wetlands: a biogeochemical study**

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*Keywords:* temperate coastal wetlands, microbial communities, greenhouse gas emissions.

Freshwater wetlands are an important source of methane, a potent greenhouse gas. However, they can also act as a carbon sink. Organic matter decomposition in wetlands is mediated by various types of bacterial metabolic activities, including respiratory, fermentative, and methanogenic. Temperate coastal wetlands are characterized by the presence of saltwater which can disrupt these processes by promoting the activity of sulfate-reducing bacteria, which compete with methanogens for electron donors. Since sulfate reduction is thermodynamically favorable compared to fermentative processes and methanogenesis, it effectively reduces gross methane production and therefore methane emissions to the environment. While sulfate reduction is a crucial process in coastal wetland sediments, the factors impacting rates and pathways in these settings remain unclear.

To address this gap, we propose new multidisciplinary research on temperate coastal wetlands along the Adriatic coast. Our goal is to determine the influence of salinity on organic matter decomposition and associated greenhouse gas emissions. Specifically, we investigated the link between the microbial community and sulfur concentrations in sediments and water at three sites along a salinity gradient. Core soil samples of 40 cm have been sampled in each location. To investigate the microbial community composition, we used the long-read capability of the Oxford Nanopore MinION to sequence bacterial ribosomal operons from soil samples. Acid volatile sulfides in soils has been assessed with a semiquantitative paper analysis. Sulphate and sulfide concentrations in waters have been measured using a field spectrophotometer.

In sites with high sulfate concentration, the presence of sulfur-reducing bacteria prevails compared to freshwater sites. In these environments, emerge the presence of obligate anaerobic species related to fatty acid degradation, denitrifying bacteria, methane-oxidizing bacteria, and bacteria typical of soils with plant residues. The work sheds light on the structure of microbial communities in wetlands, which is critical for understanding ecosystem processes and complex biological systems like wetlands, with substantial implications for wetland conservation and management, climate change mitigation, and research into biogeochemistry.

## Can crystal imperfections alter petrophysical properties of halite crystals?

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Keywords: rock salt, fluid inclusion, petrophysical properties.

Petrophysical properties of the rock salts have been extensively studied for environmental and economic reasons and for potential applications in several industries such as mining, petroleum, gas storage and waste disposal (Leiter et al., 2021 and references therein). Conventionally, rock salts are considered as homogeneous/pure bodies with low porosity (2.5 to 3.6%), permeability, and density (2.165 g/cm<sup>3</sup>), and their mechanical properties have been tested (at the macro- and meso-scale) using different methodologies such as hydrostatic confining pressure, gas-porosimeter, buoyancy method, (e.g., Lin et al., 2015; Samperi et al., 2020 and references therein). However, there is not sufficient research considering the role of the crystal imperfections at smaller scale (micro- and nano-scale). Their presence causes a modification of the crystals internal structure in term of liquid (e.g., fluid inclusions - FIs), solid (e.g., clay minerals and organic matters) and gas/vapour phase (e.g., fractures). The aim of this work is to investigate through a multidisciplinary approach, how these imperfections could affect and modify the petrophysical properties of two halite crystals belonging to the white and transparent facies and observed in a salt dome from the Crotona Basin (Southern Italy) (Cipriani, 2020). We combine petrographic investigations (optical microscope and Scanning Electron Microscopy) with chemical analyses (Raman Spectroscopy) and we carried out an accurate 3D reconstruction of the halite internal structures using synchrotron radiation X-ray phase-contrast computed tomography. This approach revealed a crucial petrographic difference in both halite facies. The crystal from the white facies, shows an alternation of milky and clear bands: milky bands are enriched in FIs, emit a bright fluorescence under UV light denoting the presence of organic materials and have a porosity between 1 and 13%. On the contrary, clear bands are devoid of FIs, do not emit fluorescence and have a porosity lower than 5%. The analysed crystal from the transparent facies has a homogenous appearance and shows individual FI trails and has a porosity of ~ 2%. These data highlighted the variation in the amount and distribution of FIs and fractures in two distinct facies of halite crystals, both primarily composed of NaCl. All these factor significantly alter the total porosity, which deviates from the literature reported value of 2.5% to approximately 13% in the milky band (white halite facies). This study provide information on how the imperfections can modify the petrophysical properties of the halite crystals and can also affect the rheological behaviour on different scale. Further results of the role of intracrystalline organic matter in estimating total porosity will be also presented. The results of this study could benefit multiple industries by enhancing geological modelling, hydrocarbon exploration, and understanding rock salt behaviour in different conditions.

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## **A fluid inclusion approach to study the evolution of fluids in the north-easternmost part of the Larderello geothermal field (well Sesta 6bis)**

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*Keywords:* fluid inclusion, Larderello geothermal field.

The Larderello geothermal field is a well-known vapor-dominated system, located in southern Tuscany, characterized by the production of superheated steam. Power production started at the beginning of the last century. Many deep wells have been drilled, among which the deep geothermal well Sesta 6bis, located in the north-eastern area of this geothermal field, which reached a total depth of 3921 m. In order to analyse fluid inclusions hosted in quartz minerals, three core samples from three different depths, 2733-2737 m, 3085 m and 3803 m b.l.g., have been selected. Indeed, fluid inclusions are known to be a powerful tool to study and characterize the different fluids that permeated the geothermal reservoir, and their analysis allows the determination of the temperature and salinity.

This work gave the opportunity to study the north-easternmost part of the geothermal system, where a more detailed study of the past circulation in the deeper reservoir was lacking, especially considering fluid inclusion analyses.

In the three samples both primary vapour-rich (V-rich) and liquid-rich (L-rich) inclusions have been found, as well as multiphase and secondary L-rich inclusions. Through microthermometric analyses, homogenization ( $T_h$ ) and first and final ice melting temperatures ( $T_{mi}$ ) were determined. Finally, in order to infer the composition of the gas fraction in V- and L-rich inclusions, Raman analyses were carried out on the vapour bubbles.

Our data track a fluid evolution process, starting from the decrease of the temperature from the primary to the secondary fluid inclusions, which are considered as representative of the present-day fluid actually circulated in the deeper geothermal reservoir. Furthermore, considering the salinities of the L-rich inclusions, variations in this value from one depth to another have been highlighted. On the other hand, multiphase fluid inclusions, found in the shallower sample, are characterized by high salinity values, which can be due to different reasons, such as the influence of a saline brine or a residual fluid after boiling process.



## Partitioning rare Earth element distribution among particulate, colloidal, and truly dissolved fractions: implications for environmental and industrial applications

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*Keywords:* technology-critical elements, volcanic groundwater, distribution coefficient.

In environmental and industrial settings, the distribution and behavior of Rare Earth Elements (REEs) are of great interest due to their unique properties and applications. One critical aspect of understanding REE behavior is distinguishing their distribution among the three main fractions in water systems: colloidal, particulate, and truly dissolved.

Particulate fractions refer to particles that are larger than 0.45  $\mu\text{m}$  and settle out of solution under the influence of gravity. Colloidal fractions refer to particles that are between 0.022 and 0.45 ( $\mu\text{m}$ ) in size and remain suspended in solution due to Brownian motion. Truly dissolved fractions include REEs that are ionized and can pass through a filter with a pore size of 0.022  $\mu\text{m}$ .

It is important to distinguish these three fractions because the mobility, bioavailability, and toxicity of REEs can vary greatly depending on their distribution among them. Colloidal and particulate fractions can act as carriers for REEs, affecting their transport and availability to living organisms while truly dissolved fractions are more readily taken up by aquatic organisms. Additionally, industrial applications of REEs often involve specific fractionations, such as the separation of colloidal and particulate fractions for purification purposes.

We collected and filtered (through both 0.45 and 0.022  $\mu\text{m}$ ) 28 groundwater samples taken on the lower flanks of Etna Volcano (Sicily, Italy). For the determination of 14 lanthanides (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) plus Y in the aqueous fractions we proposed an improved method based on the coprecipitation of REEs with  $\text{Mg}(\text{OH})_2$ , assisted by the triethylamine (TEA). The particulate fraction, retained on the 0.45 cellulose acetate filters, was assessed by microwave-assisted acid digestion. REE concentrations for the three fractions were measured through inductively coupled plasma-mass spectrometry (ICP-MS).

The comparison among the chondritic-C1 normalized patterns proved the strong influence of pH and the redox potential of the solution on the distribution of the REEs into the three phases. The complexation by carbonate and bicarbonate ions had also a major role in the relative concentrations of Heavy REEs over the Lights ones. The competitive scavenging of REEs by Hydrous Manganese Oxides (HMO) and Hydrous Ferric Oxides (HFO) was shown. The very distinct coefficient of distributions ( $K_d$ ) shown by Yttrium and Cerium demonstrated their peculiar and opposite behaviors, emphasized in the comparison of the solid fraction over the aqueous one.

## Environmental impact assessment and recoverability of metals from Municipal Solid Waste Incineration (MSWI) plants ashes during pre- and post-pandemic period

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**Keywords:** solid waste residues, characterization, pandemic, metal recovery, environmental impact.

Municipal Solid Waste Incineration (MSWI) plants are known for generating hazardous wastes in the form of solid by-products, namely Fly Ash (FA) and Bottom Ash (BA). Municipal Solid Waste (MSW) of FA and BA contain large amounts of mineable base elements such as Cu, Co, Zn, as well as Potentially Toxic Elements (PTEs) like Cr, Ni, As, Cd, Pb, and Rare Earth Elements (REE). The potential recovery of these elements from MSW is crucial for sustainable considerations towards circular economy (Funari et al., 2016; Han et al., 2021). Therefore, to investigate the recoverability and environmental significance of these elements, we collected samples of FA and BA from MSWI plants located in Ferrara (FE) and Forlì (FC) cities in Italy, during both the pre- and post-pandemic period. The samples were digested by aqua regia following the International Organization for Standardization (ISO) protocol (Santoro et al., 2017). The experimental work was conducted at the Geochemistry Lab of ISMAR-CNR (Bologna) of the National Research Council. To determine the total metal and trace element concentrations of both the total and digested samples of MSW, we analyzed the samples at the laboratory of the Department of Biological, Geological and Environmental Science (BiGeA) at the University of Bologna, Italy. The wavelength dispersive X-ray fluorescence (XRF) spectrometer was used to analyze the total composition, while an ICP-MS Perkin Elmer was used for the digested samples. Our objective was to assess the recoverability of the elements and their environmental impact by characterizing FA and BA samples collected during both pre- and post-pandemic period. Our XRF results showed high concentrations of elements in all samples from both FE and FC. These included Fe, Al, Mg, Na, K, Cl, S, P, Zn, Ti, Cu, Ba, Mn, Sr, Ba, Co, as well as Potentially Toxic Elements such as Cr, Ni, As, Cd, and Pb, indicating their significant presence in urban MSW streams. Furthermore, we observed that both the BA and FA samples showed high recoverability of these elements. However, the concentration of REEs was low in all the samples studied. Our findings suggest that the recovery of these elements from MSW could play a critical role in supporting the circular economy and promoting sustainable development.

Our XRF analysis data revealed that the concentration of base elements such as Zn, Cu, and Co as well as PTE like Pb are notably higher in BA than FA samples collected from MSWI plants from FE and FC during both pre- and post-pandemic periods. Moreover, the elemental composition of BA and FA samples in FC was relatively higher than in FE. Magnetic susceptibility and Loss of Ignition (LOI) values were also higher for FC. Interestingly, REE concentration was low in all samples. Overall, our findings underscore the potential of MSWI ashes as an alternative source for base metal and REE recovery through aqua regia digestion protocol assisted by microwave digester. This preliminary study highlights the importance of better understanding the environmental impact of anthropogenic materials like MSWI ashes.

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## Leaching of potentially toxic elements in contaminated soils amended with biochar: evidences from 2 years column experiments

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*Keywords:* soil, biochar, potentially toxic elements.

Soil is a biologically active lithosphere layer that serves numerous functions such as medium for agricultural production, water filtration, buffering and mineralization, as well as habitat for pedofauna and carbon sink. Acting as a filter medium with high sorption capacity, soil stores and transforms pollutants deriving from human activities. Since soil is a non-renewable resource, the anthropic impact could damage its functions, thus resulting in the degradation of associated ecosystems services.

Crude oil and its derivatives are among the most important sources of anthropogenic contamination that could affect the soil. Along with organic pollutants, the refinery activities lead to an excess of Potentially Toxic Elements (PTEs). Soil contamination by PTEs is recognized as a global issue and has drawn concerns worldwide because of their poor mobility, non-biodegradability and high toxicity in soil (Burges et al., 2015).

Biochar is a carbon-rich material produced by the pyrolysis industrial process of organic wastes under limited or no oxygen conditions. Recently, it has been studied for its capacity to improve soil quality, store carbon and, particularly interesting, also decrease the mobility, leachability, and availability of PTEs in contaminated soils (Gong et al., 2022).

The aim of this study is to evaluate the effects induced by vineyard-pruning-biochar amendment on leachate from contaminated soil. Different from other column experiments, this work aims to understand the long term effect of biochar under controlled conditions.

Operatively, six columns (diameter 0.15 m, height 1 m) were prepared including 3 soils amended with biochar (0.4 kg/m<sup>2</sup>), 2 control soils and a last column filled only with biochar. The experiment started on January 2022 and is still running. The soil is maintained at field condition providing deionized water as irrigation and, at selected timestep, a saturation event is generated and leachate is collected and analyzed for chemical-physical parameters and PTEs.

Until now, five saturation events performed and five leachates have been collected and analyzed. The results show that pH in leachates from treated soils has increased of almost 1 point with a maximum value at month 3. As the months went by, the pH started to decrease but the difference with untreated soils remain stable. Among the PTEs Mn, Fe, Al, Zn V, B, Cr and As are showing increasing concentrations trends in leachates from amended soils, while Sb and Cu have decreasing concentrations trends in treated soils compared to control soils.

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## Epitaxy in multiphase inclusions as driving force for olivine oxidation coupled with hydrogen production at high pressure in the mantle

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*Keywords:* multiphase inclusions, subduction zones, hydrogen.

Magnetite-bearing multiphase inclusions hosted in metamorphic olivine of harzburgites from the Cerro de Almirez (Betic Cordillera, Spain) have been interpreted as final products of the trapping of the aqueous fluid produced by the subduction-zone dehydration of former serpentinites. The chemical exchange between inclusion fluid and olivine started soon after entrapment, at peak  $P$ - $T$  conditions of 1.6–1.9 GPa and 650–700°C, and continued during cooling along the retrograde path, with the coexistence of olivine and magnetite with orthopyroxene, chlorite, talc, antigorite and the destabilisation of olivine and antigorite into brucite and low-temperature chrysotile serpentine, as recognised by Raman analyses. Thermodynamic modelling and mass balance calculations demonstrate that the water component of fluid trapped in the inclusions of metamorphic olivine is expected to trigger the oxidation of the fayalite component in olivine, producing a mineral assemblage made of magnetite + orthopyroxene and  $H_2$ , where the elemental redox processes are  $Fe^{2+}$  of olivine that oxidizes to  $Fe^{3+}$  and  $H^+$  of water that reduces to  $H_2$ . We performed quantitative mass spectrometry analyses of the fluid phase trapped in the multiphase inclusions and of the olivine crystals hosting the inclusions, revealing that 1 kg of olivine matrix contains  $6.2 \pm 0.1$  mmol of  $H_2$ . We identify two synergistic driving forces of the whole process, which has the peculiarity to produce molecular hydrogen at apparently oxidising conditions: i) the building up of an epitaxial interface between olivine and magnetite, and ii) the olivine ability to trap  $H_2$  at high pressures. The olivine +  $H_2O$  system of these natural microreactors simulates a process of oxidation of the mantle olivine by water, with production of  $H_2$  at pressure and  $fO_2$  conditions (FMQ+2) at which water reduction is considered an unlike mechanism.

## Grain size and mineralogical constrains on leaching in the bottom ashes from municipal solid waste incineration: a comparison on 5 plants from Northern Italy

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*Keywords:* MSWI-BA, PTE, leaching test.

The ever-increasing production of waste has led in recent years to a growing interest in these materials that can be considered as urban mines from which to extract economically valuable elements. Bottom ash (BA) generated from Municipal Solid Waste Incinerators (MSWI) represents a significant source of elements that can be potentially hazardous if released into the environment, but at the same time, of significant economic value if extracted and reused.

In this work BA from 5 northern Italy (Parma, Piacenza, Torino, Ferrara and Forlì-Cesena) Waste to Energy (WtE) plants were sorted based on different grain sizes. The input waste of the plants is similar, coming from a culturally homogeneous area, and with similar collection management. For each grain size, a mineralogical, chemical, and physical characterization has been done using XRF, XRD, and TGA. Therefore, standard leaching tests were done on particles of different size, following the European Normative EN 12457-2 (2004) and the variability was analysed by PCA.

The results showed that marked differences in leaching behaviour were between the two different owner corporation that is IREN for PR, PC and TO and HERA for FC and FE. Some ions, among which Cl, K, Li, Na and Cu show an opposite trend respect to grain size, suggesting higher leaching in smaller grain sized. SO<sub>4</sub><sup>2-</sup> follows the same trend of Cl in TO, PR, PC. In FE and FC the sulphates leached are one order of magnitude less than in other incinerators. Ni and Cr are more leachate in the smaller grain size such as in TO, PR and PC, but not in FE and FC. Pb does not follow a definite trend, with little change with grain size. Al is leached in significant amounts only in TO, PR and PC, but not in FE and FC.

With respect to a given particle size, the leaching of an element has been compared to the total content in the bulk sample (from XRF analysis) and calculated in percentage (all referred to mg/kg of material). The most released element is Cl with a release percentage of about 70-90%, higher in the finer fraction, suggesting the presence of very soluble salts, such as NaCl and KCl, dispersed on the surface of the grains (Mantovani et al., 2023). Other elements like Mg and Fe do not show a significant leaching, indicating that they are bonded in non-soluble oxide or silicate structures.

From a circular economy perspective, it is feasible to reuse BA as an additional material in concrete. The minerals in FE and FC that are related to cement, such as portlandite, make it suitable for reuse in concrete, facilitating the setting and hardening reactions. However, significant concentrations of Cl and S, especially in the finer grain size, could be disadvantageous for cement application, and a pre-treatment before application as cement binder may be necessary. Grain sorting could be useful in cases where leaching of the larger grain size meets the legislative limits for a given element, while the smaller grains do not, like Cr in PC and Cu in PR.

Mantovani L., De Matteis C., Tribaudino M., Boschetti T., Funari V., Dinelli E., Toller S. & Pelagatti P. (2023) - Grain size and mineralogical constrains on leaching in the bottom ashes from municipal solid waste incineration (BA-MSWI): a comparison on 5 plants from Northern Italy. *Front. Environ. Sci.*, 11. <https://doi.org/10.3389/fenvs.2023.1179272>.

## Chromium oxidation in the time-dependent response of the pyrolyzed tannery waste KEU: environmental implications

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*Keywords:* hexavalent chromium, tannery wastes, pyrolysis.

At present more than 80% of the global leather production involves tanning through chromium salts. Leather manufacturing produces high-Cr wastes that require suitable treatments before disposal, to prevent environmental threats. Even if Cr(VI) salts are generally not used in tanning, and Cr in the fresh sludge is expected to persist in its trivalent state due to the high content of organic substances, it is necessary to ensure that Cr(III) remains resistant to the conversion to the hexavalent form during disposal in oxidizing environments since Cr(VI) compounds are highly toxic and group one human carcinogens. Among the different tannery sludge treatments for re-utilization within a circular economy model, thermal treatments through incineration and pyrolysis have been widely applied. In general, pyrolysis in a controlled reducing atmosphere minimizes the Cr(VI) that forms during the heating treatment and represents a promising and cost-effective technology to treat the sludge, producing a carbon material where Cr is expected to be fixed as non-toxic Cr(III). Pyrolyzed tannery sludges residues free from toxic Cr(VI) can be safely disposed, converting tannery wastes into a recycling resource. However, few studies exist about the time-dependent stability of Cr(III) in pyrolyzed chars upon oxidation.

The present study is focused on the characterization of high Cr-bearing chars produced during pyrolysis and sintering of sludges from the tanning district of Santa Croce sull'Arno (Italy), one of the largest in Europe including more than 250 tanneries. The pyrolysis product, referred to as KEU, has been deemed as a model for circular economy. The KEU has been distributed in the environment, recycled to form inert fill and used as a base in the construction of roads. Ageing experiments demonstrate that a time-dependent Cr(III) – Cr(VI) inter-conversion in KEU at ambient temperature in the presence of air occurs. Microstructural analysis reveals that the pristine stable Cr(III) high-temperature mineralogy of KEU that forms during pyrosintering is strongly destabilized upon spray water cooling in the last stage of production, allowing Cr(III) to be released from primary phases and incorporated into newly formed  $\alpha$ -CrOOH (grimaldiite) flakes. The trivalent chromium in CrOOH oxyhydroxides has the potential to be oxidized to Cr(VI), which become easily leachable by water, making KEU a hazardous material when exposed to ordinary ambient conditions. Environmental investigations in sites contaminated by Cr(VI) released from KEU reveal that the hexavalent chromium underwent a complex fate in the water-soil system, forming Cr(VI)-bearing precipitates and being partly reduced to the trivalent state when dispersed by aqueous routes. Microcosm and field experiments indicate that Cr(VI) reduction and sorption in groundwater is strongly promoted by using hemp (*Cannabis sativa* L.), that represents a very promising candidate to mitigate contamination.



## Element mobility and spatial distribution of metals in sediments from Conca River and Reservoir, Italy

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*Keywords:* sediments, metals, mobility.

Sediments play a crucial role in catchments and river systems as they can potentially carry pollutants that degrade aquatic habitats and infrastructure, reduce storage capacity, and impact the environment (Apitz, 2012). Sediment geochemical characterization, spatial distribution, and Sequential Extraction Procedures (SEP) were conducted on sediments to assess their environmental impact and analyze metals, determining their concentrations, potential mobility, and bioavailability (Toller et al., 2022).

This study aimed to determine the geochemistry of the sediments in the Conca reservoir in Romagna, Italy, and evaluate their impact on the environment. The Conca basin reservoir has a surface area of 0.46 km<sup>2</sup> and a capacity of 1.1-1.2 × 10<sup>6</sup> m<sup>3</sup>, with a bulkhead located 1 km inland from the Conca river mouth that retains a volume of about 23,000-25,000 m<sup>3</sup>/year of sediments. The catchment area along the Conca river includes numerous civil, agricultural, and industrial settlements that influence the quality of the sediment with their activities.

The sampling campaign was conducted on sediments collected from the main river and within the Conca reservoir area, and in depth using a core of 1.80 cm. Various analytical techniques were employed, such as total components analysis by X-Ray Fluorescence spectrometry (XRF), acid digestion and leachate and residual by Inductively Coupled Plasma Mass Spectrometry (ICP-MS), organic component by Carbon, Hydrogen, and Nitrogen elemental analyzer (CHN), and polycyclic aromatic hydrocarbon (PAH) by Gas Chromatography-Mass Spectrometry (GC-MS). Data characterization, inter-element relationship, and principal component analysis (PCA) were processed by CoDaPack, PAST and R software.

The study results showed that the highest CaO contents were mainly distributed in the upstream area of the catchment, while the SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> contents occurred mainly in the downstream areas, reflecting the geological background. Urban and agricultural land use generated geochemical signals registered by the sediment with enrichments in Cr and Ni. The PCA showed the inter-element relationship and correlation between trace metals and potentially toxic elements (PTE) with the Organic Matter (Corg and LOI (Loss on Ignition)). SEP results were used to evaluate the potential risk of metal contamination for the reservoir, as well as to identify the most mobile metals in the reservoir and the most suitable remediation strategies.

In conclusion, this study provides important insights into the impact of human activities on river-reservoir systems and highlights the crucial role of sediment quality in the function of river-sea systems. By identifying the sources and potential pollutants in the Conca reservoir sediments, this research sheds light on the environmental risks associated with sediment deposition and can inform strategies for sustainable water management. As reservoirs become increasingly important infrastructure for water demand, the findings of this research underscore the importance of ongoing efforts to monitor and manage sediment quality in river-sea systems.

Apitz S.E. (2012) - Conceptualizing the role of sediment in sustaining ecosystem services: Sediment-ecosystem regional assessment (SEcoRA). *Sci. Total Environ.*, 415, 9-30. <https://doi.org/10.1016/j.scitotenv.2011.05.060>.

Toller S., Funari V., Zannoni D., Vasumini I. & Dinelli E. (2022) - Sediment quality of the Ridracoli fresh water reservoir in Italy: Insights from aqua regia digestion and sequential extractions. *Sci. Total Environ.*, 826, 154167. <https://doi.org/10.1016/j.scitotenv.2022.154167>.

## **Bulk composition and leaching tests on an environmentally dangerous production residue (KEU)**

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*Keywords:* sewage sludge, potentially toxic elements, leaching tests.

KEU (*Kraftanlagen Energie und Umwelttechnik*) is a by-product of a pyrolyzed waste of sewage sludge produced by wastewater treatment of. This material is indeed processed after inertization, being mixed with quarry aggregates, to obtain a sintering granulate. It is likely the responsible of the anomalous concentrations of Cr and CrVI and other heavy metals recovered in several domestic wells distributed along the Firenze-Pisa-Leghorn motorway (Tuscany, central Italy) since KEU was used as roadbed. The same concerns were also recently evidenced a little more to the south, close to Arezzo, as in the local groundwater system high contents of heavy metals were determined and attributed to a different type of KEU, i.e. derived from the inertization of muds from refining industries.

In this work, an extensive analytical work was carried out to characterize the mineralogical and chemical bulk composition of seven KEU-bearing samples collected from different cumulus stored in an aggregate crushing plant and one pre-treated KEU sample. Additionally, two distinct leaching tests were performed to evaluate the release of PTEs (Potentially Toxic Elements) by shaking 20 g of each sample in 200 mL of MilliQ and CO<sub>2</sub>-saturated MilliQ water, respectively, the latter simulating the interaction between meteoric waters and KEU. After 1 day of leaching, the resulting suspension was centrifuged and the supernatant was analyzed for pH, electrical conductivity, main composition, and trace elements. The post-centrifugation residue was once again leached and shaken for 7 days to evidence whether the PTEs were still released after a relatively long-term leaching. The preliminary results showed that the MilliQ water leachates of the KEU-bearing materials are characterized by high pH values (up to 11.75), whereas the CO<sub>2</sub>-saturated MilliQ water partly buffers the pH since it was in most cases <8. Our study indicates that, as expected, in most cases the CO<sub>2</sub>-saturated MilliQ water is able to remove more heavy metals than those solubilized by MilliQ water. Moreover, the 1-day leachates resulted to be enriched in many heavy metals with concentrations, in most cases, from hundreds to thousands of mg/L. Despite a general decrease in the 7-days leachates, high contents of some heavy metals were still measured, suggesting that prolonged interaction between meteoric waters and the KEU-bearing material is anyway able to transfer PTEs to the groundwater systems. Another important aspect that was highlighted is that the investigated samples are chemically heterogeneous, indicating that the inertization process was not performed by using the same amount of quarry aggregates. Notwithstanding such an inertization, aimed at stabilizing unwanted toxic elements, its efficiency is rather scarce and, consequently, its use as by-product is strongly discouraged unless a more adequate inertization process is realized.

## Realization of a prototype aimed at investigating the degradation potential of landfill gas in bio-covers

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Keywords: bio-cover, laboratory prototype, landfill gas.

Landfill gas (LFG) diffuse emissions into the atmosphere and landfill leachate (LL) uncontrolled discharges into the environment represent two of the major issues in landfill management. Recent research approaches to reduce the LFG emissions and the related environmental impacts and costs, focus on: (i) application of biochemical methane potential tests, aimed at effectively predicting the LFG generation from the deposited waste categories, with consequential optimization of the engineering systems for LFG collection and energy recovery; (ii) improvement of the efficiency of possible bio-covers in degrading CH<sub>4</sub> and non-methane volatile organic compounds (VOCs) and reducing meteoric water infiltration.

For the realization of lab-scale prototypes designed to investigate new bio-cover systems, different concepts have been reported in literature, such as: (i) columns filled with treated soil and equipped with a pump that allows the flushing of synthetic LFG mixtures from the column base, to study the LFG degradation efficiency of the bio-cover; or (ii) columns filled with a layer of waste covered with soil and equipped with a LL recirculation system, to study the effects of LL on waste degradation and LFG production.

Here, a novel prototype to reliably investigate the capability of bio-covers for degrading LFG components is presented.

The developed prototype consisted of a maceration chamber (i.e. landfill body producing the LFG), made with a 20 L tank filled with a mixture of selected waste category and anaerobic sludge (inoculum to provide microorganisms for anaerobic degradation process), connected to a column (i.e. landfill cover soil), constituted of 105 cm high dark PP cylinder (7 cm inner diameter), filled with soil. The column is equipped with 4 ports as pertaining sampling points, placed along the vertical axis (spaced 22 cm, with the upper one 9 cm from the top and the lowest one 30 cm from the bottom), hosting 5.5 cm long PA tubes (4 mm inner diameter), equipped with three-way stopcocks, and inserted in the column. Another sampling port is placed in the silicone tube connecting the maceration chamber with the column. Periodical gas sampling from both maceration chamber and column is performed using a plastic syringe and gas is stored in 12 cc vials equipped with a pierceable rubber septum. Analysis of VOCs composition is carried out by gas chromatography coupled with quadrupole mass spectrometry. The obtained analytical dataset describes temporal evolution of VOCs produced in the maceration chamber and passing through the soil column. Such experimental setup, coupled with comprehensive chemical analyses of gas samples from the maceration chamber and the soil column, allows to investigate and describe the influence of many physicochemical parameters and conditions (e.g. soil moisture and characteristics, temperature, possible addition with dewatered sewage sludge, possible LL recirculation) on VOCs degradation capacity of bio-cover systems.

## Optimization of the abatement of landfill gas diffuse emissions in cover soils treated with sewage sludge and leachate: A laboratory experiment

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*Keywords:* laboratory experiment, landfill cover soil, landfill gas emissions.

Landfilling represents the most common option for municipal waste (MW) management worldwide, also in expected temporal projection. The degradation process of deposited MW generates two potential contaminating outputs that may cause severe environmental impacts on both local and global scales: (i) landfill gas (LFG), mainly consisting of CH<sub>4</sub>, CO<sub>2</sub> and a minor fraction of non-methane volatile organic compounds (VOCs), and (ii) landfill leachate (LL).

Nowadays, several mitigation strategies are deployed to minimize the uncontrolled release of LFG into the atmosphere, including bio-cover systems, which degrade CH<sub>4</sub> and a variety of VOCs by the action of microbial population consortia, and reduce meteoric water infiltration. However, the current methods to attenuate LFG diffuse emissions are not fully effective, and a significant part of generated LFG is emitted into the atmosphere.

The purpose of this study was to identify and investigate potential low-cost and sustainable approaches to effectively manage the LFG in combination with LL and dewatered sewage sludge (SS), according to the concept of circular economy aimed at utilizing complementary waste categories (i.e. LL and SS) as resources to favor the abatement of LFG diffuse emissions in soils. Two experimental runs were conducted using lab-scale landfill prototypes developed and tested in a previous study. Particularly, the individual prototype consisted of a maceration chamber (i.e. landfill body filled with degrading waste that generated the LFG) connected to a soil column (i.e. landfill cover soil).

The first experimental run was carried out using two prototypes, with the purpose to investigate the LFG abatement potential in a new bio-cover system, realized modifying a natural soil with addition of dewatered SS and LL recirculation.

The second experimental run, using four prototypes, focused on investigating the individual contributions of dewatered SS addition and LL recirculation, also reducing the amounts of dewatered SS and LL used in the treatment of the natural soil.

In both experimental runs, gas samples were analyzed by (i) gas chromatography using a thermal conductivity detector (GC-TCD) for main gaseous components, (ii) gas chromatography using a flame ionization detector (GC-FID) for light hydrocarbons (C<sub>2</sub>-C<sub>4</sub>) and CH<sub>4</sub> at concentrations < 0.05%, (iii) cavity ring-down spectroscopy (CRDS) for carbon isotopic signatures in CH<sub>4</sub> and CO<sub>2</sub>, and (iv) gas chromatography coupled with a quadrupole mass spectrometry (GC-MS), after solid-phase micro extraction (SPME), for C<sub>4</sub>+VOCs.

The first experimental run highlighted the enhanced efficiency of the soil treatment with LL and dewatered SS in degrading CH<sub>4</sub> and selected VOCs, pertaining to alkanes and highly odorous terpenes, with respect to non-treated soil.

The second experimental run showed how the efficiency in LFG abatement by the treated soil was influenced to a larger extent by the addition with dewatered SS as compared with LL recirculation.

**S20.**

**Sustainable strategies for the design and development of  
innovative materials: from non-renewable resources to  
valorisation of anthropic wastes**

*CONVENERS AND CHARIPERSONS*

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## Reuse of waste materials in the manufacture of ceramic tiles: an experimental study

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*Keywords:* ceramic tiles, recycled resources, eco-sustainability.

The growing interest in the building sector towards the production of eco-sustainable materials has led many research groups to test the possibility of using recycled resources for the production of ceramics, mortars and concretes (Belfiore et al., 2020).

In such a scenario, this experimental study aims at evaluating the possible reuse of two waste materials in the production of ceramic tiles, namely volcanic ashes and ceramic wastes (i.e. chamotte).

Five different pastes were produced through the hand-made technique by expert ceramists, by using variously sized volcanic ashes and/or chamotte as a temper, mixed in different proportions with clay.

The volcanic ashes used for the manufacture of tiles were collected at the roadside in the territory of Giarre, a village located in the eastern flank of Mt. Etna volcano, and can be referred to the paroxysm occurred on February 2021 from the Southeast Crater. Instead, as for the chamotte, the kiln wastes of the same company that was responsible for the manufacture of our experimental ceramic tiles were used, after appropriate grinding and sieving.

To assess the quality of the products obtained and verify their technical-economic feasibility, durability and physical-mechanical resistance, the following laboratory tests have been performed: a) water absorption; b) flexural strength; c) resistance to thermal shock; d) resistance to deep abrasion; e) impact resistance.

The results obtained were then compared with data of a reference product, for several years on the market and therefore of certified quality, whose aplastic inclusions consist of azolo, namely fragments of finely ground basalt.

At the end of tests, the tiles made by using only chamotte as a temper showed better performance, followed by those made of fine-grained volcanic ash which also achieved very good results. Conversely, the other experimental pastes exhibited rather poor physical-mechanical characteristics, thus revealing to be not suitable for the production of ceramic tiles.

Belfiore C.M., Amato C., Pezzino A. & Viccaro M. (2020) - An end of waste alternative for volcanic ash: A resource in the manufacture of ceramic tiles. *Constr. Build. Mater.*, 263, 120118. <https://doi.org/10.1016/j.conbuildmat.2020.120118>.



## Influence of municipal solid waste fly ash on phosphate-based geopolymer foams properties

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Keywords: phosphate geopolymer, fly ash, foam.

There is interest in proposing geopolymer binders as ‘green’ building materials to partly replace Portland cement in the future. Phosphate-based geopolymers (PBG) gained increasing interest only in the last few years (Ma, et al., 2022). PBGs are obtained through the reaction of an aluminosilicate precursor (i.e., metakaolin, MK) with a diluted orthophosphoric acid solution, instead of the usual alkaline silicate one.

The dissolution of MK into the acid solution leads to the release of Al<sup>3+</sup> ions which polycondense with the phosphate ions into a three-dimensional amorphous hydrated aluminophosphate network. The residual hydrated silica can also form some silicate networks that may react with the remaining phosphorous entities and form Si–O–P bonds (Ma et al., 2022). The excellent thermal and mechanical performance displayed by metakaolin-PBGs has stimulated research on its possible application as foamed lightweight material for insulation. The foam porosity has been controlled by changing the content and amount of foaming agent, (namely, Al and Fe powders, H<sub>2</sub>O<sub>2</sub>, limestone, etc.), together with stabilizing additives such as surfactants (Ma et al., 2022). Total porosity up to 70-80%, together with very low thermal conductivity (i.e., 0.05 W/mK) have been achieved (Ma et al., 2022). However, the expensive costs of MK and phosphoric acid require to focus on other reactive source that could, at least partially, replace them and increase the economic sustainability of these promising materials.

Here, the feasibility of washed municipal solid waste FA introduction in foamed MK-PBG mixtures is explored. MSWI-FA forms in the incineration plant purification system and, due to the high content of chlorides and heavy metals, has to undergo a stabilization/inertization treatment (one of the most common is water washing), before being landfilled or, possibly, used as secondary/supplementary raw material (Bernasconi et al., 2022). In our previous work, the washed MSWI-FA displayed a very different reactivity in the system with respect to MK. More specifically, it acts as a cations source for the precipitation of Ca-Mg phosphates, which significantly increases the final porosity (Bernasconi et al., 2023).

In this work, the partial substitution of MK with washed MSWI-FA in PBG formulation with Al powder as foaming agent is investigated, by inquiring the changes in the porosity development with microscopy techniques (scanning electron and optical microscopy) and physical characterization (dry bulk density, water absorption, compressive strength), together with the mineralogical and structural investigation of the samples by XRPD and spectroscopies (IR and solid-state NMR). Furthermore, a thermal treatment (500-900°C) is tested, to evaluate possible improvement on the material characteristics.

Bernasconi D., Caviglia C., Destefanis E., Agostino A., Boero R., Marinoni N., Bonadiman C. & Pavese A. (2022) - Influence of speciation distribution and particle size on heavy metal leaching from MSWI fly ash. *Waste Manage.*, 138, 318-327. <https://doi.org/10.1016/j.wasman.2021.12.008>.

Bernasconi D., Viani A., Zárýbnická L., Mácová P., Bordignon S., Caviglia C., Destefanis E., Gobetto R. & Pavese A. (2023) - Phosphate-based geopolymer: Influence of municipal solid waste fly ash introduction on structure and compressive strength. *Ceram. Int.*, 49(13), 22149-22159. <https://doi.org/10.1016/j.ceramint.2023.04.042>.

Ma S., Zhang Z. & Liu X. (2022) - Comprehensive Understanding of Aluminosilicate Phosphate Geopolymers: A Critical Review. *Materials*, 15, 5961. <https://doi.org/10.3390/ma15175961>.

## Synthesis and characterization of pigmented geopolymers for sustainable conservation interventions

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Keywords: pigmented geopolymers, conservation, characterization.

Thanks to recent scientific researches, involving leading companies in the field of Italian and international conservation, in the last years, innovative alkaline-activated materials are gradually entering the field of Cultural Heritage conservation.

These categories of eco-friendly materials are very promising and, due to their versatility, are suitable for various applications, as shown by recent studies in the field of conservation with different functionalities (Barone et al., 2020), including the application on polychrome surfaces in places of exceptional historical and artistic interest (Fugazzotto et al., 2023). Their production is characterized by lower environmental impact with respect to traditional restoration products, thus opening a view to a modern and innovative restoration of Cultural Heritage, by protecting the Planet.

The present study is part of a wider project involving the development of pigmented geopolymers for sustainable restoration of a particular category of goods: mosaics.

Different kinds of inorganic and organic pigments were directly added into the geopolymer mixture in different percentages, in order to synthesize preliminary products to be tested through various investigations.

In this first stage of the study, commercial metakaolin was used as a precursor for the synthesis; in fact, this raw material, whose use is frequent and has already been tested in the literature (Davidovits, 2018), lends itself very well to the production of pigmented geopolymers, as it offers the possibility of obtaining a very light-coloured base.

Ultramarine Blue, Yellow Ochre and Green Earth were chosen among the inorganic pigments, while Red Lacquer was chosen among the organic ones.

The precursor and the pigments used were preliminarily characterized by means of Raman Spectroscopy and X-ray Diffraction. The final pigmented geopolymers, instead, were subjected to compression tests after a month of curing to investigate their mechanical properties, to colorimetric analyses at regular intervals to monitor their chromatic variation, and to chemical and physical stability tests.

According to these preliminary results, the studied materials have proven to have great potential, which this research attempts to investigate, to become promising in the conservation of polychrome Cultural Heritage.

Barone G., Caggiani M.C., Coccato A., Finocchiaro C., Fugazzotto M., Lanzafame G., Occhipinti R., Stroschio A. & Mazzoleni P. (2020) - Geopolymer production for conservation-restoration using Sicilian raw materials: feasibility studies. IOP Conf. Ser. Mater. Sci. Eng., 777, 012001. <https://doi.org/10.1088/1757-899X/777/1/012001>.

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## Geopolymer-based catalysts for pollutants removal by photo-Fenton reaction

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Keywords: geopolymer-based catalyst, wastewater treatment, photo-fenton.

The development of novel, highly-efficient and low-cost catalysts plays an important role for the achievement of the environmental governance. This work wants to contribute at the study of catalysts for "end-of-pipe" treatments (Zhang et al., 2020) of industrial waters by using metakaolin-based geopolymers. A set of seven different geopolymers was prepared using a kaolinitic clay heat-treated at 700°C for 2 hours, a sodium silicate solution, hydrogen peroxide H<sub>2</sub>O<sub>2</sub> (3 wt%) in different weight ratios (1 - 5 - 10%) and olive oil in weight ratio 20% (Bai et al., 2016). A multiphase polymerization was also applied. The XRPD and FTIR characterization showed similar results for all samples, i.e. diffraction patterns with the typical hump in the 20-35° 2θ range and the main band of infrared spectra at around 1020 cm<sup>-1</sup>, respectively, both distinctive of geopolymerization reaction occurrence. MO and SEM observations showed well-developed matrices with a proportional increase of pores size to H<sub>2</sub>O<sub>2</sub> ratio. In geopolymer in which 1 wt% of H<sub>2</sub>O<sub>2</sub> was used, circular shaped pores with regular borders (0.1-0.4 mm sized) were distinguished, whereas in geopolymers with 5 and 10 wt% of H<sub>2</sub>O<sub>2</sub> were distinguished sub-spherical (dimensions between 0.2-1 mm) and irregular or sub-rounded shaped pores (dimensions about 1-3 mm), respectively. In samples containing H<sub>2</sub>O<sub>2</sub> and oil, more homogeneous morphologies were observed in which pores size decreased and the total pores amount increased. The effectiveness of geopolymer catalysts was tested, after samples impregnation with Fe (II) (heterogeneous system), in photo Fenton process, working at neutral pH in water (O'Dowd & Pillai, 2020). Among the tested samples, geopolymer with 1 wt% of H<sub>2</sub>O<sub>2</sub> gave best results in terms of pollutants degradation (model molecules and industrial waters) in different cycles of reaction and regeneration. SEM-EDS analyses evidenced as, at the end of test, geopolymeric matrix resulted consumed of silico-aluminous components whereas no relevant Fe(II/III) leaching was detected. Furthermore the catalyst recovery operations were simplified by the 3D shape of sample. Results promoted porous metakaolin-based geopolymers as promising heterogeneous catalysts.

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## Alkali activation of mechanically pre-treated carbonate-bearing clays

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*Keywords:* mechanical pre-treatment, carbonate bearing clays, alkali activation.

In the perspective of a sustainable use of widely available raw materials, a number of studies focused on the last years to the exploration of the use of inexpensive polymineral clay resources as precursors for the preparation of alkali-activated binders (AABs), alternatively to high pure kaolinite clays. Among them, carbonate-bearing clays were less investigated, although recent studies have demonstrated that they are potential sources for the production of AABs, even though containing low amounts of clay minerals (Rakhimova, 2022). It is mainly related to the formation of high reactive CaO after the thermal treatment of the clay at temperature of about 850°C which decomposes calcite; the so formed CaO participates to the alkali activation reaction with subsequent formation of a mixture of C-A-S-H/(N, C)-A-S-H type binding gel (Rakhimova, 2022; D’Elia et al., 2020). However, the CO<sub>2</sub> emissions related the decomposition of calcite during the thermal clay pre-treatment, significantly reduces the environmental advantages of alkali-activation technology with respect to Portland Cement production, for which 60% of CO<sub>2</sub> emission is associated to the conversion of limestone to CaO. In the view of the utilization of carbonate-bearing clay as raw material for AABs, but avoiding the environmental impacts related to the thermal activation, the suitability of the mechanical activation method has been investigated in this study. Carbonate-rich clays from Apulian region (Southern Italy) were subjected to two different mechanical activation methods: 1. high energy grinding by vibro-milling according to the same procedure described in (D’Elia et al., 2018) and conventional ball miller (D’Elia et al., 2023). Characterization of mechanically activated clays and solubility tests showed advanced delamination and amorphization effects on clay minerals and significant reduction of calcite grain size (D’Elia et al., 2018). Mechanically treated clays were activated using both 8M NaOH and a sodium silicate solution (SiO<sub>2</sub>/Na<sub>2</sub>O = 2.01); different curing temperatures were also tested in order to find the best conditions for the development of well hardened samples. The best results were obtained in samples activated using sodium silicate as activating solution and cured at T = 85°C in the oven, which showed well compact matrices and achieved mechanical strengths of about 17 MPa after 28 days in the case of samples from clays activated by vibro-milling and of about 10 MPa in that activated by conventional ball miller. Based on the obtained results, mechanical pre-treatment of carbonate-bearing clays is a promising activation method for promoting their utilization for the preparation AABs, in an optic of environmental and energy-consuming sustainably.

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## Porosity influence on MK-based geopolymers for ammonium removal

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Keywords: geopolymer, porosity, ammonium removal.

Wastewater reuse has become a key issue in meeting the growing water demand, but effective disinfection is required. One of the most common pollutants in wastewater is ammonium, a frequent nitrogen species that contributes to eutrophication, acidification and degradation of water quality. Biological treatments are mainly used for this purpose. Although these systems are efficient, they require large areas of land due to slow biological conversion of nutrients and thus incur high capital costs (Yusof et al., 2010). Recent investigations suggested that adsorbent geopolymer materials can represent a new efficient, low-cost, low-carbon-footprint approach for ammonium removal by ion exchange (Luukkonen et al., 2019; Medri et al., 2022). It has also been showed that the adsorption capacity of geopolymers toward ammonium equal or higher than typically used zeolites and that their porosity influences their efficiency to pollutants removal (Bai & Colombo, 2018). The main objective of this work is the investigation of the influence of porosity of MK-based geopolymers with respect to the ammonium removal. To this purpose, metakaolinite was activated with NaOH and sodium silicate solution, and foams were obtained via the addition of two different foaming agents in different percentages: H<sub>2</sub>O<sub>2</sub> (alone) and a blend of H<sub>2</sub>O<sub>2</sub> and olive oil. The obtained moulds were cured at room temperature for 24 hours and then at 85°C for 5 hours. Samples were characterized chemically and mineralogically using XRD, FT-IR, and SEM, while physical characterization was performed by a multimethodological approach to evaluate porosity and resistance. The results showed that in all samples the geopolymerization reaction occurred. Adsorption tests were performed in laboratory on different samples using model solutions. To optimize the adsorption conditions, the initial concentration, sorbent dosage and contact time were varied. Ammonium removal percentage of each geopolymer was calculated using UV-visible spectroscopy by examining the ammonium concentration in solutions before and after the contact with the geopolymer matrix.

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## Porosity and ageing durability assessing for volcanic ash and basalt sludge-based alkali-activated materials (Mt. Etna volcano, Italy)

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Keywords: alkali-activated materials, recycle, durability.

The Ecological Transition requires to achieve environmental sustainability by saving natural resources and developing sustainable industrial processes for material production. Alkali activated materials (AAMs) have gained interest due to both their potential to use natural and/or industrial waste precursors in a circular economy and their sustainable manufacturing process. In recent years, research has focused on testing the feasibility of using volcanic ashes from Mt. Etna for building and restoration purposes in an alkaline environment (Finocchiaro et al., 2022; Fugazzotto et al., 2023). Additionally, due to the abundance of basalt mining stones in the Etnean area and their resulting processed sludge wastes, these latter have been used to produce AA-pastes with promising preliminary results (Portale et al., 2023).

This work compared volcanic ash-based AAMs (VA) and basalt sludge-based AAMs (BS) in terms of their porosity, adsorbing capacity, and ageing durability by salt crystallization. The investigation involved performing hydric tests (free and forced water absorption and drying), as well as analysing the pore size distribution of the samples by mercury intrusion porosimetry (MIP). The elastic-dynamic properties of the synthesized materials, which directly influence their mechanical resistance, were also determined using ultrasound. Finally, the sample set was subjected to salt crystallization cycles to simulate the decay resulting from the dissolution and recrystallization of mirabilite within their porous systems.

Both sets of AAMs show rapid adsorption capacity, displaying a typical behaviour of a tortuous porosity in the step of forced water absorption. Contrary, the drying appears very slow. Moreover, the MIP results show interesting differences between VA and BS, not only in the percentage of accessible porosity, but also in the main pore size distribution. The salt crystallization cycles highlight a significant weight loss, especially for VA samples, which suffer the most damage. Ultrasonic results confirm the differences found through previous analyses. Finally, the obtained results highlight a nano and micro porosity, confirmed by the fast absorption and slow drying recorded during the hydric tests, maybe can be also linked to the presence of a secondary gel formed by the interaction between the matrix's sample and water. This behaviour agrees with the salt ageing test, evidencing a moderate resistance to salt crystallization. Therefore, their final preferential destination use should be in an inside environment. However, further studies are necessary for obtaining a formulation useful for outdoor use which, otherwise, need an application of protective coatings.

This study was funded by the Junta de Andalucía Research Group RNM179 and by Research Project B.RNM.188.UGR20 of the Regional Ministry of University, Research and Innovation of the Junta de Andalucía and FEDER (a way of making Europe).

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## Different kinds of waste into a single secondary product: a chemical and mineralogical characterization of recycled waste

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**Keywords:** construction and demolition waste (CDW), industrial waste, vitrification.

According to EU environmental policy, managing and reutilizing waste is of fundamental importance to produce secondary raw materials for specific applications (e.g. for eco-sustainable buildings or for the glass industry) and improve the circular economy.

Large amounts of waste are related to the building construction and demolition sector. Construction and Demolition Waste (CDW) is the non-hazardous solid waste resulting from construction or demolition of buildings, including dismantling works related to catastrophic events (Abudurehman et al., 2021; Galderisi et al., 2022). Both regarding CDW and industrial waste, particular attention should be paid to the finest fractions, which usually are the most difficult to recycle.

Vitrification is one of the most promising treatments, producing a chemically stable material, which can also immobilize toxic elements in its vitreous structure (Stabile et al., 2019).

This work explores how the combination of different kinds of waste can allow to produce a secondary raw material that can be used to recycle the finest fractions of waste, usually destined to landfill, improving the vitrification degree of the final products.

CDW was obtained from the rubble produced by the 2016 seismic events in the Marche Region (Central Italy). The finest fractions were selected by sieving and mixed with powdered ceramics or bricks in different concentrations (e.g. 30/70, 50/50%w/w). Vitrification of waste was carried out by electric heating the different mixes in a chamber furnace at atmospheric pressure, 1200°C and 8 h duration.

The products were characterized with chemical analyses by electron microprobe and X-ray Fluorescence (Stabile et al., 2023). Mineralogical characterization was obtained with X-ray diffraction and micro-Raman spectroscopy, to investigate the crystalline and amorphous phases in the products. The increasing proportion of the waste mixed with CDW promoted a complete vitrification of the products, whereas for lower concentrations crystalline phases were also found, mainly as gehlenite and pseudowollastonite. Furthermore, accessory phases were identified by micro-Raman spectroscopy, consisting of residual crystalline phases from the starting waste materials and sulphates produced during the thermal treatment.

The multi-analytical approach provided a mineralogical and chemical characterization of the recycled products, exploring the distribution of the mineralogical phases according to the different concentrations of waste.

This investigation allowed to determine that, even starting from CDW, commonly considered only for downcycling application, it is possible to obtain a secondary raw material that could be used for upcycling uses, as component for refractory materials, tiles, glass ceramics or for incorporation of hazardous elements. In this regard, mineral sciences are essential to determine the potentials of materials for unconventional applications.

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## **Influence of environmental curing conditions on mechanical and microstructural features of water potabilization sludge – clay alkali activated blends**

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*Keywords:* alkali activation, curing parameters, water potabilization sludge.

In view of a necessary transition towards technologies and materials capable to reduce the environmental footprint, this contribute aims to evaluate the mechanical and microstructural features of alkali activated blends obtained from calcined water potabilization sludge (WPS) (Clausi & Pinto, 2023) and carbonate-rich illitic clay (LCR) (D’Elia et al., 2023). To reduce the environmental impact the follow choices were done: i) alkali activated systems were designed by substituting partially (25 -50 - 75 - 100 wt%) the natural resource (clay) with the waste-derived one (WPS); ii) the materials were sourced in the same territory, Apulia (Italy), to raise the reuse of resources locally; iii) alkali activation was promoted by using exclusively NaOH 6M, instead of quite expensive alkaline silicate solutions; iv) a room temperature curing was tested in two seasons of the year (summer - winter) to evaluate binders behaviour in real applications.

A multi-analytical characterization of blends using XRPD, MO, SEM-EDS and mechanical test, demonstrated that alkali activation reaction took place for all samples, and up to 75% of sludge could be substituted to clay. However, the matrices development were quite affected by the different environmental conditions. Samples cured in the winter season ( $RT \leq 18\text{ }^{\circ}\text{C}$  -  $RH > 75\%$ ) exhibited higher compressive strength compared to those cured in the summer season ( $RT > 25\text{ }^{\circ}\text{C}$  and  $RH > 65\%$ ), e.g. 100 wt% WPS-based sample varies from about 10 MPa to 5 Mpa. The mechanical behaviours were explained by mineralogical investigations and MO and SEM observations which showed the presence of highly crystalline zeolite-A in all samples cured in the summer season, that produced discontinuities affecting samples integrity.

The results showed that parameters control during maturation is a more suitable solution for these alkali-activated mixtures. To properly allow to replicate the systems and upgrade the manufacture, an use as precast modules rather than binders is suggested.

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## **Reusability potential of selected soil types as supplementary cementitious material: Case studies with particular regard to tunnel excavation material**

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*Keywords:* calcined clay, resource-efficient tunneling, eco-efficiency.

Economic development is coupled with an ever-increasing demand for primary mineral resources. In this context, recycling of soil has gained importance. Intense research efforts have shown that calcined clays as supplementary cementitious materials (SCMs) meet the requirements to represent a viable solution in mitigating CO<sub>2</sub> emissions related to cement production. Efficient use and recycling of mineral raw materials can thus significantly reduce the demand for primary mineral resources and improve resource efficiency. In the framework of the sustainable product policy in the EU, tunnel construction projects represent a promising feature for recycling of materials in production instead of using primary resources, as large amounts of excavated soil accumulate locally and over short time periods. In soft ground, tunnels are usually built with tunnel boring machines (TBM) with liquid or earth pressure supporting the tunnel face. During the process excavated soil often needs conditioning, TBM muck thus may need to be processed prior to reuse or disposal. Excavated material can be subdivided into material classes suitable for raw material substitution, for use in earthworks and traffic route construction, or as material for landscape structures. The aim of recycling should always be to use soil as a building material in the most ecologically sensible way possible. The focus of the present study is (1) on the determination of geotechnical properties of raw materials (i.e. clayey soils) from large infrastructure construction projects, and (2) the suitability of the processed material as a starting material for binding agents in mineral building materials. Geotechnical index tests of raw soils comprised determination of soil-mechanic parameters like water binding capacity, particle size distribution, Atterberg Limits and organic content. Characteristic crystalline mineral phases of raw soils and their calcined products was conducted via XRD coupled with Rietveld refinements. A diverse suite of clayey soils defined by disparate clay mineralogy was investigated. Calcination temperatures ranged from 650-850°C, with times of temperature exposure varying between 1-4h. The experimental strategy comprised exploration of reactivity of calcined clays in combination with low-carbon Portland-composite cement CEM II/C-M (S-LL) 42.5N as reference. The reference cement was replaced by calcined clays in supplementary proportions ranging from 10-50% by mass, at a constant water/binder ratio of 0.5. Commercial Centrilit NC powder was used as a standard for metakaolin. To rule out filler effects, powdered limestone was used as a secondary standard. Evaluation of pozzolanic activity was conducted via determining flexural and compressional strength. Results show that in terms of strength development, blended mortar mixtures with cement replacement rates of up to 20% reach equal strength or even exceed that of CEM II/C-M (S-LL) 42.5N, proving that calcined clays can significantly contribute towards the eco-efficient transition of the cement industry.

## Sustainable smart inorganic nanocarriers for corrosion inhibition in conservation of reinforced concrete based Cultural Heritage

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*Keywords:* sustainable materials, corrosion inhibition, concrete.

The technical breakthrough in the manufacture process and quality control of cement that occurred in the first half of the 1900s allowed the construction of an incredible variety of monuments and civil buildings. These type of Cultural assets can exhibit specific conservation issues due to the decrease in performance of the old reinforced cement pastes that, along with the lack of appropriate conservation methodologies, can lead to a reduction, even drastic, of their life time. Among the critical issues, corrosion of rebars is a major challenge for conservators since it affects significantly the concrete durability and, accordingly, that of the building. In the field of corrosion protection, polymer coatings are commonly used, and corrosion inhibitors are employed to improve their effectiveness, however, these solutions present several limitations, including UV sensitivity of inhibitors. Smart systems based on corrosion inhibitors can significantly improve the efficacy of a protective coating by customizing the release of anticorrosive agents in response to the onset of specific degradation conditions and preventing the deactivation of these agents due to UV radiation. An innovative solution is offered by a particular class of smart nanocarriers, the mesoporous silica nanoparticles (MSNs), that are characterized by high chemical stability, large surface area, ease of preparation and compatibility with polymer coatings. They can be conveniently loaded with corrosion inhibitor, thanks to their porous structure (Olivieri et al., 2021). Various synthetic methods can produce MSN with tunable pore size, specific textural properties and with a convenient surface chemistry, able to gate the pore, allowing a stimuli-induced, more long lasting and sustainable release of the cargo.

Here, MSNs have been prepared by means of synthetic procedures (Rizzi et al., 2021) able to control pore structure, then they have been loaded with different corrosion inhibitor compounds. In particular, after firstly using conventional BTA as a reference, green corrosion inhibitors (such as ascorbic acid, tannins....) have been then tested.

The surface of the MSNs has been also purposely functionalized grafting at their surface polyelectrolyte chains, that change their conformation as a function of pH, namely when coiled up, they close the pores, preventing the release of the cargo, while upon pH changes they extend, allowing the release of the corrosion inhibitor. The prepared smart nanocarriers MSNs have been thoroughly characterized, along their loading conditions, finally their stimuli responsive corrosion inhibitor release ability has been tested in a simulating environment. The smart nanocarriers have confirmed their potential as effective candidates for a long lasting and sustainable protection of reinforced concrete based architectural elements of Cultural Heritage.

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Rizzi F., Castaldo R., Latronico T., Lasala P., Gentile G., Lavorgna M., Striccoli M., Agostiano A., Comparelli R., Depalo N., Curri M. L. & Fanizza E. (2021) - High surface area mesoporous silica nanoparticles with tunable size in the sub-micrometer regime: insight on the size and porosity control mechanisms. *Molecules*, 26, 4247, <https://doi.org/10.3390/molecules26144247>.

## **New geo-resources for the conservation of Cultural Heritage: feasibility study on the application of stone sawing sludges-based Alkali Activated Materials**

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*Keywords:* alkali activated materials, geo-resources, cultural heritage conservation.

In this work, we present for the first time the feasibility of applying Alkali Activated Materials (AAMs) synthesized by recycling stone sawing sludges as precursors for Cultural Heritage restoration and conservation purposes. AAMs are inorganic polymeric materials originating from the dissolution of aluminosilicate powdered compounds in alkaline solutions and the consequent condensation of the resulting pastes in a solid 3D network (Davidovits, 1991). AAMs could potentially have a lower environmental impact than traditional restoration and conservation products given that they offer the possibility of recycling stone wastes, which in turn, prevents the exploitation of new raw materials, promoting a circular economy (Barone et al., 2021; Portale et al., 2023). Moreover, their synthesis takes place at room temperature and without any precursor pre-treatment. In this way, production costs, thermal energy demand and, therefore, CO<sub>2</sub> emissions are lowered (Turner & Collins, 2013). The waste materials chosen for this study are stone sawing sludges (SS) composed of powders deriving from rock cutting and polishing processes mixed together with water for cooling down the sawing tools. SS are the most abundant products resulting from the stone processing industry: they amount up to 41% of the total processed rocks (Montani, 2021). The disposal of this waste is regulated by EWC 010413 in Europe and by D.lgs. n. 156/06 in Italy. Nevertheless, disposing means deprivation of a future for these potential geo-resources and it is therefore why their reuse has become an interesting challenge in the view of a circular economy.

The present work focuses on the characterization studies carried out on both SS and SS-based AAMs to investigate their chemical, mineralogical, microstructural and physical-mechanical features by means of analytical techniques such as XRF, XRD, FT-IR, SEM, colorimetry, uniaxial compressive and bending tests. The samples were also investigated by means of Oddy test, useful to investigate the potential harmful impact when using on or displaying AAMs with real artifacts. In addition, the research presents preliminary results of the SS-based AAMs application for the conservation of archaeological pottery. Selected compositions were used as fillers on no-value ceramic pots to simulate the potential behaviour on real artifacts. Changes in the physical properties of the pastes, as well as their interaction with the ceramic bodies, were monitored over time, starting from the moment of application up to a month after that: a score from one (very bad) to five (very good) was assigned to features such as ease of mixing and application, stickiness, working time, contamination of ceramic, reversibility and flexibility. The obtained results lead us to promising outlooks in the fields of conservation and restoration.

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## Calibrating HSI-SWIR (hyperspectral imaging-short wave infrared) for rapid discrimination of CDW (construction and demolition waste)

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Keywords: CDW, XRF, SWIR.

Hyperspectral Imaging (HSI) is a powerful technique able to characterize and discriminate materials in a rapid, cheap and non-destructive way. This method is commonly used in the SWIR domain under reflectance settings, and thus it is exploited in remote sensing (Mars, 2018) and unprocessed items to identify and discriminate the spectral fingerprint of materials, rocks and waste as well. As a matter of facts, there are several studies about non-mineral waste sorting based on this technology but very few are focused on the classification and sorting of ceramic- and/or mineral-like materials via HSI-SWIR (Trotta et al., 2021). Such an approach is in principle extremely useful to recognise and differentiate the types of construction materials constituting a CDW. CDW is in fact extremely heterogeneous, since it can contain organic and metallic debris as well as concretes, natural stones, masonries, etc, plus other. However, the reliability of SWIR to identify the lithic fraction of CDW is still lacking. Here, a data set of CDW samples from Abruzzo region with fully characterized petrography, i.e. XRPD and bulk geochemistry (Galderisi et al., 2022), has been used to calibrate the average SWIR spectra obtained by HSI. In addition, the same CDW data-set was also characterised via XRF-EDS mapping.

The results from the micro-XRF-EDS surface chemistry agree with the bulk chemical analysis in Galderisi et al., 2022. CaO is abundant in concrete and natural stones, intermediate to absent for masonries and absent for tiles; the contrary holds for the SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. SWIR spectra unveil three main regions of interest. The shape and the position of the peaks in the two 1300-1700 and 1800-2150 nm regions are related H<sub>2</sub>O and/or OH species; their absence or weak intensity is indicative of anhydrous crystalline and non-crystalline (glass) phases, typical of ceramic tiles or materials fired at high-T. By contrast, the presence of broad peaks characterises the poorly crystallised cement phases in concrete, whereas sharp peaks located around 1420 and 1920 nm are typical of masonry.

The third spectral region between 2150 and 2400 nm is instead crucial to discriminate clay minerals from carbonates. Peaks located around 2250 nm are more intense in silicate-rich materials, whereas the peak at 2345 nm identifies carbonates (CO<sub>3</sub><sup>2-</sup>-bearing), contained in natural limestone and concrete aggregates. This feature (2345 nm peak) is extremely diagnostic and quantitatively related to the concentration of CaO and can be used to rapidly and accurately quantify silicates vs carbonates. All these SWIR features can be transferred to the sorting facilities to separate CDW materials with similar colour and density but extremely different in chemical/mineralogical compositions.

Galderisi A., Iezzi G., Bianchini G., Paris E. & de Brito J. (2022) - Petrography of construction and demolition waste (CDW) from Abruzzo region (Central Italy). *Waste Manage.*, 137, 61-71.

Mars J.C. (2018) - Mineral and lithologic mapping capability of worldview 3 data at Mountain Pass, California, using true- and false-color composite images, band ratios, and logical operator algorithms. *Econ. Geol.*, 113, 1587-1601.

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## **Building a circular future: raw materials sourcing and supply chains in the construction industry**

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*Keywords:* cement, circular economy, raw materials.

Sustainable Development Goal (SDG) 12 fosters the establishment of “sustainable consumption and production patterns” with the aim of mitigating the environmental impact of primary raw materials sourcing, and of waste generation and disposal. It is estimated that nearly 100 billion tonnes (Gt) of raw materials are extracted globally each year and, in a business-as-usual scenario, materials extraction is projected to grow to nearly 190 Gt by 2050. Currently, at the end of the life cycle of the material flow, over 35 Gt are emitted to the atmosphere during processing, or dispersed as unrecoverable waste, and over 30 Gt are collected as waste, and mostly disposed of in landfills. Out of this stock of waste material, only approximately 8 Gt are recycled, which corresponds to less than 10% of the current annual demand. These figures demonstrate the existence of a huge margin for improvement in waste management and recovery, and the need of creating value from waste streams.

Building and construction play a critical role in this scenario, considering that about 40% of the stock of extracted raw materials is fed into this industrial sector, which also accounts for 13.5 billion tonnes of greenhouse gas emissions and about 30% of the global energy consumption. On the other hand, building materials represents an opportunity for their potential of incorporating significant amounts of waste and by-products.

Other than deploying strategies for optimal waste management and recycling, the other need for a transition towards a sustainable raw materials supply chain in construction is promoting the use of local resources. This is especially true in the emerging economies, such as those of Sub-Saharan Africa (SSA), where materials such as cement and concrete are needed to sustain the fast pace of demographic and urban growth. The use of locally sourced raw materials for construction in SSA is also fostered by SDG target 11.c: “Support least developed countries, including through financial and technical assistance, in building sustainable and resilient buildings utilizing local materials”.

In such a scenario, the geosciences have a tremendous potential in tackling the challenge of meeting the increasing demand of construction materials, while reducing associated impacts deriving from raw material extraction, waste generation, and CO<sub>2</sub> emissions.

## **Chemical-mineralogical-petrographic characterization of building demolition waste (CDW) from Tuscany for the valorization and recycling**

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*Keywords:* construction and demolition waste (CDW), separation methods, recycling.

Waste produced in EU has been under the waste directive since 2008 (2008/98/CE) which regulates also the construction and demolition wastes (CDW), representing about one third of the total amount of waste, mostly currently disposed only in landfills or for downcycling applications.

In Italy, it can be estimated that only 10% CDW is actually recycled, so it is necessary to find methodologies helping to insert this waste stream in the circular economy. A correct CDW recycling method would have not only the advantage of committing the agreements with the EU, but it would have also a favorable effect on environment. Recycling of these materials would reduce also the demand of natural aggregates, by considering CDW as a secondary raw material and a real economic resource. Other countries, especially in North Europe, as Germany, are already decreasing the mining of stone materials favoring the industrial recycling, with profit.

CDW produced in Tuscany, in areas between Pisa and Versilia, where sampled in companies dealing with the collection and separation of these materials from building demolition and refurbishments. CDW samples were subjected to grainsize separation and have been characterized using different techniques, XRD (X-Ray Diffraction) to characterize their mineralogy, SEM-EDS (Scanning Electron Microscopy-Energy Dispersive Spectroscopy) and XRF (X-ray Fluorescence) for the chemical composition, optical microscopy and image analysis for petrographic analysis and to estimate the modal composition. Transfer tests were used to obtain information about possible leaching and determine the environmental impact of these materials.

In particular, efforts were made to enhance the sampling quality using a method based on the different opposing resistances of the various CDW components, collecting the most disposable part in finest fraction. A utilization of this fraction has been attempted by mixing it with other compounds, with the aim to create tiles and mortars from CDW. The results demonstrate that this product worsens the physical characteristics of materials in which it is introduced (cement-based mortars), but products interesting for the market requirements could be produced when the right mix design is obtained.

This work reports the preliminary results obtained from a research study carried in the frame of a Master thesis at University of Pisa, under the supervision of the late Prof. Pietro Armenti (Volpintesta, 2019).

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## **Design of experiments (DOE): a preliminary study for the optimization of alkali-activated formulations**

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*Keywords:* design of experiments, basalt sawing sludge, alkali-activated materials.

The experimentation of a material requires numerous tests that can be costly and time-consuming. The optimisation of a product is conventionally done changing one parameter at a time. Such a method, called the “cost approach”, is expensive and not always effective, because the interactions between the factors (i.e., precursors, additives, solutions, speed etc.) involved cannot be estimated. Moreover, in a mix design, the sum of the factors must be equal to one, and its final feedback will be dependent on the proportion of the ingredients in the mix (Venkatesan et al., 2019). Hence, the solution is to construct a set of selected experiments, in which all the relevant factors are varied at the same time. This is the so-called design of experiments (DOE), and it allows to reveal which factor influences the response and how to make the best decision during the optimisation of a product, with the minimum number of trials and maximum efficacy, minimising costs and efforts (Goupy et al., 2007).

In this study, funded by “CHANGES – Cultural Heritage Active Innovation for Sustainable Society” – NextGenerationEU CUP: E63C22001960006, DOE approach was used to formulate alkali-activated materials based on basalt sawing sludge deriving from Mt. Etna volcano (Italy), with the aim of finding the best formulation. The Etnean basalt sawing sludge is a by-product coming from the local rock sawing activities. It represents a non-hazardous waste with low market values that can lead to serious environmental problems (e.g., dispersion in atmosphere, soil occupation, landscape spoiling etc.) (Portale et al., 2023). DOE was carried out by using the JMP® software. In detail, the experimental plan consisted of 20 tests, where basalt sawing sludge, metakaolin, sodium hydroxide and sodium silicate were the considered factors while compressive strength was the expected responses.

The final predictive model indicates which factors are the most relevant and how their combination influences the output, helping us to find an optimal formulation based on the highest compressive strength and the lack of efflorescence. Moreover, to further investigate the differences between each formulated samples, a multidisciplinary analytical approach has been carried out by means of Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFT), X-ray diffraction (XRD) and Scanning Electron Microscope (SEM).

Preliminary results have shown that the DOE approach seems to be auspicious and more efficient rather than the experimental one used in Portale et al. (i.e., keeping the precursor constant and changing the additives and activator solutions proportion). Future study will focus on the use of the best formulation as a potential replacement of traditional products (e.g., Portland cement, mortars) in the construction and restoration fields.

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**S21.**

**Mineral crystal chemistry: a powerful tool for our  
understanding of the inner nature of geomaterials. In memory  
of Alessandro Guastoni**

*CONVENERS AND CHAIRPERSONS*

*Maria Lacalamita (Università degli Studi di Bari Aldo Moro)*

*Cristian Biagioni (Università di Pisa)*

*Ferdinando Bosi (Sapienza Università di Roma)*

## Tourmaline petrogenetic indicator highlighted in a multicolored crystal from the Mavuco area (Alto Ligoña pegmatite district, NE Mozambique)

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**Keywords:** tourmaline-supergrup minerals, petrogenetic indicator, chemical and spectroscopic investigations.

Tourmaline is well known to be an efficient geological tool for investigating P–T–X conditions in all crustal settings within the Earth given its ability to register and preserve the chemical composition and the redox conditions of the environment in which it crystallized (Dutrow & Henry, 2011). These features are well highlighted in a tourmaline grain collected from the secondary deposit of Mavuco in the Alto Ligoña pegmatite district (NE Mozambique). The marked polychromism from core-to-rim that characterize this sample, suggested studying it to reconstruct its growth history. Electron microprobe analyses of the sample revealed a wide variation in FeO- and MnO-concentrations, resulting in marked changes in color from black, yellow, blue-green, pink-red in the core zone, to dark-green at the prismatic overgrowth. The black inner core is characterized by a peculiar enrichment in Fe and Mn (FeO ~5 wt.% and MnO ~4 wt.%), as result of the availability of such elements in the pegmatitic melt. Iron is exclusively present in the divalent state, as confirmed by Mössbauer analysis. The yellow core zone shows an increase in MnO, reaching values up to 7 wt.%, and a simultaneous decrease in Fe (FeO < 1 wt.%). The increased incorporation of Mn could be promoted by the depletion of Fe in the pegmatitic melt, reflecting the competition of both elements for the Y-site in the tourmaline structure. The yellowish coloration is caused by an intervalence charge transfer Mn<sup>2+</sup>-Ti<sup>4+</sup> interaction and to a minor extent by Mn<sup>2+</sup> spin-forbidden transition, as revealed by OAS analysis. A drop in the concentration of Mn<sup>2+</sup> occurs in the blue-green core zone, reaching values too low to contribute to the color (MnO < 2 wt.%), as Mn<sup>2+</sup> is a weak chromophore. In the absence of FeO in this zone, the bluish coloration is mainly due to a slight increase in CuO, which contributes through Cu<sup>2+</sup> spin allowed transitions. In the pinkish core zone, the lacking of FeO and the presence of a strong broad band at 19000 cm<sup>-1</sup> indicates that Mn<sup>3+</sup> is the main color-causing agent as the result of a change in redox environment. However, the oxidation of Mn<sup>2+</sup> to Mn<sup>3+</sup> is not related to an opening of the geochemical system, as supported by the lack of sudden change in the chemical composition in the tourmaline crystal. The oxidation can be instead explained by the presence of a natural radiation source in the proximity of the pocket, which effects became evident when Mn content reached a low level (MnO < 1 wt.%). The dark-green prismatic overgrowth is characterized by a sharp increase in Fe and Mn, as a consequence of partial destabilization of the pocket environment (Altieri et al., 2022; 2023). A pocket rupture event, followed by leaching and corrosion processes of the early crystallized Fe- and Mn-rich minerals, allowed the release of Fe and Mn in the environment and their incorporation in the overgrowth. Moreover, Mössbauer analysis revealed a Fe<sup>3+</sup>/Fe<sub>tot</sub>-ratio of ~ 4%, confirming mild oxidizing conditions.

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## Understanding genesis and color origin of the very rare leek-green tourmaline variety

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**Keywords:** tourmaline-supergroup minerals, gem-pegmatites, chemical and spectroscopic investigations.

Tourmalines from Elba Island are easily recognizable and distinguishable from those of all other world localities for their delicate pastel colors and the perfection of their crystal shape, even in small sizes. Some colors displayed by tourmalines were recorded for the first time in crystals from Elba Island. Among these, a peculiar color is the “leek-green”. The term leek-green was firstly used by the Italian naturalist Targioni Tozzetti in 1825 for describing tourmaline crystals characterized by an unusual bright acid green-yellow coloration. In order to define the color mechanisms and the characteristics of the fluids involved in their crystallization, two tourmaline crystals, with a vivid greenish-yellow color, occurring in the Catri and the Cechi pegmatitic veins from Sant’Ilario and San Piero in Campo (Elba Island, Italy), respectively, were studied with a multi-analytical approach. This approach includes electron microprobe analysis (EMP), spectroscopic investigations (OAS and FTIR) and single-crystal XDR diffraction. Experimental data reveal that both tourmalines can be classified as fluor-tsilaisite, with MnO up to 9 wt.%. Spectra recorded on both samples show absorption bands caused by Mn<sup>2+</sup> spin-forbidden transition (~24000 cm<sup>-1</sup>) and intervalence charge transfer Mn<sup>2+</sup>-Ti<sup>4+</sup> interaction (~31000 cm<sup>-1</sup>), with TiO<sub>2</sub> up to 0.40 wt.%, indicating that the leek-green coloration is due to Mn<sup>2+</sup> and Ti<sup>4+</sup> without the influence of Fe<sup>2+/3+</sup> (FeO ≤ 0.02 wt.%). The rarity of the leek-green color in the crystals is linked to specific conditions of formation: the original pegmatite-forming melt must be enriched in Mn and, at the same time, relatively depleted in Fe during tourmaline crystallization in gem pockets. Such conditions are favored by a B-rich peraluminous melt that can remove Fe as early-crystallized schorl (e.g., Laurs et al., 2007). Furthermore, Mn must be preserved when highly evolved Li-rich tourmaline starts to crystallize; this can be only achieved when spessartine garnet, the main competitor for Mn in Elba pegmatites, is absent or has crystallized during the very early stages of pegmatite crystallization (Altieri et al., 2023). In the Catri and the Cechi veins, paragenetic observations revealed that the early-stage of cavity evolution is marked by the crystallization of abundant primary schorl and a lack of spessartine. This scenario supports a high enrichment in B in the initial pegmatitic melt, which promoted schorl crystallization rather than the formation of micas or garnet (e.g., Dingwell et al., 1996). In addition, the scarce presence of biotite aids in conserving Ti until the late stages of pegmatite evolution, thus producing the leek-green color in Elba tourmalines via Mn-Ti intervalence charge transfer. The presence of Mn only in the divalent state suggests that reducing conditions are required for the formation of such colored tourmalines.

Altieri A., Pezzotta F., Skogby H., Hålenius U. & Bosì F. (2023) – Dark-coloured Mn-rich overgrowths in an elbaite tourmaline crystal from the Rosina pegmatite, San Piero in Campo, Elba Island, Italy: witness of late-stage opening of the geochemical system. *Mineral. Mag.*, 87, 130-142. <https://doi.org/10.1180/mgm.2022.125>.

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## Axinite crystal chemistry and thermal behavior

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Keywords: axinite, crystal chemistry, thermal behavior.

Axinite-group minerals are complex hydrous borosilicates belonging to the sub-class of sorosilicates, with structural formula  $^{VI}[X1X2YZ1Z2]_2^{IV}[T1T2T3T4T5]_2O_{30}(O_wOH_{1-w})_2$ . They host tetrahedrally-coordinated B at T5, Ca at both X1 and X2 highly distorted octahedra, Al at both Z1 and Z2 fairly regular octahedra, and are classified, on the basis of Mn<sup>2+</sup>-Fe<sup>2+</sup>- and Mg-occupancy of the distorted Y-octahedra, as axinite-(Mn), axinite-(Fe) and axinite-(Mg), respectively (Andreozzi et al. 2000, 2004).

Despite their wide occurrence in metamorphic environments of low to medium grade, axinite-group minerals have never been investigated in detail and their potential as water and boron carriers in geological settings remains poorly explored.

In this work, a subset of 10 axinite crystals, selected from a set of 61 samples from all over the world, were fully characterized using scanning electron microscopy (SEM), Electron MicroProbe Analysis (EMPA), Secondary Ion Mass Spectrometry (SIMS) and single-crystal X-ray Diffraction (SC-XRD). With respect to the compositional (Mn,Fe,Mg)-ternary plot, the majority of the samples cover an area close to the Fe-corner, except for a sample from Merelani (Tanzania), which shows a rare composition falling along the Mn-Mg join, and a sample from Luning (Nevada), which shows approximately an intermediate composition in terms of Mn, Fe and Mg. Chemical and structural results have been integrated with the data reported in Andreozzi et al. (2000, 2004) and the crystal chemistry of axinite-group minerals is described in detail.

In addition, the intermediate (Mn,Fe,Mg)-sample from Luning was investigated via in situ High-Temperature powder X-ray Diffraction (HT-pXRD) to define its thermal behavior and breakdown temperature at room pressure. Results obtained evidenced that the (Mn,Fe,Mg)-axinite follows a linear expansion with temperature up to 600°C, then showing a deviation from linearity up to a temperature of 850°C, which represents its breakdown temperature. Above 850°C, the (Mn,Fe,Mg)-axinite decomposes into anorthite and a clinopyroxene-like phase, plus a possibly very minor amount of melt where boron and water are likely to be stored.

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## Ferro-bosiite, a new tourmaline species from Mavuco, Alto Ligoña pegmatite district, NE Mozambique

Bosi F.\*<sup>1</sup>, Altieri A.<sup>1</sup>, Skogby H.<sup>2</sup>, Pezzotta F.<sup>3</sup>, Hålenius U.<sup>2</sup>, Tempesta G.<sup>4</sup>, Ballirano P.<sup>1</sup>, Flégr T.<sup>5</sup> & Cempírek J.<sup>5</sup>

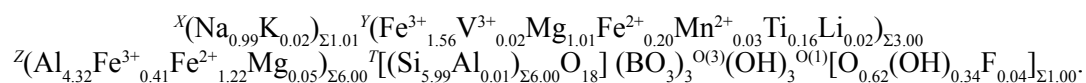
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**Keywords:** New mineral species, tourmaline, ferro-bosiite.

Ferro-bosiite, ideally  $\text{NaFe}^{3+}_3(\text{Fe}^{2+}_2\text{Al}_4)(\text{Si}_6\text{O}_{18})(\text{BO}_3)_3(\text{OH})_3\text{O}$ , is a new mineral of the tourmaline supergroup. It was discovered in a giant collapsed cavity discovered in the “Marina” granitic pegmatite, at the Mavuco locality in the Alto Ligoña pegmatite district, NE Mozambique (46°03'30.74"N – 8°48'24.47"E, 730 m asl). Ferro-bosiite occurs as black acicular late-stage overgrowth at the analogous pole of multicolored fluor-elbaite crystal. The black crystals, with a vitreous luster, have brown streak, conchoidal fracture, a Mohs hardness of ~7. Ferro-bosiite is uniaxial negative, with refractive indices  $\omega = 1.675(5)$  and  $\varepsilon = 1.645(5)$ . This new tourmaline was studied with a multi-analytical approach: single-crystal XRD diffraction, electron microprobe, Mössbauer, infrared, optical absorption and micro-laser induced breakdown spectroscopy.

It has trigonal symmetry, space group  $R3m$ ,  $a = 16.0499(5)$  Å,  $c = 7.2977(2)$  Å,  $V = 1628.03(11)$  Å<sup>3</sup>,  $Z = 3$ , calculated density = 3.216 g/cm<sup>3</sup>. The crystal structure was refined to  $R_1 = 2.55\%$  using 1547 unique reflections collected with  $\text{MoK}\alpha$  X-ray intensity data. Crystal-chemical analysis resulted in the empirical crystal-chemical formula:



Ferro-bosiite is an oxy-species belonging to the alkali group 3 of the tourmaline supergroup. The closest end-member composition of valid tourmaline species is that of bosiite, ideally  $\text{NaFe}^{3+}_3(\text{Mg}_2\text{Al}_4)(\text{Si}_6\text{O}_{18})(\text{BO}_3)_3(\text{OH})_3\text{O}$ , to which it is related by the substitution  ${}^z\text{Fe}^{2+} \leftrightarrow {}^z\text{Mg}$ . The new mineral was approved by the International Mineralogical Association's Commission on New Minerals, Nomenclature and Classification (IMA-CNMNC) (Bosi et al., 2022).

From the list of IMA-CNMNC approved minerals (Pasero, 2023), it appears that the tourmaline supergroup consists of 39 species. Tourmaline is hence the eighth grouping of minerals with similar structure on Earth, preceded by amphiboles (> 110 approved species), zeolites (> 90), spinels (~ 60), alunites, apatites, hydrotalcites and seidozerites (each with more than 40 species).

Bosi F., Altieri A., Skogby H., Pezzotta F., Hålenius U., Tempesta G., Ballirano P., Flégr T. & Cempírek J. (2022) - Ferro-bosiite, IMA 2022-069. In: IMA Commission on New Minerals, Nomenclature and Classification (CNMNC) - Newsletter 70. Eur. J. Mineral., 34, 591-601. <https://doi.org/10.5194/ejm-34-591-2022>.  
Pasero, M. (2023) - The IMA-CNMNC List of Mineral Names – Updated: May 2023. <http://cnmnc.units.it/>.

## Tourmaline life-cycle in subduction systems

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Keywords: maruyamaite, tourmaline, UHP.

For a long time, tourmaline, a boron hydrous cyclo-silicate, was just considered an accessory mineral limited to crustal conditions, and was mostly appreciated as a gemstone for the variety of its colors and high durability. Only in the last few decades tourmaline was re-evaluated as a powerful geological tool, useful to get information about the chemistry of its mineralizing fluids and possibly about the oxidative conditions of its formation environment. Particular relevance was gained by tourmaline when it was considered as a potential boron and water carrier into specific geological settings as subduction zones (e.g. Marschall & Jiang, 2011). In fact, tourmaline formation is inextricably related to the presence of boron, which is hosted in its crystal structure at a specifically dedicated site, namely *B* site from tourmaline general formula  $XY_3Z_6T_6O_{18}(BO_3)_3O_3O_1$ .

During the early subduction stages, boron is highly enriched in serpentinites both absorbed on antigorite's surface and lattice-bounded. As boron is a fluid-mobile element, it strongly partitions in the fluid phase; therefore, it can be released from crystal structure during serpentine dehydration reactions and breakdown (structural collapse) and redistributed in stable mineral phases as tourmaline, that can crystallize in such conditions. Thus, tourmaline can actually born in subduction zones, carry water and boron at greater depths and in turn release them when its breakdown conditions are reached.

The experimental work performed in this work was primarily designed to define the breakdown temperature of tourmaline, at pressure conditions comparable to those occurring in the shallowest and inner portions of a down-going slab. It turned out that tourmaline (specifically schorl composition) is stable up to 700 and 600°C at, respectively, 3.5 and 4.5 GPa.

Water is not only released during breakdown, as part of the total amount is also lost during a thermally induced oxydation-dehydrogenation process, which takes place before breakdown and is represented by following equation:  ${}^YR^{2+} + {}^{O^{3+}/O}OH^- + \frac{1}{4}O_2 \rightarrow {}^YR^{3+} + {}^{O^{3+}/O}O^{2-} + \frac{1}{2}H_2O$ , where R is a generic transition element (commonly Fe or Mn) and  $O_2$  is oxygen from the environment.

To better understand how tourmaline structure reacts to the increasing temperature up to breakdown, in situ high-temperature powder X-ray Diffraction experiments were performed at room pressure. Different tourmaline compositions (schorl, Fe-rich fluor-elbaite, Mn-bearing elbaite, uvite) were considered in this second set of experiments to check for a possible composition-dependent thermal behavior. Apparently, the same breakdown temperature of roughly 850°C was measured for all the studied compositions, suggesting that the thermal behavior of tourmaline is not directly related to the *Y* population (which is very different for all the considered species) but to the composition of the tridimensional framework of *Z* polyhedra.

Lussier A., Ball N.A., Hawthorne F.C., Henry D.J., Shimizu R., Ogasawara Y. & Ota T. (2016) - Maruyamaite,  $K(MgAl_2)(Al_5Mg)Si_6O_{18}(BO_3)_3(OH)_3O$ , a potassium-dominant tourmaline from the ultrahigh-pressure Kokchetav massif, northern Kazakhstan: Description and crystal structure. *Am. Mineral.*, 101, 355-361.

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Musiyachenko K.A., Korsakov A.V & Letnikov F.A. (2021) - A new occurrence of maruyamaite. *Dokl. Earth Sci.*, 498, 403-408.

Walenta K. & Dunn P.J. (1979) - Ferridravite, a new mineral of the tourmaline group from Bolivia. *Am. Mineral.*, 64, 945-948.

## Crystal chemistry of oxy-dravite-maruyamaite series

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Keywords: maruyamaite, tourmaline, UHP.

The potassium-dominant tourmalines known so far are very peculiar species, namely povondraite  $[\text{NaFe}^{3+}_3(\text{Mg}_2\text{Fe}^{3+}_4)(\text{Si}_6\text{O}_{18})(\text{BO}_3)_3(\text{OH})_3\text{O}]$  and maruyamaite  $[\text{K}(\text{Al}_2\text{Mg})(\text{Al}_5\text{Mg})(\text{Si}_6\text{O}_{18})(\text{BO}_3)_3(\text{OH})_3\text{O}]$ , that crystallized from mineralizing fluids extremely rich in K at unique localities on Earth, respectively: Bolivia (Walenta & Dunn, 1979) and Kazakhstan (Lussier et al., 2016).

The incorporation of large cations such as  $\text{K}^+$  in tourmaline structure is unfavored with respect to smaller cations as  $\text{Na}^+$  and  $\text{Ca}^{2+}$ , therefore specific conditions of formation (structural or environmental), aside from K abundance in the forming medium, are required.

For povondraite, the incorporation of K was hypothesized to follow from the enlargement of the cell volume due to the presence of the wide cation  $\text{Fe}^{3+}$  at Z polyhedra.

The finding of diamond inclusions in maruyamaite suggested instead a possible genetic environment of ultra-high pressure (UHP) conditions, which should have “squeezed” the large cation  $\text{K}^+$  into the structure. However, the coexistence of biotite and K-feldspar with maruyamaite undermined this formation model, apparently restraining its stability up to 1.4 GPa and 650-800°C (Musiachenko et al., 2021).

Anyway, whatever the formation model is, K content in tourmaline largely affects its structural parameters. In this work, nine single crystals from the whole compositional series oxy-dravite–maruyamaite were fully characterized through scanning electron microscopy (SEM), electron microProbe analysis (EMPA) and single-crystal X-ray Diffraction (SC-XRD). The obtained results showed that a progressive increase in K content (i.e. going from oxy-dravite to maruyamaite) through the substitution  $^x\text{Na}+^y\text{Mg}+^{\text{O}3}(\text{OH}) = ^x\text{K}+^y\text{Al}+^{\text{O}3}\text{O}$ , leads to an increase in *c* parameter length,  $\langle X\text{-O} \rangle$  and cell volume.

Lussier A., Ball N.A., Hawthorne F.C., Henry D.J., Shimizu R., Ogasawara Y. & Ota T. (2016) - Maruyamaite,  $\text{K}(\text{MgAl}_2)(\text{Al}_5\text{Mg})\text{Si}_6\text{O}_{18}(\text{BO}_3)_3(\text{OH})_3\text{O}$ , a potassium-dominant tourmaline from the ultrahigh-pressure Kokchetav massif, northern Kazakhstan: Description and crystal structure. *Am. Mineral.*, 101, 355-361.

Musiachenko K.A., Korsakov A.V & Letnikov F.A. (2021) - A new occurrence of maruyamaite. *Dokl. Earth Sci.*, 498, 403-408.

Walenta K. & Dunn P.J. (1979) - Ferridravite, a new mineral of the tourmaline group from Bolivia. *Am. Mineral.*, 64, 945-948.

## Equation of state and structural evolution of jamesonite ( $\text{FePb}_4\text{Sb}_6\text{S}_{14}$ ) at high pressure

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Keywords: jamesonite, crystal structure, high pressure.

The high-pressure behaviour of Jamesonite ( $\text{FePb}_4\text{Sb}_6\text{S}_{14}$ ,  $a = 4.08(3)$ ,  $b = 19.08(3)$ ,  $c = 15.67(3)$  Å,  $\beta = 91.68(8)^\circ$  and  $V = 1214(6)$  Å<sup>3</sup> space group  $P2_1/c$ ), a natural antimony sulfosalt, has been investigated using in-situ HP-synchrotron X-ray single crystal diffraction up to 16.6 GPa with a diamond anvil cell under hydrostatic conditions. Jamesonite is included in the group of rod-based sulfosalts structure made of infinite rods of M-S polyhedra typical of Pb-Sb sulfosalts. Jamesonite crystals has been commonly found as needle-like morphology and for this reason these types of sulfosalts attracted the scientific interest for application in selective absorption and catalysis and microstructural devices. It is an intrinsic semiconductor with an optical band gap of 0.48 eV. Furthermore, this mineral represents a valuable source of antimony, an important metal for the metallurgy and semiconductor industrial sector. Pressure could play an important role on the structural properties of these thermoelectric compounds. Measurements were made at the ID-15B beamline at ESRF (Grenoble) synchrotron. Fitting the pressure volume (P-V) data with a third order Birch-Murnaghan Equation of State (BM-EoS) we obtained the following values:  $V_0 = 1214(6)$  Å<sup>3</sup>,  $K_0 = 35(3)$  GPa, and  $K'_0 = 4.4(5)$ .  $K_0$  becomes equal to 37.0(9) fitting the data with a second order BM-EoS. The compressibilities of the lattice parameters, up to 16.6 GPa, were studied by fitting the data with a third-order BM-EoS and the following values were found:  $M_{0a} = 55$  GPa,  $M'_a = 19$ ,  $M_{0b} = 130$ ,  $M'_b = 11.0$ ,  $M_{0c} = 147$  and  $M'_c = 10$ ; by using second-order BM-EoS the data were  $M_a = 81$ ,  $M_b = 122$ ,  $M_c = 133$ . Axial and volume Eulerian-finite strain ( $f_E$ ) at different normalized stress ( $F_E$ ) were calculated. Structural refinements comparison at different P indicates that Fe and Sb do not change their coordination number over the whole investigated P range: Fe has a 6 coordination whereas the three Sb polyhedra have 5 coordination. On the other hand, both Pb polyhedra increase their coordination around 12 GPa: Pb1 passes from 6+1 to 7 coordination, whereas Pb2 passes from 7+1 to 8+1 coordination (taking into account bond lengths lower than 3 Å). The effect of temperature (T) on the baric behaviour of jamesonite will be presented by using data collected at different P along three isotherms (room T, 426K and 523K).

## Ca-REE fluorcarbonates from Cuasso al Monte (Western Southern Alps): a new (Nd)-fluorcarbonate and evidence of Ce mobility

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Keywords: Rare Earth Elements, synchysite-(Ce), REE-fluorcarbonates.

Ca-REE fluorcarbonate minerals are the main ore for Rare Earth Elements (REE). As well established, REE are critical raw materials and their role is crucial for the industrial progress, the development of modern and environmental-friendly green technologies. However, despite their importance, a lot of open questions exist about the mechanism that governs their transport and deposition. Nevertheless, the understanding of the partitioning of REE is of paramount importance for mineral beneficiation and recycling. Furthermore, Ca-REE fluorcarbonates belonging to the bastnäsite-synchysite series are important for a mineralogical and crystallographic perspective, since they form a polysomatic series (Capitani, 2019).

We studied Ca-REE fluorcarbonates from Cuasso al Monte (Western Southern Alps) found within miarolitic cavities of the granophyre. Ca-REE fluorcarbonates occur in two different morphologies: hexagonal prism and flower-like aggregates of hexagonal lamellae, both micrometer in size. This report focuses on the latter. By means of SEM-EDS and Micro-Raman spectroscopy (Conconi et al., 2022), we identified two different phases: synchysite-(Ce) and a possible new (Nd)-fluorcarbonate. In the latter, the dominant REE is Nd, followed by La and Ce, and has a Ca/(Ca+REE) ratio of 0.09-0.15, which is close to the ratio of the B<sub>5</sub>S (0.14) and B<sub>6</sub>S (0.12) unnamed polysomes. Moreover, the new phase is associated with botryoidal phyllosilicates covered by a thin Ce-oxide layer. The morphology of synchysite and the new phase is very similar, but whereas in synchysite the hexagonal lamellae are compact, with a Ca and Ce depleted rim, in the new phase they show a complex microstructure: the lamellae are highly porous and, as evidenced by TEM, they consist of an intergrowth of fluorcarbonate nanocrystals and minor hematite, chamosite and kaolinite.

Overall, these observations suggest a mechanism in which Ce is leached from synchysite-(Ce) and precipitates as Ce-oxide, leading to a remnant Nd-fluorcarbonate phase.

Capitani G. (2019) - HRTEM investigation of bastnasite-parisite intergrowth from Mount Malosa (Malawi): Ordered sequences, polysomatic faults, polytypic disorder, and a new parisite-(Ce) polymorph. *Eur. J. Mineral.*, 31, 429-442. <https://doi.org/10.1127/ejm/2019/0031-2824>.

Conconi R., Fumagalli P. & Capitani G. (2022) - A multi-methodological study of the bastnasite-synchysite polysomatic series: Tips and tricks of polysome identification and the origin of syntactic intergrowth. *Am Mineral.*, in press. <https://doi.org/10.2138/am-2022-8678>.



## Chemical characterization of geomaterials at a nanoscale with TEM-EDS: a comparison between the Standardless, Cliff & Lorimer and Absorption correction quantification methods

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Keywords: TEM-EDS, absorption correction, Cliff-Lorimer approximation.

Transmission electron microscopy (TEM) is a well-established technique for the study of geomaterials from the microscale down to the atomic scale. Other than structural and microstructural information, chemical composition at a comparable scale can be obtained. Basically, energy dispersive X-ray spectroscopy (EDS) is the most widespread analytical method installed in TEMs because it is easy to use, fast and of relatively low acquisition cost.

In TEM-EDS microanalysis, the *A* (absorption) and *F* (secondary fluorescence) corrections are generally omitted because the sample is so thin (tens of nm), and therefore the interaction volume so small, that they are negligible. However, as demonstrated in this work, this is not always the case.

Here we describe a method for the calibration of the TEM-EDS system and the application of the absorption correction method (ACM) (van Cappellen & Doukhan, 1994) to the analyses. The results are then compared with those obtained with the standardless method (STL) (Williams & Goldstein, 1991) and the Cliff-Lorimer approximation (CLA) (Cliff & Lorimer, 1975). For the purpose, cordierite, johannsenite, fayalite, spinel, biotite and antigorite, previously characterized with electron microprobe, have been tested. The results show that in all cases the ACM and the CLA give results superior than the STL method. However, whenever one has to deal with dense minerals and/or to work in thick areas of the sample, the ACM gives more consistent results. For instance, with the CLA, the relative abundances of Fe and Si in fayalite (a relatively dense mineral) diverge with increasing thickness, showing a positive slope for Fe and a negative slope for Si – which is an indication of uncorrected absorption – whereas the results for ACM show flat trends for both elements, i.e. their relative abundances with varying thickness are constant. This behaviour is only slightly noticed for Mg and Fe in cordierite (a relatively light mineral) and is not observed at all in antigorite. Furthermore, the possibility to rule out the contribution of absorption to any detected chemical difference, makes the ACM a more confident method for the study of nanoscale zoning, as evidenced in the case of johannsenite, where chemical zoning involving Mn, Fe and Mg were detected.

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## Fe-bearing vanadium dioxide - paramontroseite: structural details and high temperature transformation

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Keywords: paramontroseite, vanadium, high-temperature.

Vanadium is a multivalent transition metal, forming a large number of different oxides (Shvets et al., 2019). Interest for V has recently grown in relation to the increasing sensitivity to environmentally sustainable energy solutions. In fact, V has chemical-physical features making it suitable for use in many technological applications, as catalysis, batteries, electrochromic systems, solar windows, supercapacitors.

Paramontroseite is a V dioxide isostructural with ramsdellite ( $\text{MnO}_2$ ; Curetti et al., 2021): pairs of octahedral chains run along z and share vertices, so that empty channels parallel to z are formed.

A natural sample of Fe-bearing paramontroseite from Prachovice mine (Czech Republic; Sejkora et al., 2013) was investigated to shed light on structural details, cation partitioning and behavior upon heating. In our specimen, the crystals are strewn over a carbonate matrix and show an opaque black color and regular lamellar shape (7-8 mm). Among the lamellae of paramontroseite one can distinguish calcite and small crystals of a transparent yellow-greenish color, identified as an uraninite-like phase.

Sample fragments of the specimen were analyzed using a JEOL JSM-IT300LV Scanning Electron Microprobe; quantitative chemical analysis and composition maps were recorded to investigate the distribution of the main elements in the original sample. Idiomorphic crystals show a core-to-rim zonation (Fe and Al increase approaching the rim). The average formula unit is  $\text{V}_{0.84}\text{Fe}_{0.19}\text{Al}_{0.03}\text{O}_2$ .

XRD experiments carried out on single crystal ( $a = 4.8960(14)$ ,  $b = 9.395(3)$ ,  $c = 2.9163(5)$  Å,  $V = 134.14(6)$  Å<sup>3</sup>; S.G. *Pbnm*) showed that V and Fe are not vicariant of one another, as V occupies the octahedral site at (0.09 0.14 0.25), whereas Fe enters a tetrahedral site at (0.41 0.06 0.25), the latter expected to be empty in the ideal structure. Geometrical distance between M and T positions is 1.746(2) Å, thus suggesting that it is unlikely to have both sites occupied at the same time.

The behavior upon heating has been investigated in situ until 550°C, using an X-ray Rigaku SmartLab XE powder diffractometer equipped with a high temperature cell. The unit cell volume shows a non-linear trend with T, characterized by three intervals, in which V increases, decreases and increases again, though  $a$  shortens,  $b$  remains almost constant until 300°C and then increases, and  $c$  increases steadily. The calculated  $\beta$  coefficients are: -2.0, 3.0, 0.8 and  $1.8 \cdot 10^{-5} \text{ }^\circ\text{C}^{-1}$  for  $a$ ,  $b$ ,  $c$  and  $V$ . At T higher than 350°C, V undergoes oxidation, from [4+] to [5+], and paramontroseite decomposes into Fe-tetrapolyvanadate ( $\text{Fe}_2\text{V}_4\text{O}_{13}$ ) and V-pentoxide ( $\text{V}_2\text{O}_5$ ).

m-Raman spectroscopy analyses confirmed that paramontroseite is sensible to heating: the crystal surface invested by the laser beam degrades very quickly, leading to the phases revealed by diffraction measurements. There is no evidence for the formation at high T of a rutile-type phase, as we observed for ramsdellite  $\text{MnO}_2$ .

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## Mineralogical characterization of zoned sphalerite from the Zn-Pb ore deposit of Longobucco (Sila Massif, Calabria, Southern Italy)

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Keywords: sphalerite, Longobucco, mineral chemistry.

Polymetallic ore deposits of the Sila Massif were subjected to raw metals exploitation starting from the Bronze and Iron ages. In spite of this, the scientific literature on their mineralogical characterization is not comprehensive and mostly out-of-date, as recently reported (Fregola et al., 2023). A mineral chemistry study with special focus on some phases could certainly contribute to decipher the origin of these mineral deposits. In this contribution, we present a mineralogical characterization of zoned sphalerite samples collected from the mineralized bodies outcropping along a fault zone cross-cutting monzodiorites at the “Torrente La Manna” site in the Longobucco area (Sila Massif, Calabria). In a separate contribution, we also present results on the whole mineralogical association of this mineralized site, including paragenetic considerations (Ciccolella et al., 2023). Sphalerite from Longobucco has been analysed by optical microscopy, micro-Raman spectroscopy, scanning electron microscopy (SEM), electron probe micro analyses (EPMA), and single crystal X-ray diffraction. Chemical micro-analyses revealed that sphalerite contains minor to trace amounts of Fe ( $0.803 \pm 0.021$  to  $9.550 \pm 0.064$  wt.%), Cd (up to  $0.685 \pm 0.020$  wt.%), Hg ( $0.176 \pm 0.033$  to  $0.461 \pm 0.039$  wt.%), Cu (up to  $0.454 \pm 0.011$  wt.%), and Co (up to  $0.023 \pm 0.005$  wt.%). Sphalerite from Longobucco systematically shows colour and chemical zoning, with darker coloured growth bands due to enriched Fe-content. Sector zoning of Cd is also observed. The optical and paragenetic study allowed us to associate the different colour zones to different growth episodes. In particular, sphalerite of the first generation (sphalerite-I) is lighter coloured and Fe-poorer, with respect to the darker and Fe-richer one of the second generation (sphalerite-II). Micro-Raman spectroscopy and single crystal X-ray diffraction were performed on the different colour zones. In particular, Raman spectra show that number, position and relative intensity of the bands in the spectral range 250-400  $\text{cm}^{-1}$  are related to the colour zoning and Fe-content of the sphalerite growth bands. These results are in good agreement with the previous literature (Buzatu et al., 2013). Preliminary single crystal X-ray diffraction data detected a slight difference between the lattice parameters of the lighter sphalerite-I ( $5.4140 \pm 0.0009$  Å) and of the darker sphalerite-II ( $5.4194 \pm 0.0007$  Å). Based on the relationship between Fe-content and cell parameters found in synthetic  $\text{Fe}_x\text{Zn}_{(1-x)}\text{S}$  solid solutions (Osadchii & Gorbaty, 2010), our results would correspond to a difference from 0.06 to 0.15 mole fraction of FeS. Zoned sphalerite indicates a variation in the composition of the mineralizing fluid(s) during the geological history of the Longobucco ore deposit.

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## In situ temperature dependent investigation of natural taranakite from the Pollera Cave (Liguria, Italy)

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Keywords: HT-XRD, taranakite, francoanellite.

Taranakite is a phosphate mineral with chemical formula  $K_3Al_5(PO_3OH)_6(PO_4)_2 \cdot 18H_2O$ , crystallizing in the trigonal system (space group *R-3c*); its structure is known from single crystal X-ray diffraction and neutron diffraction experiments on synthetic analogues (Dick et al., 1998).

It occurs in natural environments as white powdery aggregates and nodules inside bat guano deposits in caves and as an important reaction product between soils and acidic phosphatic solutions derived from the dissolution of fertilizers (Liu et al., 2002). From thermogravimetric analyses, natural taranakite has been shown to partially dehydrate to form francoanellite at temperatures higher than 105°C (Marincea & Dumitraş, 2003). The occurrence of natural francoanellite was also reported from different caves around the world (Queffelec et al., 2018, and references therein). Studying the crystal chemistry and stability of these phases and their response to different environmental conditions could provide valuable information to gain a more comprehensive understanding of the minerogenetic mechanisms occurring in cave environments and of the processes controlling P diffusion and availability in soils. Moreover, their dependence on temperature and humidity conditions makes them viable candidates as environmental proxies.

The studied samples were collected from a fossil bat guano deposit inside the Pollera Cave (Liguria, Italy), specifically at the boundary between bat guano and a layer of detrital red clays (*terra rossa auct.*). The transition from taranakite to francoanellite was investigated by in situ high temperature powder diffraction ( $T = 25 - 225^\circ\text{C}$ ) in the angular range  $4 - 48^\circ 2\theta$ . Complementary data was also gathered by means of thermal analyses (TG-DTA) and in situ high temperature FTIR spectroscopy.

The variations in lattice parameters of taranakite and francoanellite along the temperature profile were studied through refinement from diffraction data with the Rietveld method and peak fitting. The refinement also allowed to estimate the rate of phase transition through the quantification of mineral concentrations.

The results of thermal analyses agree with diffraction and spectroscopic data and show that the loss of molecular water during heating is a two-step process that determines i) the destabilization of taranakite with consequent formation of francoanellite at temperatures higher than 85°C and ii) the progressive amorphization of the material from 140°C.

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## Stability and metastability of MgSiO<sub>3</sub> pyroxenes at deep mantle conditions: new insights from ab initio calculations

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Keywords: pyroxenes, thermodynamics, ab initio.

Pyroxene minerals are key to understand the structure and composition of Earth and rocky exoplanets interiors. Nevertheless, the full details of the MgSiO<sub>3</sub> phase diagram still remain unclear, in particular in the high temperature region, where the phase stability of HT pyroxenes is assessed from inaccurate, or even unphysical, thermodynamic data. According to the more recent thermodynamic assessments, pyroxenes with MgSiO<sub>3</sub> composition are known to exist in at least five different structures and undergo structural phase transitions with increasing P-T conditions. At low T and low P, monoclinic low-clinoenstatite (LP-CEn) with space group *P21/c* is the stable phase. A displacive phase transition occurs at high pressure (i.e.  $P > 6-7$  GPa) resulting in high-pressure clinoenstatite (HP-CEn) with space group *C2/c*. Orthoenstatite (OEn, *Pbca*) occurs at high T and pressures up to about 7 GPa, whereas protoenstatite (PEn, *Pbcn*) and high-T clinoenstatite (HT-CEn, *C2/c*) have small stability fields at high T and low P (Gasparik, 2003). This is further complicated by the fact that several additional metastable pyroxenes have been suggested to be preserved in the mantle (Thompson & Downs, 2003). Metastable pyroxenes could also have a role in subducting slab dynamics due to their slow dissolution rate into majoritic garnet, favouring slab stagnation at the mantle transition zone (Agrusta et al., 2014). Pyroxenes polymorphism is extremely difficult to reproduce experimentally either because some of the above mentioned minerals are unquenchable phases (like PEn and HP-CEn), or because difficulties arise during the synthesis procedure of pure MgSiO<sub>3</sub> end members (as in the case of OEn). This prevents to obtain a comprehensive knowledge on their thermodynamic properties, which are in turn fundamental for the investigation of phase equilibria of pyroxenes at mantle conditions. Hence, these phases represent the perfect ground to test the predictive power of ab initio calculations based on quantum-mechanical theory.

We present a DFT based ab initio B3LYP computational study on MgSiO<sub>3</sub> pyroxenes. All their relevant thermophysical and thermodynamic properties (e.g. heat capacity, vibrational entropy, thermal expansion, thermal EoS) have been calculated in the framework of the quasi-harmonic approximation (QHA) by full phonon dispersion calculations. The computed properties have been tested by predicting pyroxenes phase equilibria from subsolidus up to melting conditions via classical thermodynamic modelling. Theoretical phase boundaries agree with experimental results and provide new insights on pyroxenes polymorphism: for example, our calculations revealed that HT CEn is never stable at high T and low P conditions and PEn is the liquidus phase of the MgO-SiO<sub>2</sub> system (at least up to 1.2-1.9 GPa). Theoretical melting curves are also in good agreement with piston-cylinder experiments (Boyd et al., 1964). Implications for geodynamic processes are eventually shown and discussed.

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## High temperature studies of fedorite and fluorcarletonite from the Murun alkaline complex (Russia)

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Keywords: fedorite, fluorcarletonite, thermal behavior.

Over the last ten years we have investigated a selection of rare silicates from ultra alkaline rocks of the Siberian Russia (Lacalamita et al., 2019; Kaneva et al., 2020 and references therein). In some cases detailed crystal chemical studies were lacking in the literature as well as non ambient X-ray diffraction investigations (Comboni et al., 2019; Lacalamita et al., 2019).

In the present work the thermal behavior of fedorite,  $\text{Na}_{2.5}(\text{Ca}_{4.5}\text{Na}_{2.5})[\text{Si}_{16}\text{O}_{38}]\text{F}_2 \cdot 2.8 \text{H}_2\text{O}$  and fluorcarletonite,  $\text{KNa}_4\text{Ca}_4\text{Si}_8\text{O}_{18}(\text{CO}_3)_4(\text{F}, \text{OH}) \cdot \text{H}_2\text{O}$  from the Murun massif (Russia) is reported for the first time. Specifically, the combination of thermal analysis and in situ high temperature single crystal X-ray diffraction (HT-SCXRD) was employed for both minerals, whereas ex situ high temperature Fourier Transform Infrared Spectroscopy (HT-FTIR) and molecular dynamics simulations complemented the characterization of fedorite and fluorcarletonite, respectively.

In the case of fedorite, all the employed analytical techniques testified for a continuous dehydration reaction up to  $T \sim 600^\circ\text{C}$  whereas thermal analysis evidenced the complete loss of  $\text{H}_2\text{O}$  at  $650\text{-}700^\circ\text{C}$ . The release of the F atoms occurred above  $700^\circ\text{C}$  whereas the breakdown of the structure at about  $1000^\circ\text{C}$ . HT-SCXRD showed thermal expansion from room temperature to  $600^\circ\text{C}$  with a preferential increase of the *a* and *b* axes and a decrease of the *c* cell parameter as a consequence of the partial dehydration.

Fluorcarletonite is a new mineral, very recently described (Kaneva et al., 2020). It has a complex structure consisting of infinite branched *sechser* double-silicate layers (having four- and eight-membered rings of  $\text{SiO}_4$  tetrahedra), sheets of Na- and Ca-centered polyhedra linked to isolated  $(\text{CO}_3)^{2-}$  groups and  $\text{K}^+$  cations occupying the cavities within the eight-membered silicate rings. OH and  $\text{H}_2\text{O}$  groups coordinate Na-polyhedra. A continuous unit cell volume expansion was provided by XRD analysis in the  $25\text{-}550^\circ\text{C}$  T range, whereas the quality of intensity diffraction data rapidly decreased at  $T > 550^\circ\text{C}$ . Molecular dynamics simulations, preliminarily performed at constant volume (the NVT ensemble), allowed to detect the temperature range at which the rupture of the O-H bonds or the subsequent C-O bonds rupture in the  $(\text{CO}_3)^{2-}$  group take place. Besides, constant pressure molecular dynamics simulations (the NPT ensemble) were carried out, in order to investigate the crystal phases occurring at  $T \geq 1000^\circ\text{C}$ .

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## Crystal structure and disorder of layered lead oxychlorides: the cases of blixite and thorikosite

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Keywords: blixite, thorikosite, oxychloride.

Layered lead oxychlorides (hereafter LLO) are ideally composed by litharge-like PbO blocks, alternated with sheets of Cl<sup>-</sup> ions (Chukanov et al., 2019). The electroneutrality can be reached by different mechanisms such as substitution of OH<sup>-</sup> for O<sup>2-</sup> in the PbO layer, insertion of Pb atoms in the chloride sheet (with the formation of square planar PbCl<sub>4</sub> groups), substitution of Pb<sup>2+</sup> by higher-charge cations, removal of some OPb<sub>4</sub>-tetrahedra with incorporation of anionic groups, such as OH<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, SiO<sub>4</sub><sup>4-</sup>, BO<sub>3</sub><sup>2-</sup>, leading to cavities of different size and shape which are often ordered and may give rise to several superstructures. The latter case seems to occur in blixite [Pb<sub>8</sub>O<sub>5</sub>(OH)<sub>2</sub>Cl<sub>4</sub>; *a* 5.832(3), *b* 5.694(5), *c* 25.47(2) Å] (Gabrielson et al., 1958): although detailed structural studies on natural blixite have never been done so far, Krivovichev & Burns (2006) described the crystal structure of a synthetic analogue of blixite with a monoclinic *C2/c* four-fold supercell [*a* 26.069(5), *b* 5.8354(11), *c* 22.736(4) Å, β 102.612(6)°, *V* 3375.3(11) Å<sup>3</sup>]. In an ongoing investigation of disorder in LLO, we performed a SC-XRD and EPMA study of blixite from the type locality (Långban mine, Sweden). EPMA data lead to a Pb/Cl atomic ratio very close to 2. Preliminary SC-XRD results indicate a monoclinic cell with halved volume with respect to that reported by Krivovichev & Burns (2006). The resulting blixite structure exhibits a topology of the PbO layers quite similar to that observed in the synthetic analogue but with a different stacking of the layers. More detailed structural studies are in progress.

Structural studies (SC-XRD and XAS) are underway also for thorikosite [Pb<sub>3</sub>Cl<sub>2</sub>(OH)(SbO<sub>3</sub>,AsO<sub>3</sub>); *a* 3.919(1) Å, *c* 12.854(5) Å, *V* 197.4(2) Å<sup>3</sup>] (Rouse & Dunn, 1985) where, despite the entry of cations with noticeably different size than Pb, such as trivalent Sb and As, no X-ray superstructure reflections were observed. Preliminary SC-XRD data on thorikosite crystals from type locality (Thorikos, Greece) confirm the *I4/mmm* basic structure. XAS data were performed on thorikosite at As and Sb *K*-edge. XANES results confirm that both elements are present at the trivalent state. EXAFS data indicate a similar coordination environment for both As and Sb with average metal-oxygen distances of 1.79 and 2.00 Å for As and Sb, respectively, thus indicating that both elements are present in the thorikosite structure in triangular-pyramidal coordination with O atoms.

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## Crystal chemistry of phlogopite from Mount Amiata volcano: preliminary data

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Keywords: phlogopite, Monte Amiata volcano, crystal-chemistry.

Mount Amiata is a Pliocene hybrid volcano active between 305 and 231 ky (Laurenzi et al., 2015), coeval with the activity of leucite-bearing Roman volcanoes (Conticelli et al., 2015). Mount Amiata rocks are characterised by the presence of both crustal xenoliths and magmatic enclaves within lavas and domes. Here we report a study on micas from Mount Amiata magmatic (AMT202) and crustal (AMT23) rocks carried out through SC-XRD, EMPA and XAS techniques.

Three crystals from each rock sample have been selected for SC-XRD and EPMA investigations. The studied crystals belong to the phlogopite-annite solid solution and crystallize in the  $2M_1$  polytype. The presence of residual peaks in the  $\Delta F$  map located between O4 and the interlayer site indicates [310] twinning and/or the coexistence of mixed  $1M$  and  $2M_1$  stacking sequences, or even a higher grade of stacking disorder (Oberti et al., 1993).

Micas from both rock samples show similar chemical features. They have high F and Ti (ca. 0.4 apfu for both samples) with Mg# around 0.5. OH contents have been estimated exploiting structural considerations regarding the length of  $c$  parameter: the shorter the  $c$  parameter, the higher the loss of hydrogen and/or F  $\rightarrow$  OH substitution (Lepore et al., 2017 and references therein); for both samples, the OH content is approximately 0.7 apfu.

XAS measurements were performed at Fe K-edge (7112 eV) on powders obtained by crushing in acetone 10 mg of hand-picked mica crystals. The analysis of the XANES pre-edge peak indicates that, despite the similarity of the chemical features of AMT23 (crustal) and AMT202 (magmatic), the two samples show very different  $Fe^{3+}/Fe_{tot}$  ratios. Indeed,  $Fe^{3+}/Fe_{tot}$  is about 10% in AMT202 and 50% in AMT23. No indication for the incorporation of  $Ti^{4+}$  and  $Fe^{3+}$  in tetrahedra was inferred from both XAS and SC-XRD results. Local information on Fe environment derived from Fe K-edge EXAFS are in excellent agreement with SC-XRD and EPMA data.

Structural and chemical data seem to indicate that the incorporation of high charge cations in the structure is mainly balanced via a combination of an *oxy* mechanism and  $M^{3,4+}$ -Tschermak substitution. Bond-length distortion parameters suggest that  $Ti^{4+}$  and  $Fe^{3+}$  are preferentially hosted in the M2 site.

Further studies are currently in progress to better understand the substitution mechanisms occurring in the investigated samples and relate them to the crystallisation conditions.

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## Occurrence and crystal chemistry of austinite, conichalcite, and zincolivenite from the Peloritani Mountains (northeastern Sicily, Italy)

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Keywords: austinite, conichalcite, zincolivenite.

In the framework of a study of the mineralogy of the small ore deposits occurring in the Peloritani Mountains, (northeastern Sicily, Italy), an association of three distinct Zn-bearing arsenates, austinite,  $\text{CaZn}(\text{AsO}_4)(\text{OH})$ , conichalcite,  $\text{CaCu}(\text{AsO}_4)(\text{OH})$ , and zincolivenite,  $\text{CuZn}(\text{AsO}_4)(\text{OH})$ , was identified. These arsenates, sampled at the Tripi mine (Messina province), were investigated using a multi-technique approach involving X-ray diffraction (both single-crystal and powder techniques), quantitative chemical analyses (in wavelength dispersive mode) and micro-Raman spectroscopy.

Austinite and conichalcite occur as aggregates of colorless bladed crystals, up to 1 mm in length, and as bright green tabular crystals, up to 1 mm in size, respectively. Zincolivenite was observed as pale green prismatic crystals, up to 0.2 mm. Electron microprobe data, recalculated based on 3 cations per formula unit (pfu) and calculated assuming the amount of  $\text{H}_2\text{O}$  necessary to achieve the electrostatic balance, give the following empirical formulae for austinite, conichalcite and zincolivenite:  $\text{Ca}_{1.04(1)}\text{Zn}_{0.86(4)}\text{Cu}_{0.09(4)}\text{As}_{0.98(2)}\text{P}_{0.02(1)}\text{O}_4(\text{OH})_{0.98}$ ,  $\text{Ca}_{0.98(1)}\text{Fe}^{2+}_{0.02(4)}\text{Cu}_{0.69(10)}\text{Zn}_{0.30(6)}\text{As}_{0.97(2)}\text{P}_{0.03(1)}\text{O}_4(\text{OH})_{0.98}$  and  $\text{Cu}_{0.73(5)}\text{Zn}_{1.25(5)}\text{As}_{1.01(1)}\text{O}_4(\text{OH})_{1.01}$ , respectively.

X-ray diffraction data collected on the three arsenates allowed the refinement of the crystal structures of austinite and zincolivenite, whereas no grains of conichalcite suitable for high-quality single crystal data collection were found. The crystal structures of austinite and zincolivenite were refined starting from the atomic coordinates given by Giuseppetti & Tadini (1988) and Chukanov et al. (2007), respectively. Austinite and zincolivenite are both orthorhombic with the following unit-cell parameters and space groups:  $a = 7.4931(5)$ ,  $b = 9.0256(6)$ ,  $c = 5.9155(4)$  Å,  $V = 400.06(5)$  Å<sup>3</sup>, space group P212121, for austinite, and  $a = 8.4594(9)$ ,  $b = 8.5324(8)$ ,  $c = 5.9893(6)$  Å,  $V = 432.30(12)$  Å<sup>3</sup>, space group Pnmm, for zincolivenite. The crystal structure of austinite and zincolivenite have been refined to  $R1 = 0.0236$  [for 1210 unique reflections with  $F_o > 4\sigma(F_o)$  and 78 refined parameters] and  $R1 = 0.0229$  [for 523 unique reflections with  $F_o > 4\sigma(F_o)$  and 48 refined parameters], respectively.

The identification of this arsenate assemblage is noteworthy, since notwithstanding the identification of high contents of potentially toxic elements (PTE) in this sector of Sicily (e.g., Cosenza et al., 2015; Cangemi et al., 2021), no mineralogical studies were devoted to the identification of the potential hosts of these PTE. In particular, the identification of austinite, conichalcite, and zincolivenite from the Tripi mine gives new insights on the fate of As in the ore deposits of the Peloritani Mountains, with the crystallization of arsenate minerals representing a step in the dispersion of As from the primary ore minerals to the environment.

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## Batoniite, a new Al sulfate from the Cetine di Cotorniano mine (Tuscany, Italy)

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Keywords: batoniite, new mineral, crystal structure.

In recent years, the study of secondary sulfate assemblages from Tuscany has provided the mineral systematics with some interesting novelties. Among the reference localities for the studies of this secondary minerals there is the Cetine di Cotorniano mine, well known for the occurrence of several species since the first half of the 1980s (Menchetti & Batoni, 2015, and references therein).

Sabelli & Santucci (1987) reported a potential new sulfate species (UM1987-12-SO:AlH, according to Smith & Nickel, 1987), associated with jurbanite, alunogen, and gypsum, but they were not able to solve its crystal structure owing to the quality of available material. Recently, during a systematic investigation of some Tuscan specimens, a new sample of UM1987-12-SO:AlH, showing white to colorless tabular crystals, up to 1 mm in size, was found. This material was suitable for single-crystal X-ray diffraction study and was characterized both chemically and structurally, confirming it is a new sulfate species. The mineral and its name, batoniite, were approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2023-008).

The empirical formula of batoniite is  $(\text{Al}_{7.98}\text{Fe}_{0.01})_{\Sigma 7.99}(\text{SO}_4)_{5.01}(\text{OH})_{13.95}(\text{H}_2\text{O})_{18} \cdot 5\text{H}_2\text{O}$ , ideally  $\text{Al}_8(\text{SO}_4)_5(\text{OH})_{14}(\text{H}_2\text{O})_{18} \cdot 5\text{H}_2\text{O}$  ( $Z = 2$ ). Batoniite is triclinic, space group  $\text{P}\bar{1}$ , with the following unit-cell parameters:  $a = 9.1736(12)$ ,  $b = 12.0826(16)$ ,  $c = 20.912(3)$  Å,  $\alpha = 82.949(4)$ ,  $\beta = 87.389(5)$ ,  $\gamma = 87.137(5)^\circ$ ,  $V = 2295.7(5)$  Å<sup>3</sup>. The crystal structure was refined to  $R1 = 0.0964$  for 5207 unique reflections with  $F_o > 4\sigma(F_o)$  and 631 refined parameters. Batoniite is characterized by isolated  $[\text{Al}_8(\text{OH})_{14}(\text{H}_2\text{O})_{18}]^{10+}$  octamers, H-bonded with five interstitial  $(\text{SO}_4)^{2-}$  and five  $\text{H}_2\text{O}$  groups. The peculiar Al-octamer occurring in batoniite was previously reported in some synthetic compounds, e.g.,  $\text{Al}_8(\text{OH})_{14}(\text{H}_2\text{O})_{18}(\text{SO}_4)_5 \cdot 16\text{H}_2\text{O}$  (Casey et al., 2005).

The genesis of batoniite is probably related to the action of  $\text{H}_2\text{SO}_4$  on Al-bearing rocks of Paleozoic age cropping out in the Garibaldi tunnel, the lowest mining level of the Cetine di Cotorniano mine.

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## **Minor cations or anions as key components for the stabilization of complex sulfosalts: a review**

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*Keywords:* sulfosalts, minor chemical constituents, crystal-chemistry.

Sulfosalts represent the main part of sulfide minerals. Since the development of electron probe micro-analysis (EPMA) during the 1960s, and later automating of EPMA as well as X-ray crystal structure resolution, numerous sulfosalts with complex crystal chemistry have been characterized. Among them, one knows today about 80 species where one chemical component, constituting 1/10 of cations or anions, or less, has a peculiar role in the crystal structure. Cations are mainly monovalent (Cu, Ag, Tl), or divalent (Fe, Mn, Hg). Examples with anions ( $O^{2-}$ , Cl) are rarer. ( $As_2$ )<sup>4+</sup> or ( $S_2$ )<sup>2-</sup> pairs are exceptional. Cations generally form single chains according to specific coordination polyhedra. As exemplified by the crystal structures of various lead sulfosalts discovered in Italy, minor cations or anions act as the structural interlocking between constitutive ribbons.

## Exploring disorder in complex mineral structures through single-crystal X-ray diffuse scattering: preliminary data

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Keywords: diffuse scattering, mineralogy, crystallography.

Diffuse scattering is the weak and continuous scattering that lies beneath and between Bragg reflections in a diffraction pattern. It arises from any deviation from the ideal model of a crystal, defined as comprising a perfectly repeating configuration of atoms. It is widespread in the crystalline world, both in simple and complex systems. Diffuse scattering has been long considered as a niche topic, which could offer valuable insight into the structure of crystal, but mostly in a qualitative way. In the last decade, diffuse scattering studies have been facing a growing return in popularity. The rise in computational capacity and the advent of third- and fourth-generation synchrotrons together with the development of new area detectors (e.g., single photon counting hybrid pixel detectors) have paved the way for a renaissance of this method. New approaches, such as the 3D- $\Delta$ PDF (Simonov et al., 2014), codes and software have been developed to allow for a more efficient data treatment, yielding quantitative results, and a better insight on old and new problems.

In light of this recent progress, we analysed single-crystal diffuse scattering in minerals with well-known complex structures, namely cupropearceite (Bindi et al., 2013) and several members of the layered oxychloride group, such as janchevite, thorikosite and schwartzembergite (Chukanov et al., 2019). Pearceite-polybasite minerals show composite modulated structures and diffuse scattering that have been characterized at room temperature by means of electron diffraction (Withers et al., 2008). Oxychloride minerals comprise a rich variety of layered structures, whose diffuse scattering was never studied in detail so far. Data collection was performed at beamline ID28 at the European Synchrotron Radiation Facility (ESRF) using the continuous rotation method with a wavelength of 0.6968 Å and Hybrid pixel detector (PILATUS3 1M). For cupropearceite, the measurements were carried out at different temperatures for the characterization of diffuse features as a function of temperature.

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## Adding new species to the tetrahedrite group: three new members of the hakite series

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Keywords: tetrahedrite group, crystal structure, new mineral species.

Within the tetrahedrite group, cubic chalcogenides with general formula  $M^{(2)}A_6M^{(1)}(B_4C_2)^{X(3)}D_4^{S(1)}Y_{12}^{S(2)}Z$  ( $Z = 2$ ), those species with  $A$  and  $B = \text{Cu}$ ,  $D = \text{Sb}$ , and  $Y = \text{Se}$  belong to the hakite series (Biagioni et al., 2020). So far, hakite-(Hg) was the only approved mineral (Škácha et al., 2016). During the study of selenide specimens from the U and base-metal Příbram ore district, Central Bohemia, Czech Republic (Škácha et al. 2017), three new members belonging to this series have been found: hakite-(Cd), hakite-(Fe), and hakite-(Zn). All these species have been approved by the IMA-CNMNC.

These minerals occur as anhedral, grey metallic grains; studied samples were collected in the dumps of the shaft No. 16 - Háje which mined the Bytíz ore deposit of the Příbram ore district. Associated minerals are represented by other selenides and uraninite, in calcite gangue. The new minerals have been characterized through single-crystal X-ray diffraction and electron microprobe analyses.

Hakite-(Fe) and hakite-(Zn) were the first new hakite series minerals to be discovered. The empirical formula of the former is  $(\text{Cu}_{5.82}\text{Ag}_{0.18})_{\Sigma 6.00}(\text{Cu}_{4.29}\text{Fe}_{0.81}\text{Zn}_{0.50}\text{Hg}_{0.26})_{\Sigma 5.86}(\text{Sb}_{3.72}\text{As}_{0.41})_{\Sigma 4.13}\text{Se}_{12.65}\text{S}_{0.12}$ , whereas the latter has chemical formula  $(\text{Cu}_{5.76}\text{Ag}_{0.24})_{\Sigma 6.00}(\text{Cu}_{4.27}\text{Zn}_{0.61}\text{Fe}_{0.53}\text{Hg}_{0.45})_{\Sigma 5.86}(\text{Sb}_{3.55}\text{As}_{0.60})_{\Sigma 4.15}\text{Se}_{12.82}\text{S}_{0.08}$ . Unit-cell parameters are  $a = 10.7983(4) \text{ \AA}$ ,  $V = 1259.12(14) \text{ \AA}^3$  and  $a = 10.8116(14) \text{ \AA}$ ,  $V = 1263.8(5) \text{ \AA}^3$  for hakite-(Fe) and hakite-(Zn), respectively. The crystal structure of both species was refined, converging to  $R_1 = 2.56\%$  for hakite-(Fe) and  $R_1 = 3.02\%$  for hakite-(Zn). These species are isotypic with other tetrahedrite-group minerals. In both Fe- and Zn-species, selenium atoms hosted at the S(2) site have a relatively high  $U_{\text{eq}}$  value and they are probably displaced from the special position (0,0,0) in order to achieve a more reliable  $M(2)$ -S(2) distance, avoiding too short contacts.

Hakite-(Cd) is the third new addition to the hakite series. It has empirical chemical formula  $(\text{Cu}_{5.76}\text{Ag}_{0.24})_{\Sigma 6.00}(\text{Cu}_{3.95}\text{Cd}_{1.51}\text{Hg}_{0.43}\text{Zn}_{0.03})_{\Sigma 5.92}(\text{Sb}_{3.94}\text{As}_{0.13})_{\Sigma 4.07}\text{Se}_{11.35}\text{S}_{1.57}$ . Unit-cell parameters are  $a = 10.8860(6) \text{ \AA}$ ,  $V = 1290.0(2) \text{ \AA}^3$ . Crystal structure was refined to  $R_1 = 2.30\%$ . With respect to hakite-(Fe) and hakite-(Zn), hakite-(Cd) has a higher S content. Sulfur was preferentially hosted at the S(2) site, which is a S-dominant site in this species, with site occupancy ( $\text{S}_{0.80}\text{Se}_{0.20}$ ). This is another possible mechanism favouring the achievement of reliable  $M(2)$ -S(2) bond distances.

The definition of these three new members of the hakite series is not only an addition to the systematics of tetrahedrite-group minerals, but it sheds light on the crystal chemistry of this selenides through the first refinements of their crystal structure based on high-quality single-crystal X-ray diffraction data. Indeed, the crystal structure of hakite-(Hg) was reported by Škácha et al. (2016) on the basis of precession electron diffraction data only, with a high  $R$  value ( $R = 24.4\%$ ).

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## Tennantite-(In) from Pefka (Greece): occurrence and crystal chemistry

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Keywords: tetrahedrite group, new mineral, crystal-chemistry.

The variable crystal-chemistry of tetrahedrite-group minerals has been recently studied by several authors, following the new nomenclature proposed by Biagioni et al. (2020). Among the most exotic species, the recently approved mineral tennantite-(In) is noteworthy. This species was first reported by Voudouris et al. (2022) as “indium-bearing tennantite” from the Pefka ore deposit (Western Thrace, Greece), with an In content up to 6.5 wt.%. This ore deposit is an epithermal mineralization hosted in andesitic lavas and rhyodacitic pyroclastics (Repstock et al., 2015). In type material, tennantite-(In) is closely associated with roquesite, galena, and tennantite-(Fe), with the latter species occurring as rims around the In-isotype. Other sulfides identified in type material are bournonite, seligmannite, and watanabeite.

Quantitative chemical analysis of tetrahedrite-group minerals from Pefka were performed on several grains. The empirical formula of the grain of tennantite-(In) used for the structural study and recalculated on the basis of  $\Sigma Me = 16$  atoms per formula unit, is  $Cu_{10.82}In_{0.69}Fe_{0.18}Zn_{0.14}Mn_{0.06}Cd_{0.02}Pb_{0.02}As_{3.01}Sb_{1.00}Te_{0.06}S_{12.81}$ ; the In-richest analysis corresponds to the formula  $Cu_{10.93}In_{0.93}Zn_{0.07}Pb_{0.07}Fe_{0.06}Mn_{0.05}Cd_{0.01}(As_{2.40}Sb_{1.50}Te_{0.04})S_{12.90}$ . The ideal end-member formula of tennantite-(In) is  $Cu_{11}InAs_4S_{13}$  ( $Z = 2$ ). Associated tennantite-(Fe) has composition  $Cu_{10.11}Fe_{1.72}Pb_{0.02}In_{0.01}As_{4.09}Sb_{0.05}S_{13.51}$ .

Single-crystal X-ray diffraction study of tennantite-(In) indicated a cubic unit-cell, with  $a = 10.285(2)$  Å,  $V = 1088.1(6)$  Å<sup>3</sup>. The crystal structure refinement, performed in the space group  $I-43m$ , converged to  $R_1 = 0.0253$  for 240 unique reflections with  $F_o > 4\sigma(F_o)$  and 23 refined parameters. Indium is hosted at the tetrahedrally coordinated  $M(1)$  site. The average bond distance at this site, 2.340 Å, agrees with the value calculated using the empirically observed Me–S distance for tetrahedrally coordinated metals (i.e., In, Fe, Zn, and Mn, neglecting minor constituents, i.e., 2.330 Å). No other peculiar structural features have been observed:  $M(2)$  is split and occupied by Cu, whereas the  $X(3)$  site is a mixed (As/Sb) site, with only very minor Te.  $S(1)$  and  $S(2)$  are fully occupied by S atoms.

Tennantite-(In) is the 15<sup>th</sup> mineral having In ( $Z = 49$ ) as a species-forming chemical constituents. This finding confirms the role played by tetrahedrite-group minerals in hydrothermal settings as host for medium-to-small size variably charged cations having both economic and environmental significance.

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## **Alessandro Guastoni and his world: minerals and pegmatites**

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*Keywords:* pegmatite, minerals, museum.

In December 2022, the Italian mineralogical community lost one of its most recognized experts in pegmatite mineralogy, Dr. Alessandro Guastoni. Alessandro was the curator of the Museum of Mineralogy at the University of Padova where he also gained a reputation for teaching excellence. He dedicated his working life to the study of minerals and collaborated with geoscientists from around the world on countless impactful research projects. Alessandro was also a skilled mineral collector who imparted his enthusiasm for mineralogy on everyone around him. This contribution honours his memory as a great mineralogist, a great colleague, and a great friend.

## The columbite supergroup: crystal-chemical classification and nomenclature issues

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Keywords: columbite supergroup, ixiolite group, nomenclature.

A proposal for the establishment of the columbite supergroup has been approved by the IMA-CNMNC. The criteria for a mineral to belong to the columbite supergroup are: a) the general stoichiometry  $MO_2$ ; b) the crystal structure based on the hexagonal close packing (*hcp*) of anions (or close to it); c) the six-fold coordination number of *M*-type cations (augmented to eight-fold in the case of slight distortion of *hcp*); and d) the presence of zig-zag chains of edge-sharing *M*-centered polyhedra.

The columbite supergroup is divided into 5 groups: ixiolite, wolframite, samarskite, columbite, and wodginite. The crystal-chemical features of those five groups and the systematics (currently the supergroup includes 37 species) will be briefly outlined.

Some ambiguities with the mineral formerly known with the name ixiolite have been fixed up. Historically ixiolite was assigned the formula  $(Ta,Mn,Nb)O_2$ , which does not clearly show which are the species-forming constituents. In ixiolites the dominant cation has charge 5+, therefore given the general stoichiometry  $MO_2$  any ideal formula must contain a cation with lower charge or a vacancy, based on both the dominant-valency rule and the site total charge approach (Hatert & Burke, 2008; Bosi et al., 2019). Following the approval of the columbite supergroup, any “ixiolite” must match either of the following ideal formulae:  $(M1^{5+}_{0.5}M2^{3+}_{0.5})O_2$ ,  $(M1^{5+}_{2/3}M2^{2+}_{1/3})O_2$ ,  $(M1^{5+}_{0.75}M^{+}_{0.25})O_2$  or  $(M1^{5+}_{0.8}\square_{0.2})O_2$ . The root name is ixiolite (for  $M1 = Ta$ ) or nioboixiolite (for  $M1 = Nb$ ). For instance, holotype “ixiolite” (after Skogsböle, Finland) has  $Ta > Nb$ , and  $Mn^{2+}$  is the dominant charge-compensating cation, therefore it has been renamed ixiolite-( $Mn^{2+}$ ) with ideal formula  $(Ta_{2/3}Mn^{2+}_{1/3})O_2$ . At the same locality analyses are known of ixiolite with  $Fe^{2+}$  as the DCCC, therefore ixiolite-( $Fe^{2+}$ ),  $(Ta_{2/3}Fe^{2+}_{1/3})O_2$ , has been approved as a distinct mineral species as well, concurrently with the approval of the columbite supergroup. And shortly thereafter, two new mineral species have been approved by the IMA-CNMNC: nioboixiolite-( $\square$ ),  $(Nb_{0.8}\square_{0.2})O_2$ , from China, and nioboixiolite-( $Mn^{2+}$ ),  $(Nb_{2/3}Mn^{2+}_{1/3})O_2$ , from Russia.

Within the columbite group, the formulae for polycrase-(Y) and euxenite-(Y) were given as  $Y(Ti,Nb)_2(O,OH)_6$  and  $(Y,Ca,Ce,U,Th)(Nb,Ta,Ti)_2O_6$ , respectively. Based on the site total charge approach, and in agreement with the general features of the minerals of the columbite group, their formula must match the stoichiometry  $M^{3+}(M^{5+}M^{4+})O_6$ . Hence the two minerals have the same ideal formula, namely  $Y(NbTi)O_6$ . As euxenite (1840) is older than polycrase (1844), the latter mineral has been discredited.

Finally, some issues which start from columbites and could have a wider impact on the mineralogical nomenclature overall will be addressed.

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## **Crystal chemical investigations on rare zirconium-niobium silicates of the Alfred Lacroix collection of the Muséum National d'Histoire Naturelle (Paris)**

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*Keywords:* zirconium-niobium silicates, Muséum National d'Histoire Naturelle, crystal chemical studies.

The material collected at the end of the 19<sup>th</sup> century in the former French colonies and preserved in the mineralogical collections of MNHN represents a heritage of relevant scientific and historical interest, an “unicum” deserving a relevant valorization. There are more than 600 samples studied by Lacroix catalogued as nepheline syenites and associated acid differentiates, possibly hosting Zr Ti Nb silicates. Nearly 250 samples come from Madagascar, 100 from Morocco and Algeria, and 250 from the Los Archipelago (Guinea). For several samples it is reported the presence of minerals such eudyalite, lavenite, catapleite. According to Lacroix’s study approach, most of these identifications are based on optical studies, with some chemical data from wet analytical techniques. Considering the several easy and common isomorphic substitutions possible between phases within each group, one can easily understand why optical data chemical composition only cannot lead to a sure species identification. The aim of the present study of a series of rare Zr-Nb-Ti disilicates, to fully define their true nature through a combined multidisciplinary approach.

The study material was collected during the SYNTHESYS+ FR-TAF\_Call3\_034, screening 620 specimens selected within the rocks database leading to a final selection of 15 specimens for physical-chemical characterization. We focused on nepheline syenites from Tamazeght mountain range, Maroc; Andevenanaomy, Angalavozy, Madagascar and Los Archipelago, Guinea.

The material sampled during the visit was prepared for mineralogical studies currently in progress. Raman spectroscopy and powder X-ray diffraction data were collected, showing interesting results, especially for minerals of the wohlerite and eudialyte groups. Electron microprobe (EMPA) data collection and single crystal intensity data collection, for the determination of the crystalline structure of the studied phases, are currently underway. EMPA and single crystal data collected on samples from Tamazeght mountain range, Maroc allowed to detect the presence of lavenite and normandite, two phases belonging to the wohlerite group.

Some new data are available from the Los archipelago samples. Among these, the presence of a Mn-dominant member, closely related to raite, of the palygorskite-sepiolite group (Guggenheim & Krekeler, 2011), together with ongoing crystal chemical study of eudialyte. Single crystal structural and EMPA chemical data point to the presence of two distinct members of the eudialyte group, related to kentbrooksitite and sergevanite (Moreau et al., 1996; Johnsen et al., 2003).

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## The aluminium sulfate- and kaolinite-rich deposits from the Tolfa volcanic district (Latium, Italy): texture and mineral chemistry

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Keywords: Tolfa, aluminium sulfate, kaolinite.

The Tolfa Volcanic District (Latium, Central Italy) is characterized by a sulfate alteration associated with a pervasive deposition of opaline and/or microcrystalline silica, consisting of mineral replacements, veins and agate druses, in the volcanic host rocks (Conte et al., 2022). Alunite and kaolinite represent late-stage hydrothermal alteration products of volcanic successions, possibly combining both hydrothermal alteration and weathering (Lombardi & Sheppard, 1977). Although the hydrothermal alteration products have received attention in the old literature, providing some petrographic and isotopic studies of sulfates and clay minerals, as well as scattered and incomplete rock geochemistry (Lombardi & Sheppard, 1977), systematic mineralogical study for the aluminium sulfate-rich mineralizations are scarce. Recent studies essentially focused on the geochemistry of thermal springs, aquifers (Cinti et al., 2011) and pools and on agate and chalcedony veins (Conte et al., 2022). This study is focused on the aluminium sulfate-rich and kaolinite-rich deposits of the Tolfa hydrothermal alteration area, aimed to investigate the alteration materials and the hosted mineral phases, and in particular to characterize texture and chemical composition of alunite, kaolinite and oxides. We have conducted a field campaign in the area between Tolfa, Allumiere and Santa Severa Montains, allowing to sample various alunite, kaolinite and mineralized limestone quarries, and one boiling pool as well. Samples have been investigated by X-ray diffraction (XRD), scanning electron microscopy with microanalysis by energy-dispersive spectroscopy (SEM-EDS) and Fourier-transform infrared spectroscopy (FT-IR). Whole-rock geochemistry data were also obtained for the collected samples. The mineralogical investigations show a wide morphological and compositional variability of the sulfates mineralization. The alunite are present as solid solutions. We identified alunite, natroalunite as well as walthierite, usually characterized by lamellar/tabular and pseudocubic habits; instead, aluminium-phosphate-alunite (APA) are present as pseudocubic crystals. The kaolinite occurs as well-shaped grains often in vermicular packages. Quartz is abundant in most of the samples. Iron and titanium oxides show significant amounts of Cr, V, Ni. Alunite can characterize for high Ba or Sr content and a well-distinguishable P-rich core. The data collected are an useful background (i) to improve the knowledge of mineral chemistry of these deposits and to characterize in detail alunite and kaolinite minerals; ii) to evaluate the nature and the possible economic importance of the raw materials largely used in the past economy, (iii) to constrain the sulfate mineralizations by the hydrothermal fluids and (iv) to compare this case study with hydrothermal alteration and processes from extinct and quiescent volcanic districts, such as Campi Flegrei and Ischia.

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## QUANTAS, an open-source Python code for the analysis of mineral thermodynamics and elastic properties

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*Keywords:* mineralogy, thermodynamics and elastic properties, computer program.

An important issue for mineralogists, petrologists, and material scientists “lato sensu” is to obtain a clear picture of the physical and chemical properties of solid phases at different pressure and temperature conditions. This fundamental knowledge is also of utmost importance for driving the research to innovative technological applications of minerals and materials, being every day always more and more demanding and challenging. In this context, the characterization of both natural and synthetic materials plays a key role. Among the several properties of interest, fundamental and advanced applications often need knowledge of the thermodynamics and mechanical stability of solids.

Elastic properties are commonly studied regarding hydrostatic compression behaviour, leading to the definition of the equation of state of the material (Anderson, 1995), or by analysing the uniaxial/biaxial deformation, determining the fourth-rank elastic tensor from the stress-strain relationship (Nye, 1957). Besides the elastic stability, both analyses can reveal many details about both single-crystal and polycrystalline behaviour that can be exploited, for example, for the design of materials with tailored mechanical properties. Regarding the thermodynamics of solids, a lot of information can be obtained from experimental approaches, such as differential scanning calorimetry, and, recently from ab initio simulations of the lattice dynamics, e.g., using the quasi-harmonic approximation (Anderson, 1995).

It is worth noting that, nowadays, theoretical methods (e.g., quantum mechanical simulations) have reached an accuracy level that almost matches that of experiments, making them a competitive and powerful tool in characterising minerals and materials. For this reason, to aid both theoreticians and experimentalists, we developed QUANTAS (Ulian & Valdrè, 2022), an open-source Python-based software that can provide a fast, flexible, easy-to-use and extensible platform to calculate the thermodynamics and elastic behaviour of crystalline solid phases, starting from both experimental and/or “ab initio” data.

At present, QUANTAS allows calculating: (i) the thermodynamics and thermoelastic properties of a material at selected pressure and temperature conditions from ab initio quantum mechanical results; (ii) the equation of state of crystalline phases from both theoretical and experimental data; (iii) the elastic properties derived from the second-order elastic moduli, independently on the way they are obtained. The present contribution briefly presents the theory behind the different implementations that provide the above-mentioned issues, together with some examples in mineralogy and material science.

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Nye J.F. (1957) - Physical Properties of Crystals. Oxford University Press, Oxford, UK.

Ulian G. & Valdrè G. (2022) - QUANTAS, a Python software for the analysis of solids from ab initio quantum mechanical simulations and experimental data. *J. App. Crystallogr.*, 55, 386-396. <https://doi.org/10.1107/S1600576722000085>.

## Disorder and Fe-enrichment in thermally treated ankerite

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Keywords: ankerite, disorder, high-pressure.

The mineral physics of ankerite is studied as dependent on both cation disorder and Fe content. Ankerite thermal treatments were performed by means of piston-cylinder apparatus at  $P = 3$  GPa and  $T = 25 - 1000^\circ\text{C}$  on natural ankerites (space group  $R\bar{3}$ ) with different Fe-content (0.3 - 0.7 a.p.f.u.). A 1:1 mixture of (dis)ordered ankerite and Fe-oxalate, as Fe-bearing phase, was used for studying the Fe-enrichment in ankerite structure.

The run products were analyzed coupling Scanning Electron Microscopy, Electron Microprobe Analysis, ambient pressure (P) and high pressure (HP) up to 24 GPa Single Crystal X-ray Diffraction (SC-XRD) both in-house and at synchrotron facility.

Results showed that complete disorder (space group  $R\bar{3}c$ ) was achieved and that the critical T for disordering increases as the Fe content decreases in ankerite. The ankerite mineral physics is characterized by a phase transition to ankerite-II that has the same crystal structure as dolomite-II (Merlini et al., 2012; Zucchini et al., 2014; 2017). Transition P was located between 12 and 14 GPa for the ordered ankerite, whereas, disordered ankerite is stable in the investigated P range, in analogy with dolomite (Zucchini et al., 2014; 2017). The stability of disordered ankerite at HP conditions increases its potentiality to store C into the deep Earth and further experiments in more complex systems following the Earth geotherm are planned.

Both ordered and disordered ankerites show similar compressibility behavior and 3<sup>rd</sup> order Birch-Murnaghan EoS calculations yield  $K_0 = 94(2)$  and  $99(2)$  GPa, and  $K' = 3.7(5)$  and  $2.7(1)$ , respectively. On the contrary, ankerite-II EoS data show a larger  $K'$  value with respect to the low-pressure polymorph, suggesting a steep increase in stiffness after the phase transition.

Results also pointed out that the HP thermally-treated ankerite could incorporate larger amounts of Fe than the naturally occurring ordered structure. This hypothesis sheds light on the open questions about Fe enrichment in the lower mantle and gives ankerite the role of Fe-bearing phase in the Earth's interior.

The project was partially founded by “DFG core facility for high pressure research” funding program in 2018 and “SIMP Research Grant in Crystal - chemistry, in memory of Prof. Fiorenzo Mazzi” in 2022.

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## **S22.**

### **Mineral science for waste recycle and circular economy**

#### *CONVENERS AND CHAIRPERSONS*

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## Estimation model of attached mortar paste volume on the surface of recycled aggregates combining Rietveld refinement of X-ray powder diffraction and image analysis

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Keywords: CDW, sorting, Rietveld.

The use of sand and gravel is extensively devoted to building materials production where account for 60-75% of the total volume of concrete, as natural aggregates constituents. At the same time volume of waste streams from construction and demolition activities account for approximately 35% of the total amounts of materials that reached an end-of-life stage. Half of this demand of raw materials for concrete production may be avoidable using several material efficiency strategies. Recycling and reusing construction and demolition wastes as recycled aggregates (RAs) could be one of that. Unfortunately, lower mechanical performances and reduced workability are often reported when RAs are incorporated instead of natural aggregates inside concrete (Cantero et al., 2019). This is mainly due to the established issue related to the presence of residual adhered mortar paste (AM) attached on the surface of RAs resulting from the standard mechanical recycling treatment procedures of construction wastes (Bonifazi et al., 2018). In this complex contest, the quantification of AM to the RAs surface appears as a straightforward parameter to assess the quality of RAs. To achieve this target, 300 RAs have been divided after a preliminary digital image analysis into 30 groups of 10 individual clasts. Comparable values of superficial area coverage have been estimated upon specific thresholding of the starting dataset and measured by ImageJ software (Schneider et al., 2012). Three macro-groups (C, M, D) emerged in agreement with previous classifications (Kim, 2022) within clean RAs (C) almost comparable to natural aggregates, mortar-covered RAs (M) with just partial areas of surface mortar paste attached and (D) mortar-based RAs, this latter mainly equivalent to pure hydrated cement paste. An autogenous cleaning procedure has been then conducted placing RAs samples in a rotating mill drum. The powder detached resulting from each group has been sieved and weighted and furthermore analyzed using X-ray powder diffraction (XRPD). A deep mineralogical analysis is furthermore conducted by applying the Rietveld refinement procedure to the X-ray diffraction patterns collected. The results of the ratio between powder mass from mechanical detachment and a weighted mean density product for the minerals phase distribution (wt.%) gives volumetric quantitative phase information (QPA) on AM within each group. Aggregates mean volume reconstruction is then performed by bidimensional image analyses measurements of the RAs total areas calculating a mean radius value for each group, and then a total mean volume. In conclusion, combining the data a percentage of the average volume of AM (mm<sup>3</sup>) covering the surface is estimated for each group by bidimensional image analysis and tridimensional XRD-QPA microscopic crystalline information.

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## Characterization of MSWI fly ash solid residues after steam washing treatment, for their potential reuse

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Keywords: MSWI fly ash, steam washing, reuse.

Municipal solid waste incineration fly ash (MSWI FA) is classified as hazardous waste due to its high content of heavy metals and soluble salts (Li et al., 2022). The aim of this work is to characterize the composition of the MSWI FA solid residues before and after a washing treatment with steam, to show the decrease of soluble salts, mainly chlorides, and heavy metals, to reach a condition of non-hazardous waste, or even to make it suitable to be reused into geopolymers or cement. In fact, chlorine is considered the main “unconvenient” component in FA cement recycling because it can cause corrosion and clogging during co-processing in the cement kiln system (Wei et al., 2022). The application of steam washing, already tested successfully on bottom ash (Destefanis et al., 2020) represents both a sustainable and optimized utilization of water, to reduce the waste-water volumes, and to exploit the power of the heat generation to dissolve most of the soluble salts; moreover, the steam is a resource usually available at the thermovalorization plant. Several steam washing experiments were performed, applying different conditions of flux, humidity, temperature and time (from 5 to 15 minutes), to optimize the consumption of water and energy, keeping a low enthalpy steam ( $T < 100^{\circ}\text{C}$ ). FA samples before and after steam washing treatment were characterized by X-Ray fluorescence and X-ray diffraction, to analyze the chemical and mineralogical composition, to investigate its solubility in water and the effectiveness of steam to remove chlorides and sulfates, as well as the main heavy metals (Zn, Pb, Ni, Cr, Sb, Cd); by SEM-EDS microscopy to analyze both the morphology and the chemical composition. The results of these tests are coupled to leachates analyses of solid residues, which show that steam washing is efficient in removing water-soluble chlorides including sodium chloride, potassium chloride (up to 80%) and sulfates (by 30%); while for heavy metals, like Cd, Zn, Pb, the removal was up to 80%. Thus, the steam washing can be considered an efficient method to improve MSWI FA by decreasing its release concentrations under the legal limits provided for non-hazardous waste.

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## Exploitation of 13X zeolite for the recovery of REEs from spent fluorescent lamps: evaluation of the exchange selectivity and cation exchange capacity

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Keywords: zeolite, ree, circular economy.

Domestic Material Consumption (DMC) measures the total amount of materials needed by an economy to meet the demands for goods and services from within and outside a country. DMC increased globally by more than 65% from 2000 to 2019 and it was up to 14.1 t per person in Europe in 2021. The main factors influencing DMC value are the global population, industrialization, and the outsourcing of material-intensive production from developed to developing countries. A direct consequence of the increase of DMC is the always bigger request of natural resources that, other than putting pressure on the ecosystem, ultimately affect human health, geopolitics, and economy (UN, 2022). In order to mitigate the dangers of this growth, it is particularly important to study and improve the recycling of those materials nowadays classified as critical raw materials. The availability of these materials is strongly decreasing due to their extensive use and because of their scarce overall abundance. Rare Earth Elements belong to this category and they are fundamental for the development of new technologies and the transition from fossils to green energy. Different wastes have been proven to be rich in REEs, especially WEEE (waste from electrical and electronic equipment), but only few works investigated their possible recovery. With this study we want to exploit the cation exchange property of zeolite for the recovery of REEs from wastes. The first part of the work was aimed at the evaluation of the selectivity of a synthetic 13X zeolite towards four different REEs with concentrations mimicking the ones obtained from a two-step leaching of spent fluorescent lamps (Eduafio et al., 2015). NH<sub>4</sub> exchanged 13X zeolite was put in contact with four different mono-elemental solutions: Ce 0.03M, La 0.04M, Eu 0.006M and Y 0.17M. Three different solid/liquid ratios (g/ml), 1/10, 1/50 and 1/100 were tested for each solution. Further NH<sub>4</sub> exchanges were performed in order to recover REEs from the zeolites so obtained. Both powders and solutions were analysed after the REE exchange. The results showed that different Rare Earths show different exchange behaviours. In particular Y, despite being the more concentrated REE in the starting solution, reached exchange values clearly lower than those obtained for Ce and La, that instead gave very similar results. Eu starting concentration was too low to being able to compare it with the other REEs. After the final NH<sub>4</sub> exchange, half of La and Y were recovered, while almost all Ce and Eu remained in the zeolite. The data obtained thus suggest a selectivity both in the exchange of REEs and in the release of them from the zeolite. Further experiments are being performed to evaluate the selectivity of two 13X zeolites - a pure one, commercially available, and a second one synthesized from coal fly ashes - towards solutions containing different REEs and other cations.

Eduafio P.M., Strauss M.L. & Mishra B. (2015) - Experimental investigation of recycling rare earth metals from waste fluorescent lamp phosphors. TMS Annual Meeting, 253-259. <https://doi.org/10.1002/9781119093244.ch29>.

United Nations (2022) - The Sustainable Development Goals Report 2022. United Nations Publications, New York, 68 pp.



## Sequential extraction procedure and grain size in bottom ashes from MSWI

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**Keywords:** bottom ashes, potential toxic elements, sequential extraction procedure.

In waste management, incineration of Municipal Solid Waste (MSW) is an effective way to reduce waste volume and recover energy from waste burning for public use; the drawback stays in the inherent production of ashes. MSW ashes are made up of Bottom Ashes (BA), which account for about 20% of the disposed waste, and Fly Ashes (FA), about 4% of the original waste. In general, BA are made of crystalline phases, such as silicates, carbonates, oxides, sulphates, amorphous compounds (e.g. glass) and metallic inclusions. BA are mainly composed of Si, Al, Fe, Ca, Mg, K, Na, S, Cl. However, they also contain Potentially Toxic Elements (PTE) such as Zn, Pb, Cu, Cr, and Ni. Their potential hazard depends on the mineralogical phases they are embedded in, which control the potential release in the environment. Sequential Extraction Procedure (SEP) can help to correlate minerals and leachate PTE because the sequential chemical attack can destroy only specific fractions, even if standardized extraction procedures such as BCR 3-steps (Rareut et al., 1999) in BA analysis is relatively limited. Only few authors modified and adapted the standard procedure to investigate these materials (Bruder-Hubscher et al., 2002; Haberl & Schuster, 2019). In this work, a new SEP has been set up and tested on different grain size classes (0.063-0.2, 0.3-0.5, 2-4, and < 4 mm) of BA sampled from Parma Waste-to-Energy (WtE) plant. The procedure was done in five steps. XRD and XRF were performed on the residue of each step and chemical analysis were also carried out on their leachate by ICP-MS. The main results are:

1. The highly basic environment of BA made the application of BCR inefficient, requiring a calibrated procedure for this type of material.
2. A major weight loss occurs in second step linked to dissolution of carbonates and amorphous matrix. The dissolution is much higher in smaller grain sizes, and accounts for most of the difference between the different grain sizes. A second moderate loss is also displayed at step 3 linked to dissolution of oxidizable phases.
3. Amorphous represents a very large fraction of the investigated residues, especially in the smaller grain sizes. Combination of XRF and RIR-Rietveld analyses at the different sequential steps allowed us to distinguish between different amorphous' types, possibly Na/K-bearing soluble gels, organic matter, C-S-H products, melt glass and Si-enriched residue, with the latter three as the larger in content.
4. Among crystalline phases in steps 1 and 2 the cement related phases like hydrocalumite, larnite and portlandite disappear, whereas feldspars and quartz are not significantly changed during the SEP.
5. Common trends with previous investigations were found for several elements: Pb and Zn are significantly released during the step 2, whereas metals like Cu, Ni, Co, and Sb are leached in the reduction and oxidizing step, indicating that they are present as hydroxides and metals rather than in carbonates.

Bruder-Hubscher V., Lagarde F., Leroy M.F., Coughanowr C. & Enguehard, F. (2002) - Application of sequential extraction procedure to study the release of elements from municipal solid waste incineration bottom ash. *Anal. Chim. Acta*, 451(2), 285-295. [https://doi.org/10.1016/S0003-2670\(01\)01403-9](https://doi.org/10.1016/S0003-2670(01)01403-9).

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Rauret G., López-Sánchez J.F., Sahuquillo A., Rubio R., Davidson C., Ure A., & Quevauviller P. (1999) - Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials. *J. Environ. Monitor.*, 1, 57-61. <https://doi.org/10.1039/a807854h>.

## **PTE speciation in bottom ashes from municipal solid waste incinerator: a combined SEM-EDS, XRF and XANES by synchrotron radiation study**

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Keywords: bottom ashes, chemical speciation, XANES.

A considerable amount of anthropogenic material is introduced into environment through urban wastes. In 2016, world waste production amounted to 2.01 billion tons and due to economic and demographic growth, is estimated it will reach the 3.40 billion tons by 2050. An important portion of such waste, up to 11% of the global production, is incinerated (Kaza et al., 2018). In industrialized countries, the incineration is entrusted to Waste to Energy (WtE) plants, which recover energy as heat and/or electricity through controlled combustion of Municipal Solid Waste (MSW). Bottom Ashes (BA) are the main outputs of WtE processes. BA are classified as non-hazardous waste and can be recycled into different construction materials. However, several investigations of BA prove that Potential Toxic Elements (PTE) are present and their concentration and release are major in finer grain size (Alam et al., 2019). Toxicity and mobility of an element towards an environmental matrix is strictly connected to its chemical and mineralogical characteristics. Therefore, a method to identify PTE chemical speciation in ashes matrix is needed. In this work, the distribution and chemical speciation of PTE like Pb, Cu, Zn, Co, Cr and Ni has been determined on BA grain sample from Parma WtE plant by means of SEM-EDS coupled with synchrotron-based XANES and  $\mu$ -XRF mapping. This multi-technique approach allowed to deep examine PTE, providing a general picture of mineralogical and chemical properties such as the oxidation state and coordination geometry. The main results are:

- a) core and rim structures were generally found for each grain. The core consists of high temperature phases, mingled with glass of different composition, in local equilibrium, whereas the rim is made by fine grained carbonates, sulphates, oxides, hydroxides, chlorides and organic residual matters, likely coming from weathering;
- b) SEM-EDS analyses show the presence of Zn (willemite  $[\text{Zn}_2\text{SiO}_4]$ , hardystonite  $[\text{Ca}_2\text{Zn}(\text{Si}_2\text{O}_7)]$ , zincite  $[\text{ZnO}]$ , gahnite  $[\text{ZnAl}_2\text{O}_4]$ ) and Pb (Ca-plumbate) in minerals and in glass matrix. Cr oxide and chromite ( $\text{FeCr}_2\text{O}_4$ ) has found whereas Cu and Co are present as metal inclusions or alloy;
- c)  $\mu$ -XRF maps show that some elements, namely Ca and Si, but also Mg, Al, Fe, P, Cr, Ti, Co, and Pb are generally present within the core of the grains. Zn and Cu are found both in the rims and in the core, whereas others, like S and Cl and, to a lesser extent, Na and K, mostly at the rims.
- d) analysis of XANES spectra show that Cu has a variable oxidation state (0, +I, +II) suggesting its presence as oxide, hydroxide, acetate and metal form. Zn is mainly in the +II oxidation state, in agreement with SEM-EDS data. Cr has been found always as +III, whereas the +VI oxidation state was never identified. Pb spectra are all similar and have a good match with oxides. Ni and Co were found either as oxides and metal form.
- e) the speciation of PTE occurs in a wide range of minerals, due to different waste input, combustion temperature, local equilibria, grain size and ageing.

Alam Q., Schollbach K., van Hoek C., van der Laan S., de Wolf T. & Brouwers, H.J.H. (2019) - In-depth mineralogical quantification of MSWI bottom ash phases and their association with potentially toxic elements. *Waste Manage.*, 87, 1-12. <https://doi.org/10.1016/j.wasman.2019.01.031>.

Kaza S., Yao, L., Bhads-Tata P. & Van Woerden F. (2018) - What a waste 2.0: a global snapshot of solid waste management to 2050. World Bank, Washington, DC. <https://doi.org/10.1596/978-1-4648-1329-0>.

## C-capture by mineral carbonation in fresh cement vs. recycled masonry aggregates

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Keywords: C-capture, rubble, carbonation.

Cement manufacturing accounts for 8% of the world's carbon dioxide emissions and the reduction of its huge carbon footprint is a priority for the cement industry. The decarbonization of the cement industry goes through a combination of techniques ranging from reducing cement burning temperatures to CO<sub>2</sub> capture and storage (CCS). Carbonation spontaneously occurs both in nature (e.g., silicate carbonation) and in anthropic environments when CO<sub>2</sub> reacts with concrete, calcium hydroxide, calcium silicates hydrated (C-S-H), and some other phases in the concrete that, become carbonates. Unfortunately, carbonation penetrates at relatively small depths below the concrete surface and 'only' 5% of the amount of CO<sub>2</sub> emitted for cement production is sequestered by spontaneous carbonation. This quantity can be increased by exposing cement waste and rubble to high CO<sub>2</sub> pressures to produce carbonated aggregates with better mechanical properties than simple recycled aggregates. In this work, thermodynamic and kinetic aspects of carbonation are examined to identify the key factors for effectively implementing a forced carbonation process. Moreover, a comparison between the carbonation effect on fresh cement and recycled masonry aggregates is made. Carbonation products were analysed with X-ray Powder Diffraction (XRPD), Thermogravimetric Analysis (TGA) and density measurements using a gas pycnometer. The results of the analysis on fresh cement show that: (i) carbonation occurs according to a sequence of reactions involving portlandite first, then ettringite and then C-S-H phases; (ii) the factors that most influence the rate of carbonation are grain size and partial pressure of carbon dioxide; (iii) the rate of the overall reaction follows complex kinetics resulting from the combination of the kinetics of the individual minerals. The most relevant result regarding the applicability of forced carbonation, is that the fractional increment of the overall reaction follows a power law with respect to time. The reaction rate, given by the first derivative of the fractional increment/time curve, decreases with time. This implies that it is possible to achieve carbonation values of 50-60% in a relatively short period of time, but to achieve values above 90%, one or two orders of magnitude longer times are required. Carbonation, although in a smaller percentage with respect to fresh cement, also occurs in the rubble, where the percentage of calcite increases goes from 26 to 32 wt.% after 24 hours of CO<sub>2</sub> curing, while in the fresh cement the increase of calcite had been from 8.9 to 23.7 wt.%. The effect of grain size, of CO<sub>2</sub> treatment in both over- and under atmospheric pressure, as well as the possible reactivation processes of rubble, on the carbonation, will be illustrated taking into account the treatment effect also on massive samples.

The work was carried out under the contribution of the Fondazione Perugia: project code n° 21042(2022.0407) p.i. Paola Comodi.

## The effect of CDW (Construction and Demolition Waste) type and crystalline phases on the physical-mechanical performance of mortars

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**Keywords:** CDW (Construction Demolition Waste), recycled mortar, mineralogy.

The overexploitation of natural resources and the shifting to a circular economy require that CDW, the most abundant non-hazardous solid waste, substitute natural materials in the construction sector. CDW is composed of different components, variable in time, geographical and geological area and architectural styles; in turn, it is highly heterogeneous and difficult to recycle. The peculiar mineralogical and petrographic attributes of CDW strongly affect the physical-mechanical properties of new construction materials made with them. However, mineralogical and petrographic attributes and variations of CDW are only little investigated (Galderisi et al., 2022) and the actual effects on new construction materials prepared with them are still poorly known, even at the lab scale.

To fill this gap, post-seismic CDW rubbles from Central Italy were manually sorted, after removing organic and metallic portions. Selected samples were mesoscopically divided into 6 classes: concretes (CO), natural stones (NS), tiles (TI), bricks (BR), perforated bricks (PF) and roof tiles (RT). A natural aggregate (NA, sand from Lisbona) was used for comparison. The type and amount of crystalline phases (wt.%) in each of the 6 CDW classes was determined by XRPD using the Rietveld method. Density and water absorption were also quantified. NA samples are made of quartz and minor feldspars, NS and, to a lesser extent CO samples, are mainly composed of calcite (plus quartz and other minor silicates), TI samples contain primarily quartz, mullite and feldspars, whilst BR, PF and RT samples are made of similar quantities of feldspars, sheet-silicates and pyroxenes. In all the TI, BR, PF and RT samples calcite is also present, as mortar fractions adhering to the surface. Water absorption increases from natural aggregate to BR (NS).

The 6 CDW classes plus NA were then used to prepare 7 types of standardised mortars with nearly identical cement and water contents. The shrinkage of solidifying mortars is the lowest for the NA mortar and increases progressively from NS-, CO-, TI-, RT-, PF- to BR-rich mortars. Compressive and flexural strengths of mortars decrease from the NA-bearing mortar to NS-, CO-, TI-, PF RT- to BR-bearing mortars. Similar trends are observed for modulus of elasticity, ultrasonic test and electric resistivity. Hence, the physical-mechanical properties of mortars reflect the type and abundance of crystalline phases in each CDW and porosity (Galderisi et al., 2023). Therefore, determining and predicting the physical-mechanical performances of new construction materials made with CDW require detailed mineralogical-petrographical characterisations. Also, the separation of heterogeneous CDW into homogeneous groups is essential for the production of new construction materials with constant and foreseeable properties.

Galderisi A., Iezzi G., Bianchini G., Paris E. & de Brito J. (2022) - Petrography of Construction and Demolition Waste (CDW) from Abruzzo Region (Central Italy). *Waste Manage.*, 137, 61-71. <https://doi.org/10.1016/j.wasman.2021.10.028>.

Galderisi A., Bravo M., Iezzi G., Cruciani G., Paris E. & de Brito J. (2023) - Physico-Mechanical Performances of Mortars Prepared with Sorted Earthquake Rubble: The Role of CDW Type and Contained Crystalline Phases. *Materials*, 16, 2855. <https://doi.org/10.3390/ma16072855>.

## Recycling of disposable face masks into geopolymetric matrices for lightweight materials for green building

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*Keywords:* face mask waste (FMW), geopolymer binders, upcycling applications.

The enormous use of disposable face masks during and after the COVID-19 pandemic, raised concern connected to the production, use and discharge of the protection aids. As an example, if considering that facial masks have a very short life-time, limited to few hours, it is evident how their utilization has a large impact in the waste management. This represents an urgent environmental problem to be addressed, with a view to reducing the landfilling or incineration of these materials, but also keeping in mind the need to find new applications for this type of waste.

Saberian et al., (2021) showed how, by incorporating shredded masks into recycled concrete aggregate for road base applications, just 1 km of a two-lane road would use up about 3 million masks, preventing 93 t of waste from landfilling. Other studies investigated the possibility to incorporate these materials into asphalts mixtures, also improving their performances (Zhao et al., 2022). However, still carbonization (i.e., extreme pyrolysis), pyrolysis (i.e., rapid carbonization), catalytic conversion, chemical treatments, are the proposed methods to recover face mask wastes (FMWs) avoiding landfilling, with high environmental costs (Pourebrahimi, 2022).

With the aim to find an effective and greener way to recycling/upcycling FMWs into value-added materials, in this study we investigated the possibility to use FMW for applications in the construction sector, by inserting them into geopolymetric matrix (e.g., Ossoli et al., 2023). Polypropylene fragments, obtained from the mechanical reduction of FMW previously spectroscopically characterized, were added to metakaolin and K/Na silicate. The production of a geopolymetric reaction allows to find a stable chemical and physical allocation for FMW, incorporating up to 2 wt.% material in the binder.

Geopolymer-based products can present good mechanical (high compressive strength and good abrasion resistance), chemical (resistance to attack by acids and bases) and thermal (low thermal conductivity) properties. For instance, the materials produced in this study showed to have compressive and flexural strengths values of 12.7 and 3.1 MPa, respectively, with a material density of 1.68 g/cm<sup>3</sup>. These preliminary data suggest that the geopolymers-based products produced with FMW could be practically used for upcycling applications, like the production of insulating panels.

The confinement in geopolymetric binders allows to avoid the dispersion in the environment of this non-biodegradable polymer-based polypropylene waste, but also avoids the use of less environmental-friendly methods for their recycling.

Ossoli E., Volpintesta F., Reggiani A., Stabile P., Santulli C. & Paris E. (2023) - Upcycling of composite materials waste into geopolymer-based mortars for applications in the building sector. *Mater. Lett.*, 333, 133625. <https://doi.org/10.1016/j.matlet.2022.133625>.

Pourebrahimi S. (2022) - Upcycling face mask wastes generated during COVID-19 into value-added engineering materials: A review. *Sci. Total Environ.*, 851, 158396. <https://doi.org/10.1016/j.scitotenv.2022.158396>.

Saberian M., Li J., Kilmartin-Lynch S. & Boroujeni M. (2021) - Repurposing of COVID-19 single-use face masks for pavements base/subbase. *Sci. Total Environ.*, 769, 145527. <https://doi.org/10.1016/j.scitotenv.2021.145527>.

Zhao Z., Wu S., Liu Q., Xie J., Yang C., Wang F. & Wan P. (2022) - Recycling waste disposable medical masks in improving the performance of asphalt and asphalt mixtures. *Constr. Build. Mater.*, 337, 127621. <https://doi.org/10.1016/j.conbuildmat.2022.127621>.



## Fine industrial waste in geopolymer foam binders for new insulation materials

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*Keywords:* fine industrial waste, geopolymers, lightweight materials.

Among the industrial waste produced during the operations related to the manufacture of building materials or ornamental stones, the sludge produced during cutting and polishing operations represent a problem of increasing concern for companies, due to increasing environmental and economic costs of landfilling. This waste materials, in fact, find no practical applications in the common recycling of rocks and building materials swarfs, as for backfilling operations, due to the fine grainsize and in spite of the absence of organic or polluting chemicals.

In this study we tested the possibility to recycle finest waste fractions from companies dealing with ornamental stones and stone-composites. The aim is to obtain a lightweight geopolymer mortar for applications in the construction sector as insulation materials, thanks to the properties of geopolymer materials, like those related to good mechanical properties, low thermal conductivity and environmental impacts usually lower if compared to cement binders.

The industrial fine wastes (< 0.5 mm) were characterized by powder X-ray diffraction and then added to a geopolymeric binder produced by metakaolin and K- or Na silicates to which a foaming agent is added, to form a light geopolymer foam mortar. The waste fraction used in the demo mixes accounts for about 30 wt.% of the total sample and an attempt was made to avoid the addition of raw materials, to increase the “green” character of the materials produced.

Flexural and compressive strengths vary, respectively, in the ranges 1.3-2.5 MPa and 4.8-5.1 MPa (at 7 days), and compressive strength was found as 5.7-7.7 MPa at 28 days. Samples were also characterized by physical properties determinations: dry bulk density, material density, open porosity and water absorption. Preliminary results show densities between 1.09 and 1.24 g/cm<sup>3</sup> (at 7 days) reaching 0.98 to 1.00 g/cm<sup>3</sup> at 28 days, well below the limit for lightweight mortar products (< 1.5 g/cm<sup>3</sup>).

The data obtained, compared to other data from the literature, reveal interesting application of these products as lightweight insulating materials, where there are ample possibilities to fine-tune the mix composition as a function of the final utilizations envisioned.



## **Application of biomass ashes in the stabilization of road pavements subgrade soils: a multimethod approach**

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*Keywords:* clayey soils, biomass ashes, mechanical behaviour.

Recent international climate commitments promote the use of renewable energy sources to make waste recycling possible and reduce the use of fossil fuels and so the carbon dioxide emissions. Following these goals, biomass-fuelled thermal power plants, which are considered a zero CO<sub>2</sub>-emission sources, are expected to increase. Notwithstanding, the large amount of biomass combustion ashes (may be up to higher than 10% of the raw material) represents a major concern to be addressed, encouraging its reuse instead of landfilling. In this context, the project aims to develop new strategies to reuse these industrial waste materials, not only as fillers but also as stabilizing agents on road pavement subgrade layers as an alternative to traditional treatments. In this light, preliminary studies show that ashes could generate mineralogical and chemical reactions similar to those induced by lime (pozzolanic reactions) on clayey soils, as required for the improvement of mechanical properties. Specifically, in this research, the usage of biomass ashes from the combustion of wood chips as stabilizing agent of a soil (A) taken in the centre of Italy with a high percentage of clay was investigated. The results of ICL test (Initial Consumption of Lime) showed how biomasses can replace lime for the stabilisation of local clayey soils used in embankments and road subgrades guaranteeing a sufficiently alkaline environment and making possible eventual pozzolanic reactions. Based on the results of the ICL test, different samples were prepared adding to the clayey soil those amounts of lime and biomass ashes which determine a 12.4 pH value, respectively. Furthermore, densification properties of studied mixtures were investigated carrying out both standard Proctor compaction and a downscaled compaction tests. Data collected from these tests, performed on both the raw soil and the stabilized mixtures, made it possible to relate for each blend the Optimum Moisture Content (OMC) to the maximum dry density (MDD). Based on such values, target compaction levels were set to investigate the mechanical performance of studied mixtures. The mechanical behaviour of samples was investigated through unconfined compressive tests, which were carried out under different curing times and loading conditions. The chemical-mineralogical evolutions of the different mixtures monitored using X-Ray Powder Diffraction analysis (XRPD) combined with Quantitative Phase Analysis (QPA) by use of Rietveld method, Fourier transform infrared spectroscopy (FT-IR) and energy dispersive X-ray spectroscopy coupled with scanning electron microscopy (EDS-SEM), will be presented.

## Re-using Ladle Furnace Steel slags as filler in asphalt mixtures

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Keywords: steel slags, asphalt mixtures, circular economy, waste characterization.

Nowadays, worldwide, the amount of steel and iron is increased up to 161.7 million tonnes (World Steel Association, 2021), and its production outputs are characterised by 64.4% of steel, 32.9% of so-called “by-products” and 2.7% of wastes. Basically, steel-making operations is distinguished by the type of furnaces: Basic Oxygen Furnace (BOF), Electrical Arc Furnace (EAF) and Ladle Furnace (LF). The necessity to move towards the circular economy has been requiring the possibility of reusing steel disposed by-products, which are not considered wastes since September 1995 (Motz & Geiseler, 2001). The use of LFS has been spreading in different fields such as road application, soil stabilisation, earthwork and armour stones for hydraulic structures (Ortega-López et al., 2014; Bocci, 2018). LFS composition is characterised by silicates and aluminates of calcium and magnesium. Their content is non-uniform and both the free-calcium oxide (CaO) and magnesium oxide (MgO), among others, generally represent 50-60% of the total weight of LFSs, which is strictly furnace type-depend.

This study aims at investigating the feasibility of using LFS as filler in the HMA, in order to enhance the sustainable level of road infrastructures. The chemical, mineralogical (XRF, the XRD, and the SEM-EDS) and the mechanical characterisation of LFSs in asphalt materials were investigated, considering both hydrated- and not hydrated-LFSs. In particular, the effect of time-dependency of the hydration process were evaluated involving three different periods (48 h, 7 days, and 15 days), and using three different hydration conditions (natural weathering, 0.32, and 2 H<sub>2</sub>O/CaO ratio)

LFSs are mainly composed by silicates which exhibited no hydration effects. The huge presence of periclase (MgO) in all the samples show that hydration and consequently volumetric expansion does not occur for this phase. Therefore, despite the great presence of elemental Ca in the bulk material, no lime (CaO) was found suggesting that Ca reacted very quickly hydrating (CaOH<sub>2</sub>) or forming silicates and aluminates. This indicates that a controlled production chain could reduce or eliminate the CaO presence reducing the LFS slags volumetric-expansion potential.

The use of the LFS in both mastics and HMAs increases the brittleness of the materials reducing the deformability while not significantly modifying chemical and mineral composition. This important finding is likely due to both the presence of the high hydrated lime content and the fineness of grains. This effect was exacerbated especially for the HMAs containing the non-hydrated LFS. The effects of the hydration procedures did not lead to significant difference between the hydrated- and non-hydrated LFS slags.

Bocci E. (2018) - Use of ladle furnace slag as filler in hot asphalt mixtures. *Constr. Build. Mater.*, 161, 156-164. <http://dx.doi.org/10.1016/j.conbuildmat.2017.11.120>.

Motz H. & Geiseler J. (2001) - Products of steel slags an opportunity to save natural resources. *Waste Manage.*, 21(3), 285-293. [http://dx.doi.org/10.1016/S0956-053X\(00\)00102-1](http://dx.doi.org/10.1016/S0956-053X(00)00102-1).

Ortega-López V., Manso J.M., Cuesta I.I. & González J.J. (2014) - The long-term accelerated expansion of various ladle-furnace basic slags and their soil-stabilization applications. *Constr. Build. Mater.*, 68, 455-464. <http://dx.doi.org/10.1016/j.conbuildmat.2014.07.023>.

World Steel Association (2021) - Steel - The permanent material in the circular economy. URL: <https://worldsteel.org/publications/bookshop/steel-permanent-circular-economy/>.

## Recovery of molybdenum from exhaust catalyst with a green process based on agri-food wastes

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*Keywords:* green process, metal recovery, spent catalyst.

Metals recovery from industrial waste is a mandatory target in the framework of green and circular economy. Given the huge amount of solid waste production in Europe (i.e., annual production of incineration bottom ash is about 20 Mt in European community) (Šyc et al., 2020) and the end-life of ore natural reserves, the research based on technological process aimed to extract metals from waste or creating secondary raw materials is important both for circular economy and to reduce the dependence of domestic economic from foreign suppliers. China is the largest producer of most of the heavy metals and the rare earth elements (Blengini et al., 2020).

The aim of this work is developing a cost-effective and sustainable hydrometallurgical process. For this way we propose the use of Tartaric Acid in order to recover critical metals in industrial wastes. Tartaric acid is an eco-friendly weak organic acid that occurs naturally in many fruits (mainly in grapes but also in bananas, tamarinds and citrus) and can be recovered from various natural by-products, mostly from winery ones. (Kontogiannopoulos et al., 2016). It is also a perfect substitute for common strong inorganic acids, such as  $H_2SO_4$ , HCl, and  $HNO_3$ . In other words, using agri-food wastes it is possible to process another waste, the industrial one, to recover and reintegrate precious metals compounds for an efficient circular economy. For this work tartaric acid was supplied by Distillerie Mazzari S.p.A. (Italy).

For this work a selective catalyst for formaldehyde production containing significant amounts of Mo and Fe was used. The starting waste was characterized by X-ray Diffraction (XRD) to determine the mineralogical composition and the degree of crystallinity; by Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray Spectroscopy (EDS) for a morphological study followed by an elementary analysis; by inductively coupled plasma (ICP-OES) to investigate the concentration of every metal in the sample. The leaching experiment were carried out at different solid to liquid ratios, reaction times, temperature and acid concentrations to evaluate the conditions to achieve best efficiency of metal recovery.

Blengini G.A., Latunussa C., Eynard U., Torres de Matos C., Wittmer D., Georgitzikis K., Pavel C., Carrara S., Mancini L., Unguru M., Blagoeva D., Mathieux F. & Pennington D. (2020) - European Commission, Study on the EU's list of Critical Raw Materials – Final Report (2020). Publications Office of the European Union, Luxembourg. <https://doi.org/10.2873/11619>.

Kontogiannopoulos K.N., Patsios S.I., Karabelas A.J. (2016) - Tartaric acid recovery from winery lees using cation exchange resin: Optimization by Response Surface Methodology. Sep. Purif. Technol., 165, 32-41. <https://doi.org/10.1016/j.seppur.2016.03.040>.

Šyc M., Simon F.G, Hykš J., Braga R., Biganzoli L., Costa G., Funari V. & Grosso M. (2020) - Metal recovery from incineration bottom ash: State-of-the-art and recent developments. J. Hazard. Mater., 393, 122433. <https://doi.org/10.1016/j.jhazmat.2020.122433>.

## **Properties of M25 concrete filled with different amounts and types of waste: proteinic, lignocellulosic, and ceramic**

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*Keywords:* concrete, waste filling, mechanical testing.

Due to the large production of concrete worldwide, even the introduction in it of a small amount of waste filler can be of interest, since it could significantly reduce its cost and at the same time possibly preserving the structural properties of the material, without affecting the curing process. On the other side, reusing waste in the construction industry does represent a relatively simple option.

In particular, this study concentrates on the cyclic behavior of concrete grade M25, whenever three different types of waste filler are added: in particular, one is a ceramic (nanosilica from calcination of rice husk, such as suggested in Sarkar et al., 2021), one is lignocellulosic (60 mm long coir fibers from coconut fruit waste, considered for the purpose in Syed et al., 2020), and the third is proteinic (60 mm human hair waste, such as suggested also by Bheel et al., 2020). As from reports literature, the specific interest of the work is concentrated on the acquisition of a possible synergy of the three fillers in improving, or at least not reducing, the properties of the concrete, therefore the amount of the three fillers for introduction in understandably limited.

The results do indicate that the improvement of cyclic flexural and number of cycles to failure, other than compressive, split tensile and static flexural properties, are effective and consistent up to a global 1.5% volume of the two waste fibers and a 3% volume of nanosilica. Also crack patterns appear neater in the presence of the filler, which possibly suggests a higher ductility of the material up to this amount (Madani & Dolatshahi 2020). It is sensible to propose that to increase the quantity of waste introduced, it further work on the repeatability and consistency of data would be required.

Bheel N., Awoyera P., Aluko O., Mahro S., Vilorio A. & Sierra C.A.S. (2020) - Sustainable composite development: Novel use of human hair as fiber in concrete. *Case Stud. Constr. Mater.*, 13, e00412. <https://doi.org/10.1016/j.cscm.2020.e00412>.

Madani H.M. & Dolatshahi K.M. (2020) - Strength and stiffness estimation of damaged reinforced concrete shear walls using crack patterns. *Struct. Control Health Monit.*, 27(4), e2494. <https://doi.org/10.1002/stc.2494>.

Sarkar J., Mridha D., Sarkar J., Orasugh J.T., Gangopadhyay B., Chattopadhyay D., Roychowdhury T. & Acharya K. (2021) - Synthesis of nanosilica from agricultural wastes and its multifaceted applications: A review. *Biocatal. Agric. Biotechnol.*, 37, 102175. <https://doi.org/10.1016/j.bcab.2021.102175>.

Syed H., Nerella R. & Madduru S.R.C. (2020) - Role of coconut coir fiber in concrete. *Mater. Today-Proc.*, 27, 1104-1110. <https://doi.org/10.1016/j.matpr.2020.01.477>.

## Sea-derived ceramic waste for application in geopolymers

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Keywords: geopolymers, aragonite, seashells.

The production of metakaolin-based geopolymers using some form of calcium carbonate as an additive calcite, has received a considerable attention. This led to some interesting results, for example in evaluating that calcite performs better than e.g., dolomite, in the formation of the geopolymer gel by surface binding, however, it did not become an extensive practice, also due to the cost and debatable sustainability of the operation (Yip et al., 2008). The boost to this possibility can be offered by the use of waste, instead of newly extracted minerals. In particular, mixing with geopolymer binders does represent an upcycling strategy for mineral waste, in particular for carbonate ones, even if its composition is markedly heterogeneous, such as it is in the case of construction and demolition waste (CDW) (Volpintesta et al., 2023).

In this work, seashells powder of different granulometry, obtained from ground clams and mussel exoskeletons, were studied, which have already obtained some attention e.g., in the field of concrete coating (Martínez-García et al., 2019). The materials were outsourced as waste from the food-related sector and are locally collected in areas by the Adriatic Sea in the Marche region, are considered. The shell powders are formed from aragonite of significant purity to the point that extraction of the mineral from these has also been considered elsewhere (Triunfo et al., 2022). The shells, powdered after mechanical removal of the protein conchiolin, are characterised as for compositions introduced in different amounts into geopolymers and then compared with geopolymers containing the same amount of calcium carbonate obtained by quarry sources. The aim was to prove the suitability of substitution of calcite with aragonite and the possible drawbacks and limitations of such a replacement into geopolymers.

Martínez-García C., González-Fonteboa B., Carro-López D. & Martínez-Abella F. (2019) - Design and properties of cement coating with mussel shell fine aggregate. *Constr. Build. Mater.*, 215, 494-507. <https://doi.org/10.1016/j.conbuildmat.2019.04.211>.

Triunfo C., Gärtner S., Marchini C., Fermani S., Maoloni G., Goffredo S., Gomez Morales J., Cölfen H. & Falini G. (2022) - Recovering and Exploiting Aragonite and Calcite Single Crystals with Biologically Controlled Shapes from Mussel Shells. *ACS Omega*, 7(48), 43992-43999. <https://doi.org/10.1021/acsomega.2c05386>.

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Yip C.K., Provis J.L., Lukey G.C., van Deventer J.S. (2008) - Carbonate mineral addition to metakaolin-based geopolymers. *Cement Concrete Comp.*, 30(10), 979-985. <https://doi.org/10.1016/j.cemconcomp.2008.07.004>.

## **Closing the loop: transforming sewage sludge into alkaline cements through hydrothermal and alkali-activation processes**

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*Keywords:* sewage sludge, alkali activated materials, nutrients recovery.

The path towards a more sustainable future passes through a road with an efficient use of resources (energy, water, land, minerals), optimization of waste management and value creation. The increased use of secondary and renewable resources will likely be key in achieving sustainable materials use.

Sewage sludge is an inevitable highly hydrated residue generated by the wastewater treatment process. Sewage sludge management is currently a great problem for all the operators and managers of the Waste Water Treatment Plants, as very large volumes are produced every year. Our research group is currently involved in a project aimed at demonstrating the validity of a novel approach to tackle the environmental problem linked to sewage sludge (LIFE19 ENV/IT/000165, <https://life-freedom-project.eu/>). A plant for the transformation of sludge by Hydrothermal (HT) process has been realized and connected to the municipal sewage treatment plant of Cassano d'Adda. The hydrothermal processes eliminate pathogens in wastewater treatment effluents; avoid loss of water by reinserting the water trapped in the sludge into the WWTP and allows to recover nutrients, such as phosphorus and ammonia contained in the sludge. The hydrothermal process generates a solid side stream HTD cake. Valorization of the HTD has been addressed by the alkali activation process. AAMs obtained by different proportions of binary mixtures of HTD cake and metakaolin were synthesized using 8M and 12M NaOH solutions and curing samples at 85°C and 100% R.H. for 20 hours. Materials were characterized by X-ray power diffraction, Fourier transform infrared spectroscopy, scanning electron microscope, TG-DTA, leaching tests and mechanical tests. Metakaolin-based AAMs were used with the aim to produce valid construction materials and mainly to deal with a system model, being metakaolin one of the most studied precursors, due to its high reactivity and the good properties in terms of resistance and durability of the final products. Experiments showed how the addition of cake to the mixture induces the formation of microporosity, which might be useful for environmental applications or for thermal insulation purposes.

The results obtained highlight a promising path of transformation of biosolids waste into secondary raw materials, and their beneficial use in building materials to take a step forward towards the implementation of closed loop material flows.



## **Deep characterization of bottom ashes from municipal solid waste incineration: mineralogical and geochemical data from 5 plants of Northern Italy**

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*Keywords:* MSWI, bottom ash, characterization.

Bottom ash (BA) generated from Municipal Solid Waste Incinerators (MSWI) is currently classified by the European Waste Catalogue as industrial non-hazardous waste. It is an often-overlooked byproduct that can be a valuable resource in the circular economy if properly investigated and reused. Thorough analysis of its chemical composition and mineralogy is necessary to ensure the safe reuse of BA. The BA samples from five Waste-to-Energy plants in northern Italy are being characterized using various techniques such as X-ray fluorescence (XRF), X-ray powder diffraction (XRD), Rietveld refinement, Thermogravimetric analyses (TGA), and leaching tests. The results provide detailed information on the metal-bearing phases, their amounts, and their physical-chemical behavior over time. Interestingly, there are significant differences in the chemical and mineralogical composition of BA across the five plants. For example, the bulk mineralogical composition of the ashes varied depending on grain size and the proportion of each grain size. The analysis revealed that the amorphous content is more prevalent in the BA of three plants (TO, PR, PC), whereas bulk amorphous is, on average, less than 35% in FE and FC plants. Furthermore, some plants exhibit the presence of larnite and portlandite, which could support the reuse of BA in concrete, facilitating the setting and hardening reactions. These findings confirm some general trends already found in the literature, but also differ not only from previous studies but also among the five plants analyzed in this project. Therefore, conducting a mineralogical, chemical, and physical analysis before reusing BA is essential. This analysis should evaluate BA on several fronts, such as reuse in concrete, where significant concentrations of Cl and S, especially in the finer grain size, could be disadvantageous for cement application. Interestingly, pre-treatment before application as a cement binder could be envisaged since these elements are easily mobilized after water washing. Overall, this study provides detailed insights into the chemical and mineralogical characteristics of BA from five Waste-to-Energy plants in northern Italy. The findings contribute to the development of efficient treatment strategies and the reuse of BA, but also highlight the need for a more thorough investigation of BA samples to ensure their safe reuse. By understanding the composition and properties of BA, it may be possible to find innovative ways to reuse this byproduct, promoting the circular economy and sustainable waste management practices.

## Influence of CDW composition in geopolymer mortars based on volcanic ash, fly ash and metakaolin using Na and K solutions

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*Keywords:* construction and demolition waste (CDW), geopolymers, mortars.

Around 30% of all EU waste is attributed to Construction and Demolition Waste (CDW), representing environmental and economic challenges. These latter stem from both the rising amount of buildings that require refurbishment and the limited recycling of CDW, which is mostly used for backfilling. CDW is a serious problematic waste stream due to its heterogeneity: different lithotypes (depending on the area and geological provenance) and different material typology used in the building sector, namely masonry, drywall, roofing, wood, plastics, metals (Galderisi et al., 2022; 2023). However, a convincing way to recycle/upcycle this waste is still missing, especially for the finest fractions, usually landfilled.

On the basis of the interesting previous results (Volpintesta et al., 2023), the possibility of recycling two CDWs coming from Camerino (CM) and Catania (CT) areas to produce geopolymer mortars was tested. In detail, this work is focused on three specific topics: a) investigate how different CDW compositions can affect the physical-mechanical performances; b) determine the effectiveness of use as precursors of other waste materials like fly ash (FA) and volcanic ash (VA) in substitution to metakaolin (MK) to optimize the recycle process; c) test the maximum CDW amount usable as aggregates, maintaining physical-mechanical performance; d) evaluate the influence of type alkaline solution on the final properties.

Both CDWs were sampled and standardized in the particle size distribution, choosing the fraction 0.08-2 mm. XRF and XRPD results evidenced large differences between each other in chemistry and mineralogy. Eighteen mortars based on FA, VA and MK were produced with waste contents up to 50 wt.% CDWs. A multidisciplinary approach was performed for the characterization of the mortars. In the hydric test, the samples with CDW from CT evidenced lower open porosity and higher density than CM-samples, variable as a function of waste type/content and presence of VA, FA or MK. The compressive strength values are mostly in the range of structural materials (20-60 MPa), with best performances for mortars based on MK. The use of FA and VA produces a general decrease of mechanical performance regardless of the CDW type, although CM-bearing samples are the most affected due to the high Ca reactive content of CM. Best performances were obtained in the mortars produced with K- instead of Na-silicate.

This study highlighted the high potentiality of using CDW as aggregate in geopolymeric materials. However, further characterization and mix design test are needed to produce geopolymeric mortars tuning the best performances for the different applications.

Galderisi A., Iezzi G., Bianchini G., Paris E. & De Brito J. (2022) - Petrography of construction and demolition waste (CDW) from Abruzzo region (Central Italy). *Waste Manage.*, 137, 61-71. <https://doi.org/10.1016/j.wasman.2021.10.028>.

Galderisi A., Bravo M., Iezzi G., Cruciani G., Paris E. & De Brito J. (2023) - Physico-Mechanical Performances of Mortars Prepared with Sorted Earthquake Rubble: The Role of CDW Type and Contained Crystalline Phases. *Materials*, 16(7), 2855. <https://doi.org/10.3390/ma16072855>.

Volpintesta F., Ossoli E., Reggiani A., Stabile P., Santulli C. & Paris E. (2023) - Geopolymers-based application for the up-cycling utilization of Construction and Demolition Waste from the 2016 Central Italy earthquakes. *Mater. Lett.*, 133849. <https://doi.org/10.1016/j.matlet.2023.133849>.

## **S23.**

### **Biomineral, environment and gemmological studies**

#### *CONVENERS AND CHAIRPERSONS*

*Fabio Bellatreccia (Università Roma Tre)*

*Giovanni De Giudici (Università di Cagliari)*

*Valerio Funari (Istituto di Scienze Marine, CNR, Bologna)*

*Giovanna Agrosí (Università degli Studi di Bari Aldo Moro)*

*Maria Cristina Caggiani (Università di Catania)*

*Alessandra Costanzo (University of Galway, Ireland)*

## **Biominerals and Environment: Advances in infrared spectroscopic investigations at micro and nano scale**

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*Keywords:* infrared spectroscopy, synchrotron radiation, biomineralization.

Fourier Transform infrared (FTIR) spectroscopy is a non-destructive analytical technique that allows the user to perform a full chemical characterization of the inspected sample. Since early '90 FTIR its use has been extended from the chemistry laboratories to the analysis of biological samples, (Diem et al., 2004) and in over 30 year, manifold improvements in instrumentation, sampling techniques and data analysis approaches have kept high the interest on this analytical technique.

SISSI-Bio is the Chemical and Life Sciences branch of the infrared beamline SISSI (Synchrotron Infrared Source for Spectroscopy and Imaging – SISSI-Bio) at Elettra-Sincrotrone, Trieste, Italy. The laboratory is up-to-date with the latest equipment for Fourier Transform InfraRed (FTIR) analysis and currently hosts three endstations: one for spectroscopy, one for microscopy and one for nanospectroscopy. The synchrotron radiation (SR) allows for measurements at the diffraction limit over the full IR spectral range, and all the three end stations can alternatively be operated with SR or benchtop sources, increasing their usage time beyond the infrared synchrotron radiation availability. SISSI-Bio's activities have been covering a wide range of research fields including material science, biochemistry, biomedical diagnostics, cultural heritage, forensics, geology, and many others. In the last few years, at the SISSI-Bio, the collaborations and the users proposing experiments related to the environmental sciences grew substantially. In this presentation I would like to first provide a quick excursus on the aforementioned advancements in the FTIR field over the last 10 years, starting from the improvements in the instrumentation, now capable of collecting vibrational spectra at the nanoscale, far beyond the diffraction limit. Then I will be moving to present the improvement in the data treatment, thanks to the application of multivariate tools to explore and analyze large datasets and hyperspectral images. In the end I would like to present the most recent works in the fields of environmental sciences and bio mineralization in which we were involved by our collaborators (Birarda et al., 2021; Bergami et al., 2023; Bordiga et al., 2023).

Bergami E., Ferrari E., Löder M.G.J., Birarda G., Laforsch C., Vaccari L. & Corsi I. (2023) - Textile Microfibers in Wild Antarctic Whelk *Neobuccinum Eatoni* (Smith, 1875) from Terra Nova Bay (Ross Sea, Antarctica). *Environmental Research*, 216, 114487. <https://doi.org/10.1016/j.envres.2022.114487>.

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Diem M., Romeo M., Boydston-White S., Miljković M. & Matthäus C. (2004) - A Decade of Vibrational Micro-Spectroscopy of Human Cells and Tissue (1994-2004). *Analyst*, 129(10), 880-885.

## Synthesis of pyroxenes of gems quality and size

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Keywords: pyroxenes, gems, synthesis.

In recent years the introduction of synthetic gems in the jewellery industry has provided a wide variety of aesthetic and decorative solutions. Doped enstatite and doped diopside have been grown by flux growth technique (Bloise et al., 2011) using  $\text{MoO}_3$ - $\text{V}_2\text{O}_5$ - $\text{Li}_2\text{CO}_3$  as flux and  $\text{SiO}_2$ ,  $\text{MgO}$  and  $\text{CaO}$  as nutrients. Several starting mixtures were first held at 1350°C, 1250°C, 1050°C and 950°C in a vertical furnace, then cooled down to 750-600°C (according to the field stability of the pyroxenes) with different cooling rates and finally, rapidly quenched down to room temperature. The gem quality of pyroxenes was achieved by synthesising based on the above experiments. Various colouring agents, such as Mn (II), Ni (II), Fe (II) and Fe (III) were added to obtain the different colours of the gem. In high-temperature synthesis, these chromophore ions enter in the crystalline lattice, replacing the ions naturally present and changing the natural colour of the mineral. Pyroxenes, such as enstatite ( $\text{MgSiO}_3$ ) and diopside ( $\text{CaMgSi}_2\text{O}_6$ ) are very good host matrices for transition metal ions and are considered excellent for producing a broad palette of gem-quality pyroxenes with variable concentrations of the same chromophore. After the separation from the solidified flux by sonication in hot water, the final products were studied and characterized by a binocular microscope, X-ray Powder Diffraction (XRPD) and scanning electron microscopy with energy-dispersive spectrometry (SEM-EDS). The effects of growth parameters on the yield and size of crystals were discussed. Physical properties, such as hardness and refractive index, were also measured. The results show that synthetic pyroxenes have the same properties as the natural ones. Reds Mn-doped enstatite, green Ni-doped enstatite and orange-brown Fe-doped diopside single crystals were euhedral. The maximum size of synthetic pyroxenes produced here as a gem was up to 9 mm long. Overall, in this work, we point out that the conditions for producing pyroxenes crystals with a homogeneous distribution of dopant occur by cooling to 650°C from 1050°C of a suitable starting mixture at a cooling rate of 1.7°C/h.

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## **An insight in Baltic amber: determining the origin and the nature of the inclusions trapped in the natural organic gem**

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*Keywords:* amber, inclusions.

Amber is a fossilized resin ancient trees (coniferous and deciduous), which underwent the process of fossilization in various epochs and depositional environments and which has been used for a long time as a source of paleobiologic information via the preservation of paleobiota. However, the resin does not just trap organisms but amber can also preserve vapour phases of various composition. They may represent ancient air trapped at the time the original resin was exuded from its host tree but may also indicate modern air (Berner & Landis, 1987). Roedder (1984) also suggested that the trapped air might be mixed with volatile components of the amber. The processes used to prepare the samples, such as grinding and polishing, may force the entrapment of inclusions that have nothing in common to the original entrapment, therefore, post-processing water, impurities or alteration materials need to be described and differentiated from the naturally entrapped inclusions. In this study, Baltic amber Eocene in age is investigated. Numerous samples of raw (not processed) and non-raw (processed) material are used with the aim to investigate, through a multidisciplinary approach, the nature of the inclusions and to determine their origin. The samples vary in size and weight (from 1 to 5 grams) and have been all selected according to their inclusions appearance. They consist of air bubbles, liquid and solid phases (e.g. marcasite) as well as spores. Previous studies (Jiang et al., 2022) demonstrate that resin and amber are not always closed systems. Fluids (e.g. sediment pore water, diagenetic fluid and ground water) at different burial stages have chances to interact with amber throughout its geological history and affect the preservational quality and morphological fidelity of its organic inclusions. There are indeed numerous problems with preservation of original compositions in the amber matrix and therefore experiments considering any man-made inclusions are also carried out. Data from light microscopy, scanning electron microscopy (SEM), energy-dispersive and wavelength-dispersive X-ray spectroscopy (EDX and WDX), X-ray micro-computed tomography (Micro-CT) and Raman spectroscopy will be presented.

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## The effect of different evaporation rates on gypsum habit: mineralogical implications for natural gypsum deposits

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Keywords: gypsum, twins, evaporation.

Gypsum (calcium sulfate dihydrate,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) is the most abundant natural sulfate mineral on Earth's surface and is mostly found in evaporitic environments. Remarkably, the history of Earth, from the Neoproterozoic to the Phanerozoic, is punctuated by dramatic episodes of evaporitic deposition that resulted in the accumulation of thick gypsum or anhydrite-bearing sedimentary successions.

Gypsum is characterized by single and twinned crystals. Single crystals show acicular, tabular, prismatic, and lenticular habits. In some cases, gypsum can also form distinctive curved crystal structures such as the ram's horn gypsum - found in caves - and sabre gypsum observed in Badenian gypsum deposits. Five different twin laws are possible for gypsum structure, each described by a contact and penetration twin mechanism (Rubbo et al., 2012a,b). Thus, gypsum may show at least ten different twin habits.

Since the pioneering studies of Lacroix (1986), such a wide array of habits was believed to reflect peculiar growth conditions. A better understanding of the environmental factors responsible for different gypsum habits may have crucial implications for the interpretation of the origin of the gypsum deposits formed in the geological past.

To recognize the effect of impurities on gypsum habit, the impurity-free gypsum habit must be known. Starting from a solution saturated in  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , when evaporation occurs gypsum crystals precipitate. Remarkably, gypsum precipitation by evaporation is the most common phenomenon in natural environments, and the more easily reproducible process in laboratory. Moreover, by modifying the evaporation rate, it is possible to observe whether and how gypsum habit changes.

Starting with a pure solution saturated in  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , we show that an increase in evaporation rate promotes the precipitation of gypsum crystals (i) with curved habit and (ii) twins according to the 100 and -101 penetration twin laws, with different precipitation frequencies and habits. The crystal length/width ratio is proposed as a quick measure to identify between 100 and -101 penetration twin laws, and a homo-epitaxial mechanism is invoked to explain the curved habit. Moreover, the occurrence of 100 and -101 penetration twin laws in sedimentary environments is suggested, and a formation mechanism of ram's horn and sabre gypsum crystals (naturally occurring curved gypsum crystals) is hypothesized. These results describe which ones of the twin laws of gypsum are possible in a pure solution, and correlate for the first time different gypsum habits with different evaporation rates contributing to a better understanding of the gypsum habit in evaporitic environments.

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## New insights on gypsum twinned crystals: mineralogical implications for natural gypsum deposits

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Keywords: twins, fluid inclusions, evaporites.

Gypsum twins are frequently observed in nature, triggered by a wide array of impurities that are present in the depositional environments and that may exert a critical role in selecting different twin laws. Identifying the impurities able to promote the selection of specific twin laws has relevance for geological studies aimed at interpreting the depositional environment of gypsum-bearing sedimentary successions, such as those formed ~6 Ma in the Mediterranean basin during the Messinian salinity crisis (MSC).

Here, the five twin laws of gypsum are geometrically described to give a theoretical background for the twin law identification by means of optical microscopy. The precipitation of twinned gypsum crystals has been experimentally obtained (-101 contact twin law) by adding carbonate to the solution, and the involvement of rapidcreekite ( $\text{Ca}_2\text{SO}_4\text{CO}_3 \cdot 4\text{H}_2\text{O}$ ) in selecting the -101 gypsum contact twin law was invoked, suggesting an epitaxial mechanism. This is the first evidence of the effect of Ca-carbonate as a specific impurity promoting the formation of the -101 contact twin law. Moreover, we compared the natural gypsum twin morphologies observed in evaporitic environments with those obtained in our experiments and suggested the occurrence of -101 gypsum contact twins in ancient successions. We claim that -101 gypsum contact twins in such successions are probably more common than previously considered which suggests high carbonate concentration in the brines from which they precipitated. Experimental results also show that the different orientation of primary fluid inclusions (of the negative crystal-shaped) with respect to the twin plane, and the main elongation of the sub-crystals making the twin, is a useful tool to distinguish between 100 and -101 twin laws, whose geometry is otherwise very hard to distinguish especially in rock samples (Cotellucci et al., 2023).

Interestingly, no fossilized remains of calcifiers like foraminifera and coccolithophores are preserved in Messinian gypsum crystals, although other microfossils consisting of silica (diatoms) or of authigenic clay (filamentous microfossils) are very common. Such circumstance suggests that dissolution of biogenic calcite, most likely induced by pore water acidification *via* microbially-mediated redox reactions (Aloisi et al., 2022; Mancini et al., 2022), may have triggered the formation of the -101 twin law of gypsum during the MSC.

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## Geochemistry and mineralogy of antimony in enriched riverine water and mineral phases

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*Keywords:* mining impact, metals, mopungite.

Antimony (Sb) is a critical material and one of the top ten mined elements worldwide. Centuries of Sb extraction generated tons of mining waste enriched in Sb and dispersed in riverine and coastal ecosystems. Geochemical and physical weathering of mining waste mobilises Sb and other metals, posing an environmental risk. Antimony is a non-essential element with the European guideline threshold value of 5 µg/L for drinking water, and still critical to sustainable technologies. Understanding Sb geochemistry and mineralogy is fundamental to implementing remediation, Sb recovery, and mining, limiting the risk it can pose to the environment and human health.

Historical Sb mining in southeast Sardinia (Italy) offers a case study where Sb can be found in outcropping rocks, mine wastes, foundry slags, and the impacted riverine system. Mineralogical investigations (XRPD and SEMEDS) highlighted the presence of various Sb-bearing phases such as Sb<sub>2</sub>O<sub>3</sub> (valentinite/sénarmontite), stibnite (Sb<sub>2</sub>S<sub>3</sub>), metallic Sb, and the rare mopungite (NaSb(OH)<sub>6</sub>). The weathering of these Sb-bearing phases released Sb into the water, with the water samples showing a median of 323 µg/L (range 48 - 4,020 µg/L). The most common Sb<sub>(aq)</sub> phase found in the waters was Sb(OH)<sub>6</sub><sup>-</sup> with Sb(V) species. Reaction with high concentrations of carbonate and Na-phases are suspected to react with the Sb<sub>(aq)</sub> and precipitate as mopungite (NaSb(OH)<sub>6</sub>). The presence of these phases contributes to the attenuation of Sb in the riverine systems limiting its mobility. This process is of high relevance since the river system draining the mine system feeds the Flumendosa River, an important water source for the downstream valley characterised by agricultural and urbanised land use. These findings highlight the geochemical process driving Sb mobility in impacted river systems and natural attenuation processes. Further research is required to implement such an understanding to monitoring, remediation, and land use of Sb-enriched areas.

## Guano derived biominerals from the Pollera Cave (Liguria, Italy)

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Keywords: bat guano, minerals.

Bat guano is the most common type of organic deposit found in cave environments. Over time, guano is transformed by bacterial and fungal processing, which cause the degradation of organic matter and the release of strongly acidic solutions enriched in nitric, sulfuric and phosphoric acid. The reaction of these fluids with rocks, cave sediments and speleothems induce the precipitation of a large variety of authigenic mineral phases (Audra et al., 2019; Hill & Forti, 1997). Studying guano derived (bio)minerals could provide valuable insights on the minerogenetic mechanisms taking place in environments where geological and biological processes are closely intertwined. Moreover, the definition of these minerogenetic processes could be a very useful tool to gain a better understanding on the environmental conditions in which these minerals were formed.

For this work, we have sampled and characterized representative guano-derived minerals from a fossil bat guano deposit hosted in the Pollera Cave (Liguria, Italy), a 2.4 km long natural cavity developed in the Miocenic Pietra di Finale Fm. in the Finale Ligure karst area. A multi-method approach was adopted to investigate the mineralogical and geochemical features of the samples, including X-ray powder diffraction, SEM-EDS analyses, Raman and FTIR spectroscopy, XRF and ICP-MS. The samples were collected i) from the horizons of the guano deposit, ii) from the boundaries between guano and detrital clay deposits, iii) from cm-thick yellowish white to orange crusts covering calcareous blocks near the guano accumulation.

The authigenic mineral associations forming in the shallower levels of the guano mound are composed of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), brushite ( $\text{CaPO}_3\text{OH} \cdot 2\text{H}_2\text{O}$ ), ardealite ( $\text{Ca}_2(\text{PO}_3\text{OH})(\text{SO}_4) \cdot 4\text{H}_2\text{O}$ ) and taranakite ( $\text{K}_3\text{Al}_3(\text{PO}_3\text{OH})_6(\text{PO}_4)_2 \cdot 18\text{H}_2\text{O}$ ). In the deeper parts of the deposit, taranakite is common while hydroxylapatite ( $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ ) is occasionally present.

The boundaries between guano and clay deposits are characterized by the presence of white powdery aggregates and nodules of taranakite, and dark brown mm-thick crusts of leucophosphite ( $\text{KFe}^{3+}_2(\text{PO}_4)_2(\text{OH}) \cdot 2\text{H}_2\text{O}$ ). Both these phases are  $\text{NH}_4^+$ -bearing and probably derive from the interaction between bat excreta-derived leachates and detrital Fe- and Al-rich clay minerals.

The phosphatic crusts overlaying fallen calcareous blocks are mainly constituted by hydroxylapatite with the rare occurrence of ardealite. Raman and FTIR spectra of hydroxylapatite show characteristic  $\text{CO}_3^{2-}$  peaks (Antonakos et al., 2007), while EDS measurements denote Zn contents ranging from 0.3 to 1.2 wt%.

Further investigations are needed to find other potential phases associated to the guano deposit, constrain the minerogenetic mechanisms that brought to their formation and evaluate the possible direct or indirect microbiological control on the formation of these mineral deposits.

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## Investigating the strontium isotope linkage between human urinary stones and drinking waters from South Italy

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Keywords: uroliths, water, strontium.

This study aims at characterizing the strontium isotope signature ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) of twenty-two pathological biominerals (human urinary stones) collected at the Department of Urology of the San Pio Hospital (Benevento, Italy), from patients admitted between 2018 and 2020. The morpho-constitutional characterization of these samples had been previously made by Mercurio et al., 2021 and Izzo et al., 2022. A targeted sampling strategy allowed to collect 29 samples of drinking water, both bottled (twenty-four) and tap (five), were also analysed for their Sr-isotope ratio and compared to those of the examined urinary stones. Bottled waters were mostly from springs located in different Italian municipalities and four of them from the Campanian Region. Tap water samples were collected in the municipalities of Piedimonte Matese (Caserta), Naples (downtown), Ceppaloni (Benevento) and Montoro (Avellino).

Urinary stones display  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios ranging from 0.70761, for a uricite sample (ideal composition  $[\text{C}_5\text{H}_4\text{N}_4\text{O}_3]$ ), to 0.70997 for a weddellite (ideal composition  $[\text{CaC}_2\text{O}_4 \cdot (2+x)\text{H}_2\text{O}]$ , where  $x < 1$ ). Phosphates-based uroliths are characterized by a Sr-signature of 0.70862 in carbonated (hydroxyl)apatite (ideal composition  $\text{Ca}_{10-x+u}\text{O}_x(\text{PO}_4)_{6-x}(\text{CO}_3)_x(\text{OH})_{2-x+2u}\text{O}_{x-2u}$ ; where squares correspond to vacancies or additional cations and anions and  $04 \cdot 2(\text{H}_2\text{O})$ ). The purine samples included a kidney stone made of ammonium urate (ideal composition  $[\text{NH}_4\text{C}_5\text{H}_3\text{N}_4\text{O}_3]$ ) with a corresponding  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of 0.70875.

Most of the analyzed drinking waters show a Sr isotope signature in the range of values obtained for the analyzed biominerals. In details, water samples from the Pliocene-Quaternary volcanic aquifers of the Mt. Vulture provide an  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio around 0.70656, whereas those from the Paleozoic metamorphic aquifers of the Italian Alps are characterized by more radiogenic Sr isotope signatures (0.71747 and 0.72736). Bottled waters from aquifers in the Mesozoic carbonate-rocks display an  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio ranging from 0.70764 to 0.70889. Tap waters from the Campania region show a narrower range: from 0.70774 to  $\sim$  0.7080. Higher values can be observed for drinking waters bottled from aquifers in the sedimentary siliciclastic rocks and in the Quaternary glacial deposits. Intermediate isotope ratios are observed for the drinking waters collected from aquifers in the Miocene carbonate sequence and in the Late-Pliocene calcareous hemipelagic sedimentary rocks of the Lazio and Tuscany regions.

When comparing these results with data from the literature it can be noticed that the strontium isotope signature of urinary stones analyzed in the present study generally reflects the signature of the surroundings environmental matrices, including drinking waters. This clearly suggests a potential for the implementation of these pathological biominerals for biomonitoring purposes.

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## Similarities and differences among the most relevant varieties of chalcedony in gemmology: chemistry, mineralogy and microstructure

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*Keywords:* aquaprase, chemical composition, microstructure.

Chalcedony, a micro- or crypto-polycrystalline variety of quartz, is a highly valued archaeo-gemmological material due to its durability and attractive colorations. While it is commonly found in association with the silica microcrystalline polymorph moganite, chalcedony should be considered as a mineralogical assemblage (Gliozzo, 2019). Given its wide variety of patterns and colours, it is widely employed in gemmology nowadays. Among its most renowned varieties are the apple-green chrysoprase and the banded agate. In 2013, a new variety of chalcedony, named aquaprase, was discovered in Africa, and its vibrant inhomogeneous bluish-green coloration quickly made it a valued addition to the gemmological trade. Despite its popularity, a comprehensive understanding of the mineralogical features of aquaprase is lacking. This study aimed to provide the first detailed characterization of aquaprase, with particular attention to the cause of its unique colour, as well as a comparison with representative varieties of chalcedony such as blue agate from Türkiye and green chrysoprase from Australia.

Optical microscopy revealed a complex microstructural heterogeneity in the different colour intensity areas/bands of aquaprase and agate, whereas chrysoprase exhibited a more homogeneous coexistence of micro- and cryptocrystalline quartz. High-resolution synchrotron XRD was essential for highlighting the complex assemblage of various types of  $\alpha$ -quartz in aquaprase and agate. Micro-Raman spectroscopy revealed  $\alpha$ -quartz and moganite in all three chalcedony varieties and the presence of the nickel-bearing layered silicate mineral, willemsite, in chrysoprase responsible for its green coloration. Chemical analysis showed a homogeneous composition of agate, high nickel content in chrysoprase (0.1 - 1.7 wt. %), and significant content of minor elements in aquaprase (0.02 - 1.2 wt. %), which are characteristic of its formation environment. The high values of Cr (0.05 - 0.3 wt. %) are thought to be responsible for aquaprase's bluish-green colouration.

This study provides valuable insights into the unique characteristics of aquaprase and highlights its potential as a prized gemmological material.

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## Arsenic in the *Piscine Carletti* Thermal Spring System (Viterbo, Italy): a XAS speciation study

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Keywords: arsenic, XAS, calcite, biofilm.

A study aimed at unravelling arsenic (As) speciation by means of XAS spectroscopy in the carbonate sediments and the total suspended particulate (TSP) occurring at the *Piscine Carletti* spring system (CSS), part of the larger Bullicame (Viterbo, Central Italy) thermal area, has been undertaken.

At CSS, hot water emerges in an artificial pool and flows along a constructed channel (ca. 100 m long) covered by travertine deposits partially coated by differently coloured microbial mats indirectly favouring mineral deposition (Venturi et al., 2023). In this spring system, As occurs as a geogenic anomaly, and its mobility is affected by inorganic and microbiological processes which can differentiate its speciation and mobility. The determination of As speciation in both the rock and TSP is essential to validate the models on the fate of As in this “natural laboratory”.

8 rock and 8 TSP samples were collected in the CSS, in step of 14 m along the channel starting from the water spring and following the change in temperature and physico-chemical features of the system. Some water samples for the determination of the chemical and physical parameters of the environment were also collected. Solid samples were analysed, without manipulation, by means of X-ray Absorption Spectroscopy, at the As K edge (11864 eV) in fluorescence mode, and at low temperature (range 77-20 K). Experiments on rock and TSP samples were carried out at BM08 and BM26, respectively.

The main results point to an almost constant As(III) over As(tot) ratio over the whole spring system in the rock samples, As(III) being about 30% of the As(tot). Considering samples discriminated by the colour (with reference to different abundances and speciation of microbiologic populations), no apparent spectral changes were observed.

TSP samples, analysed with a specific procedure due to their ultra-diluted nature, appear also constant, and, compared to the corresponding rocky samples, slightly enriched in As(III).

These data have to be compared to a water environment, which evolves towards more oxidising and higher pH conditions while increasing the distance from the spring, as testified from the change of the As(III)/As(tot) ratio from an initial 70% down to a final 40% (unpublished data).

This complex set of experimental results will be discussed on the light of two possible interpretations schemes, i.e., a kinetically constrained precipitation mechanism, and a microbiologically constrained change of As speciation.

Venturi S., Crognale S., Di Benedetto F., Montegrossi G., Casentini B., Amalfitano S., Baroni T., Rossetti S., Tassi F., Capecchiacci F., Vaselli O. & Fazi S. (2023) - Interplay between abiotic and microbial biofilm-mediated processes for travertine formation: Insights from a thermal spring (*Piscine Carletti*, Viterbo, Italy). *Geobiology*, 20, 837-856. <https://doi.org/10.1111/gbi.12516>.

## Bio-geo interaction in mining-impacted environments

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Keywords: biominerals, metals, natural remediation.

Since the 1960s, the biominerals' ubiquitous presence and composition diversity have been increasingly recognised, and to date, 160 biogenic minerals has been listed (De Giudici et al., 2023). Biomineral formation processes and their resilience gained attention due to their capacity to persist in hostile environments. Understanding the bio-geochemistry driving these processes would enhance the development of sustainable technologies and risk assessment for degraded environments. Worldwide historical mining areas are notorious for negatively impacting the riverine and coastal ecosystems. In this study, researchers concentrated their effort on understanding the environmental response to metal contamination focusing on the ability of organisms to naturally mitigate metal water concentration by forming bio-minerals.

Rivers draining the Arburese mining district (SW Sardinia, Italy) alone contribute 2200 kg/day of Zn to the Mediterranean Sea Zn load (Dore et al., 2023). Along these rivers, biominerals were identified through metal source apportionment investigation to quantify Zn sources and attenuation areas at a catchment scale. Biomineralisations along the riverbed, hyporheic zone, and rhizospheres could attenuate riverine Zn load. Geochemical and mineralogical investigations (XRD, SEM, XRF, and XAS synchrotron light analysis) distinguished various biominerals and ongoing processes: i) metal intake in roots-soil-water soil interface driven by *Phragmites australis* and *Juncus acutus* root and stem apparatus; ii) Zn-rich phases (hydrozincite and amorphous Zn-silicate) bio-precipitate by cyanobacteria; iii) Fe-rich phases (oxy/hydroxides, green rust, and framboidal pyrite) whose formation is enhanced by organisms and able to adsorb other metals. These results highlighted the variety of biomineralisation and the organism's role in forming metal-enriched phases able to abate riverine metal load at a catchment scale.

Mechanisms ruling on bio-mineralisation are controlled by the bio-water-soil spheres interactions, which variables can be observed at a molecular, cell, metric, and kilometeric scale. For instance, at the interface between cellular and mineral surfaces, organisms can influence pH, Eh, oxygen, and CO<sub>2</sub> pressures and therefore control their surrounding environment driving the formation of mineral phases. Furthermore, this interface and the occurring processes vary depending on the presence of water, elemental soil and water composition and concentrations, water permanence time, soil porosity and permeability. These nano-kilometer scale variables intensifies the complexity behind these processes. Ongoing interdisciplinary studies aims to shed light on these processes to contribute to the restoration of impacted ecosystems, bioleaching technologies, and sustainable remediation or monitoring plans.

Dore E., Fancello D., Rigonat N., Medas, D., Cidu, R., Da Pelo, S., Frau, F., Lattanzi, P., Marras, P.A., Meneghini, C., Podda F., Rimondi V., Runkel R.L., Kimball B., Wanty R. & De Giudici G. (2020) - Natural attenuation can lead to environmental resilience in mine environment. *Appl. Geochem.*, 117, 104597. <https://doi.org/10.1016/j.apgeochem.2020.104597>.

De Giudici G., Medas D. & Meneghini C. (2023) - Bio-mineral Interactions and the Environment. In: Tribaudino M., Vollprecht D. & Pavese A. (Eds), *Minerals and Waste*, Earth and Environmental Sciences Library, 66-116. [https://doi.org/10.1007/978-3-031-16135-3\\_4](https://doi.org/10.1007/978-3-031-16135-3_4).

## **Imperial topaz, from commercial name to new gemmological variety: a new definition for chromium bearing topaz**

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*Keywords:* gemstones, topaz, coloured stones.

Topaz,  $\text{Al}_2\text{SiO}_4(\text{OH},\text{F})_2$ , is one of the main fluorine bearing silicates that occurs as accessory minerals in fluorine rich silicate rocks associated with magmatic or hydrothermal events (Alberico et al., 2003; Zhang et al., 2011). Because of this characteristic, topaz deposits are spread worldwide and can form in very different environments. The structure consists of  $[\text{SiO}_4]_4^-$  groups linking octahedral chains of  $\text{Al}[\text{O}_4(\text{F}, \text{OH})_2]$  in a zig-zag arrangement parallel to the c-axis. Four out of the six anions surrounding the  $\text{Al}^{3+}$  ion belong to  $[\text{SiO}_4]_4^-$  tetrahedra; and two form  $\text{F}^-$  or  $\text{OH}^-$  groups. Natural topaz crystallizes in the orthorhombic Pbnm space group. Often overshadowed by gems such as diamonds or the so-called ‘big three’, emerald, ruby and sapphire, topaz remains a key player in the jewellery world. Most of topaz found are colourless or very pale yellow, but they can appear in other colours. The varieties peach, pink, champagne, medium reddish orange to range red, orange-yellow and yellowish brown are all named “Imperial topaz”. Today, “Imperial topaz” is used just as a trade name and there is not a standardization of mineralogical and chemical features that could raise it as a gemmological variety in its own right. Petrov (1977) distinguished three different causes of color in topaz, highlighting how  $\text{Cr}^{3+}$  paired with colour centres plays a fundamental role in the yellow to orange to pink and pinkish-violet topaz. In this work, we have fully characterized two topaz “families” from two areas famous for the production of “imperial topazes”: Ouro Preto region in Brazil and Pakistan (uncertain Mardan or Gilgit district). These samples cover a wide range of “imperial topaz” colours from intense yellow, to orange to vivid pink. The successful strategy to combine LA-ICP-MS analyses for trace elements with X-Ray diffraction measurements and fluorescence spectroscopy allowed to accurately determine the relationship between chemical and structural features of these topaz. On the basis of these results, therefore, we would like to propose a way of recognising imperial topaz as a gemmological variety based on  $\text{Cr}^{3+}$  content, along the lines of what has been done with Cu and Mn bearing tourmaline (Tourmaline Paraiba).

Alberico A., Ferrando S., Ivaldi G. & Ferraris G. (2003) - X-ray single-crystal structure refinement of an OH-rich topaz from Sulu UHP terrane (Eastern China)—Structural foundation of the correlation between cell parameters and fluorine content. *European Journal of Mineralogy*, 15(5), 875-881.

Petrov I. (1977) - Farbuntersuchungen an Topas. *Neues Jahrb. Mineral., Abh.*, 130, 288-302.

Zhang Z.M., Shen K., Liou J.G., Dong X., Wang W., Yu F. & Liu F. (2011) - Fluid-rock interactions during UHP metamorphism: A review of the Dabie–Sulu orogen, east-central China. *Journal of Asian Earth Sciences*, 42(3), 316-329.

## **Raman spectra comparison between untreated and treated colored tourmalines from different localities**

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*Keywords:* tourmaline, Raman spectroscopy, treatments.

Tourmalines are the most popular gemstones in the world due to their wide spectrum of colors reflecting high chemical and structural complexity. Like many minerals for gemological use, tourmalines are also treated with radiation sources and/or thermal processes to intensify their color and to increase their commercial value on the market. However, color change mechanisms in treated tourmaline are still poorly known. In the present study, six tourmalines with different colors (colorless, pink, red and blue) and from different provenances, were characterized using Raman spectroscopy before and after two different types of manipulations: electron-beam irradiation and heat treatment. In the first case, the samples have been irradiated in air, through a linear electron accelerator, at a dose of  $5.1 \times 10^4$  Gy. The temperature on the sample holder has been maintained at a maximum value of 20°C using an aluminum plate equipped with a specially designed cooling system. After irradiation, samples showed a visible intensification of the original color. Successive thermal treatments, performed up to 600°C, caused a further change towards paler colors; in some cases, the sample turned into colorless. A comparison of Raman spectra, acquired on untreated, e-beam irradiated and heated samples and collected in a spectral range from 200 to 3800  $\text{cm}^{-1}$ , provide modified feature in the spectra related to the color change induced by the two different treatments.

## **Biominerals occurrence at Montevecchio mine (SW Sardinia)**

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*Keywords:* biominerals, environmental mineralogy, hydrozincite.

The “Cantieri Sanna” (Montevecchio Mine - SW Sardinia) was exploited from 1849 to the 80s of the last century for the extraction of oxidized minerals. On the site, there are many landfills with residues from the treatment of oxidized minerals. The interaction of these residues with surface waters leads to the release of contaminants that are transported by Rio Roia Cani. Along the riverbed of the Rio Roia Cani white patinas referable to biomineralization were sampled. These patinas were investigated in order to know their composition and their potential to uptake pollutants and critical raw materials (CRM).

Nine samples were collected and analyzed by X-ray diffraction (XRD), in order to detect their mineralogical composition, and by scanning electron microscope (SEM-EDS), to study their morphology and their chemical composition. Finally, after acid digestion, analyses were performed by inductively coupled plasma optical emission spectroscopy (ICP-OES) analyses and inductively coupled plasma mass spectroscopy (ICP-MS) to know their whole chemical composition.

XRD analyses showed that all samples are composed of hydrozincite, with the exception of two samples, which are composed of zincite. The SEM-EDS analysis allowed us to observe tubular and filamentous structures characteristic of biominerals, previously observed in the hydrozincites of the Rio Naracauli (Ingurtosu - Sardinia SW - Medas et al., 2014). The ICP-MS and ICP-OES analyses highlighted important concentrations of Al, Fe, and Pb within the analyzed samples and the presence of some Rare Earth Elements (REE) in significant concentrations.

In conclusion, this study leads to a state that the patinas visible along the riverbed of the Roia-Cani stream are made of hydrozincite, likely produced by bacteria and biological organisms which, by precipitating mineral phases such as hydrozincite, carry out bio- remediation, by removing the metal ions from the aqueous solution, also allow to remove and stabilize the REE present from the solution.

Medas D., Lattanzi P., Podda F., Meneghini C., Trapananti A., Sprocati A., Casu M. A., Musu E. & De Giudici G. (2014) - The amorphous Zn biomineralization at Naracauli stream, Sardinia: Electron microscopy and X-ray absorption spectroscopy. *Environmental Science and Pollution Research*, 21(11), 6775-6782. <http://dx.doi.org/10.1007/s11356-013-1886-4>.

## Historical ecclesiastic jewelry from 18<sup>th</sup> century Sicily: non-invasive gemological investigation

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*Keywords:* historical ecclesiastic jewellery, portable x-ray fluorescence investigations, Raman spectroscopy.

Monstrances, jewelries and *ex voto* represent the core of the ecclesiastic historical patrimony. Most of them, coming from the 18<sup>th</sup> century, are now stored and exposed in numerous Diocesan and Sacred Art Museum, which boast centuries of history and the property of unique objects. Refined designs, golden finishing and set gemstones give these objects a very precious appearance. But are these objects really valuable? Does the nature of the gemstones really correspond to the declared one? Often, the identification of a gem in this context is assigned according to autoptic observations and historical documents. No scientific studies are usually performed. Traditional techniques, indeed, do not allow to analyze set gems, which could be studied only with non-invasive instruments, better if portable directly in situ.

Raman spectroscopy, coupled with portable X-ray Fluorescence (pXRF) could be considered well-suited analytical techniques for this purpose, but few are the examples of their application on these kinds of art and historical remains.

With the aim of deepening the knowledge about the Sicilian production of ecclesiastic objects, confirming or not the declared gemstones identifications, a set of objects from the Diocesan Museums of Catania and Caltagirone (Italy) were studied by in situ portable Raman spectroscopy (with 785 nm excitation wavelength) and portable X-ray Fluorescence (XRF). The series of objects investigated included different monstrances with stylistic similarities and set gemstones, dated back to the 18<sup>th</sup> century; bishop's adornments, as a miter with differently coloured gems, a pastoral ring with a large green stone surrounded by colourless ones (supposed to be an emerald and little diamonds) and a pectoral cross with light orange centimetric stones surrounded by colourless little ones (supposed to be topazes and diamonds). Furthermore, an *ex voto* ornament, used for the Immaculate Conception statue for a religious ritual in Caltagirone, was also extensively analysed. It is an elegant combination of jewellery parures sewn together on a textile bustier. Numerous reddish and pinkish gemstones are set, together with small colourless ones; moreover, a cameo appears at the centre of the jewel. According to a kind of traditional Sicilian production of European derivation in vogue, especially in the 18<sup>th</sup> century, the gems mentioned were supposed to be rubies and diamonds. Interesting results emerged from the analytical investigations. In some cases, precious gemstones, such as rubies, emeralds and diamonds, are detected together with quartz or garnet, while in some others the presence of precious gems must be discredited due to the identification of glass.



## Laser Induced Breakdown Spectroscopy of gem quality topaz from different localities

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Keywords: topaz, LIBS, gems.

Topaz is an orthorhombic nesosilicate mineral with formula  $Al_2SiO_4(F,OH)_2$  and space group *Pbnm*. A cause of its hardness 8 on the Mohs scale and the variable color (yellow, brown, blue, pink, red, and colorless) it is widely used in jewellery. The compositional variation of topaz, in term of minor and trace elements, depends on the geographic provenance. Some samples containing relatively high concentrations of chromophorous elements, such as chromium (Cr), manganese (Mn), iron (Fe) and few traces of light element like lithium (Li). Li is not a common element in topaz, and its presence in the mineral is usually in trace amounts. The amount of Li in topaz can vary depending on the geological setting in which the mineral was formed (Agangi et al. 2016). We analyzed by Laser Induced Breakdown Spectroscopy (LIBS) several samples colorless or very light blue from different source (Brazil, Madagascar and Tanzania) and unknown blue topaz deeply treated sample, comparing the results with those from other localities (Pakistan and Siberia) (Rossi et al., 2014; Abbasi et al. 2021). The analyses allow to find out the main emission lines of all the elements, except F and OH, also those in traces like Li not always found in other studies. This study could be useful in understanding the role of impurities in natural topaz and the capability of the LIBS for qualitative and quantitative analyses of gemstones.

Abbasi S.A., Rafique M., Khan T.M., Khan A., Ahmad N., Faruque M.R.I., Khandaker M.U., Ahmad P., Saboor A. (2021) - Chemical Analysis of Thermoluminescent Colorless Topaz Crystal Using Laser-Induced Breakdown Spectroscopy. *Minerals*, 11, 367.

Rossi M., Dell'Aglio M., De Giacomo A., Gaudiuso R., Senesi G.S., De Pascale O., Capitelli F., Nestola F. & Ghiara M.R. (2014) - Multi-methodological investigation of kunzite, hiddenite, alexandrite, elbaite and topaz, based on laser-induced breakdown spectroscopy and conventional analytical techniques for supporting mineralogical characterization. *Phys. Chem. Minerals*, 41, 127-140.

Agangi A. Gucsik A., Nishido H., Ninagawa K. & Kamenetsky V.S. (2016) - Relation between cathodoluminescence and trace-element distribution of magmatic topaz from the Ary-Bulak massif, Russia, *Mineralogical Magazine*, 80(5), 881-899.

## UV-Vis spectroscopy of gemstones: comparison between portable and laboratory instruments

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*Keywords:* UV-Vis spectroscopy, gemstones, portable and laboratory instruments.

The traceability and characterization of gemstones is getting increasingly important in the diamond, colored stone and pearl industries. The gemological studies have several stakeholders: i) consumers seek detailed information on the provenance and quality; ii) banking investors aim to reduce risks; iii) industries aspire greater transparency; iv) governments need higher control on supply chains. In this perspective, a combined approach of diverse analytical techniques (e.g. IR, UV-Vis, Raman spectroscopies, electron microscopy, X-ray fluorescence) is of paramount importance in providing robust gemological data. However, the coexistence of instruments differing for accessibility, cost, accuracy, and setup rises questions on the comparability of the obtained results.

This study, beside characterizing 15 gems by traditional gemological techniques, compared their UV-Vis spectra obtained by portable and laboratory instruments. Particularly, the capability was stressed of the two instruments in discriminating natural and synthetic gems, and detecting the presence of artificial treatments (flux healing and glass filling).

The portable instrument is a GL Gem Spectrometer™, which is designed for gemological samples. It is supported by the GLGemSpec software which contains a wide database of spectra. The employed laboratory instrument is a UV-Vis/NIR Spectrophotometer JASCO V-770, equipped with an integrating sphere. The instrument available for this work is designed for the analysis of liquids and solids (generally powders), with no predisposition for gemstones. To overcome this limit, the sample holder for powders was employed as follows: the gem was inserted with the table facing the inner quartz-glass window and then surrounded and packed by reagent-grade BaSO<sub>4</sub> powder. The pure BaSO<sub>4</sub> was employed for baseline correction. The results obtained with these two instruments were compared between each other and to the reference spectra available in the GLGemSpec database.

The response of the two instruments varied depending on the dimension, mineral species, and color intensity of the gemstones. Both instruments failed in identifying the flux healing and glass filling treatments to which two of the rubies had been subjected.

Overall, the portable spectrometer provided spectra more similar to those present in the database (which collects indeed spectra from portable instruments). The portable spectrometer appears useful for a primary and quick identification of gemstones. The major unsolved issues, linked to both instruments, are: 1) the ability to identify the presence of treatments; 2) the distinction between natural and synthetic gemstones; 3) the difficulty of examining a gem with a particularly pale color, or a particular cut or of small size.

## Mechanisms of crystallization inhibition of struvite-K by citric acid

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Keywords: struvite-K, citric acid, phosphates.

K- Struvite ( $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ ), is a component of the so-called infectious urinary (kidney) stones. Its precipitation occurs when the urinary tract is colonized by bacteria and may cause severe damage to the renal tissue (Mclean et al., 1988). It is also known to form scale deposits on pipe walls and equipment of the wastewater treatment industry (Mohajit et al., 1989). Moreover, the controlled crystallization is a sustainable and economical method for the recovery of phosphorus from wastewaters and from the ashes of biomass combustion (Gao et al., 2018), thus compensating the increasing demand for phosphorus and mitigating the exploitation of phosphate rock deposits.

In these different contexts there is interest in controlling/inhibiting crystal growth by acting on thermodynamic parameters or by exploiting additives. Between them, citric acid (CA) is of great interest also because of its biocompatibility. Compounds containing carboxyl groups have been already found to reduce crystal growth in struvite ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ), the isomorphic ammonia form.

In this work, the influence of citric acid in the spontaneous precipitation of struvite-K has been studied at room temperature and  $\text{pH} = 9$  under different conditions of energy of mixing and concentrations of the reactants. The additive increased induction time, reduced the apparent crystal growth rate and the amount of precipitate (up to 87 wt. %). Crystallization was observed to be controlled by the formation of Mg-citrate complexes in solution and by the adsorption of citric acid at the surfaces of the growing nuclei and crystal faces. This was confirmed by the decrease in the equilibrium concentration of additive in solution; by a more negative zeta potential of struvite-K (from  $-13.1 \pm 1.0$  to  $-16.2 \pm 0.4$  mV); by the changes in the O 1s and Mg 2p binding energy, measured with XPS. Hindered nucleation and crystal growth reduced crystal size, whereas supersaturation conditions and selective adsorption at crystal faces, in reason of their residual charge density, altered the crystal habit. The evidence is that citric acid strongly binds at (001) faces reducing crystal elongation, thereby reducing the aspect ratio.

Mclean R.J.C., Nickel J.C., Cheng K.J., Costerton J.W. & Banwell J.G. (1988) - The ecology and pathogenicity of urease-producing bacteria in the urinary tract. *Crit. Rev. Microbiol.*, 16, 37-79. <https://doi.org/10.3109/10408418809104467>.

Mohajit, Bhattarai K.K., Taiganides E.P. & Yap B.C. (1989) - Struvite deposits in pipes and aerators. *Biol. Wastes.*, 30, 133-147. [https://doi.org/10.1016/0269-7483\(89\)90067-0](https://doi.org/10.1016/0269-7483(89)90067-0).

Gao Y., Liang B., Chen H. & Yin P. (2018) - An experimental study on the recovery of potassium (K) and phosphorous (P) from synthetic urine by crystallization of magnesium potassium phosphate. *Chem. Eng. J.*, 337, 19-29. <https://doi.org/10.1016/j.cej.2017.12.077>.

Viani A., Zárbybnická L., Ševčík R., Mácová P., Machotová J. & Veltruská K. (2022) - Struvite-K crystal growth inhibition by citric acid: formation of complexes in solution and surface adsorption effects. *Journal of Crystal Growth*, 126858. <https://doi.org/10.1016/j.jcrysgro.2022.126858>.

## **Biotechnological evaluation of calcite biomineralization induced by the marine bacteria *Lysinibacillus sphaericus* PG22**

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**Keywords:** biomineralization, marine bacteria, calcium carbonate.

In the last decades, marine bacteria, due to their peculiar characteristics, have emerged as a source of potential biotechnological applications particularly for enzymes and natural products. However, they are still poorly exploited for bioremediation and biomineralization. Calcite biomineralization is among those activities of considerable interest. It is a natural process and, when performed by microbes, it is defined as Microbially Induced Calcite Precipitation (MICP). MICP is a biochemical process through which the microbial cell can secrete one or more metabolic products that react with ions (Ca<sup>2+</sup>) in the environment resulting in the subsequent precipitation of minerals (Rodriguez-Navarro et al., 2012). Many marine microorganisms can perform carbonate mineralization mainly by precipitation via urea hydrolysis and reverse hydration of CO<sub>2</sub> by carbonic anhydrase (CA) (Vincent et al., 2022).

In this study we investigate the MICP potential of a marine bacteria isolated offshore Rosignano Marittimo, Tuscany, Italy, characterised by carbonatic sediments and industrial discharges. The strain was named PG22 and growth experiments in the presence of i) only calcium chloride and ii) calcium chloride and urea, demonstrated the occurrence of a MICP process in the second experimental condition characterised by a consistent amount of mineral precipitates. This evidence was further validated by XRD analysis that confirmed CaCO<sub>3</sub> precipitation. The effect of pH, temperature and calcium/urea concentration was quantitatively evaluated for PG22 through Thermogravimetric Analysis (TGA).

PG22 biochemical characterization highlighted the presence of both urease and CA activities. Genome sequencing and annotation of strain PG22 revealed the presence of genes encoding for both urease and  $\beta$  &  $\gamma$  carbonic anhydrases confirming biochemical analyses. In addition, genes responsible for the resistance to some metals, such as Co, Zn, Cd, and As, were identified. Genome-based taxonomic identification revealed that PG22 belongs to the *Lysinibacillus sphaericus* species. Further investigations are evaluating the MICP potential of PG22.

It is known that MICP can produce a high quantity of calcite (CaCO<sub>3</sub>) in a short amount of time (Dhami et al., 2013) that could be easily employed as a smart nanomaterial in many industrial sectors, e.g., concrete, bio-cement, paper-making factories, etc. On the other side, the MICP via CA is also coupled with the removal of CO<sub>2</sub> from the environment (Mitchell et al., 2010). Finally, due to the natural tolerance of this strain for toxic metals, we are evaluating co-precipitation reactions in which suitable divalent metal cations (e.g., Pb<sup>2+</sup>) are incorporated into the carbonate mineral, substantiating *Lysinibacillus sphaericus* PG22 potential use in remediation.

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## **S24.**

### **Asbestos and hazardous dust in geomaterials in the frame of European green economy: new strategies for monitoring, treatment, and reuse in view of exposure assessment**

#### *CONVENERS AND CHAIRPERSONS*

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## **Respirable crystalline silica and feldspar particles in respiratory apparatus of equines in riding arenas: a diffuse and non-conventional exposure for animals and humans**

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*Keywords:* respirable crystalline silica and respirable feldspar particles, soil, air, respiratory system investigation.

Soils used in equine riding arenas, commonly described as riding surfaces, are a mixture of several natural sandy rocks frequently enriched with organic additives.

According to commercial information, the most common and abundant minerals composing these soils are quartz, feldspars, and some types of phyllosilicates.

Respirable crystalline silica (RCS), i.e. < 4 µm quartz grains and other silica polymorphs, are classified as carcinogens of IARC group 1. The literature presents few studies on the potential toxicity of respirable feldspar particles (RFP). It may be similar or greater than quartz and different feldspars correlate with different toxicities and pro-inflammatory effects (Grytting et al., 2022).

Therefore, the presence of quartz and feldspars in equine riding surfaces could be a risk factor for health problems in humans working closely with these animals because mineral particles result from the continuous crushing of the soil and consequent air dispersion of dust caused by the trampling of horses during work in the field. Since horses themselves can suffer from pneumoconiosis, they are considered sentinel animals. Moreover, the hypothesis that horse riding represents an unconventional occupational exposure to RCS and RFP is likely.

The present study investigates the presence of minerals and inorganic particles present in soils and air in equine riding arenas and equine bronchoalveolar lavage samples. The investigations were carried out by SEM-EDXS, TEM-EDXS, XRPD, and cytopathological analyses (accordingly to the type of sample).

The result highlights the abundant presence of RCS and RFP in soils, air, and equines respiratory system in different riding arenas.

The present study provides a way to characterize the exposure of horses to RCS and RFP and highlights the problem relating to a potential increased exposure risk for equestrian workers and people attending riding arenas.

Grytting V.S., Refsnes M., Låg M., Erichsen E., Røhr T.S., Snilsberg B., White R.A. & Øvrevik J. - The importance of mineralogical composition for the cytotoxic and pro-inflammatory effects of mineral dust. *Particle and Fibre Toxicology*, 19(1), 1-22. <https://doi.org/10.1186/s12989-022-00486-7>.



## Natural occurrence of asbestiform minerals (NOA) in the Timpone Seluci metabasites (Pollino Massif, southern Italy)

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*Keywords:* asbestiform minerals, NOA, Pollino Massif.

Worldwide studies have been done about the toxicity and carcinogenicity of asbestos minerals occurring in different kind of rocks. It is well known that inhalation of asbestos could cause health problems such as malignant mesothelioma and lung cancers in particular when they occur in the nearby of residential areas. The main constituent of the asbestos minerals in metabasites is actinolite with the presence of further minerals not regulated by the directive 2003/18/EC of the European Parliament and the European council of the 27 March 2003 such as glaucophane. The aim of this work is the petrographic and mineralogical characterization of metabasites of the Frido Unit of the Liguride complex in the southern Apennines, which were found and sampled near Timpone Seluci (Lauria, PZ). Macroscopically, the metabasites have a massive structure and show dark green to blue colours; in outcrops they have been found in large, irregular bodies. Petrography was performed with optical microscopy (OM) and Scanning Electron Microscope (SEM) while bulk mineralogical composition was assessed by using X-Ray Powder Diffraction analysis (XRPD). The studied rocks show a heteroblastic structure, characterized by the presence, as main minerals, of plagioclase, quartz, clinopyroxene, blue amphibole, green amphibole, lawsonite, epidote, pumpellyite while accessory minerals are apatite, opaque minerals and rutile. Regarding secondary minerals, chlorite and sericite were also detected. Actinolite shows acicular and fibrous habitus and is from colourless to pale green. Petrographic features show that metabasites have undergone a metamorphic history characterised by high-pressure conditions, as evidenced by the presence of glaucophane and lawsonite, attributed to Alpine metamorphism. The metabasites were subsequently affected by a retrograde event under greenschist facies, evidenced by the presence of albite, chlorite and actinolite. XRPD and SEM analysis confirmed the presence of some of the main mineralogical phases observed in the petrographic study.

## Asbestos burden in lungs of women from Broni (Pavia, Italy): a postmortem sem-eds study

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Keywords: asbestos, malignant mesothelioma, SEM-EDS.

In Italy the incidence of Malignant mesothelioma (MM) among women is remarkably high, due to the several contexts in which women had been exposed to asbestos. However, very few studies in literature focus on the inorganic lung content in women.

The aim of this study is to characterize the asbestos burden in lungs, in terms of concentration, dimensions and type of asbestos, in 42 women who died from MM and had been exposed to asbestos (anthropogenic environmental exposure and household exposure) during the activity of the asbestos-cement plant located in Broni, (Pavia, Northern Italy) where mainly chrysotile, crocidolite and amosite were used.

Also the concentration of inorganic fibers (other than asbestos) in line with the “regulated fiber definition” (length  $\geq 5 \mu\text{m}$ , width  $\leq 3 \mu\text{m}$ , aspect ratio greater than or equal to 3:1 (WHO, 2000), fibers shorter than  $5 \mu\text{m}$  (classified separately as short fibers), and asbestos bodies were considered.

Autoptic lung samples have been investigated by SEM-EDS.

No asbestos has been detected in six lung samples. Overall, the most represented kind of asbestos was amosite, followed by crocidolite, tremolite/actinolite asbestos and chrysotile.

The concentration of all inorganic fibers was significantly higher in women with anthropogenic environmental and household exposures compared with those with only anthropogenic environmental exposure ( $p = 0.025$ ), as well as the concentration of asbestos fibers ( $p = 0.019$ ) and asbestos bodies ( $p = 0.049$ ).

We found a significant correlation between the concentration of asbestos fibers and the duration of exposure ( $p = 0.008$ ), as well as with the latency of MM ( $p = 0.005$ ).

The distance of the residential address from the factory and the time spent daily in contact with asbestos did not influence the lung asbestos burden.

Our data confirm the relevance of non-occupational exposure in determining asbestos concentration in lungs and highlight the importance of household exposure.

Given the absence of asbestos in some samples taken from subjects who were certainly exposed and the very scarce representation of chrysotile, in a context where it was largely used, we can conclude that, although SEM-EDS is considered the most reliable tool for assessing previous exposure to asbestos, its results should be interpreted with caution, especially in a legal context.

WHO Regional Office for Europe (2000) - Air quality guidelines for Europe.

## **Cristobalite dusts: on the hazard connected to exposure to such particulate**

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*Keywords:* cristobalite, spectroscopy, health effects.

The long-lasting investigation on the health effects due to exposure of crystalline silica respirable dusts has determined a huge improvement in the knowledge of the specific features able to determine these effects as a variable entity. The molecular and mechanistic foundations of the crystalline silica toxicity have been explored both under controlled laboratory conditions and directly in occupational settings, so as to allow close comparisons between model and actual exposure conditions.

By far, this research has been focused on quartz, the most abundant and ubiquitous silica polymorph (even in the occupational context) while only side research has been carried out on cristobalite, the other natural polymorph having distinctive economic interest. In the past, scientific research focussed mainly on the occupational settings connected with the process of calcination of diatomaceous earth.

This study provides a state-of-the-art review on the mineralogical, physical and chemical characteristics of the cristobalite dusts in some occupational settings, selected on the basis of recently traced epidemiological clusters of silica-related diseases. The aim of this work is the comparison of the results from experimental studies carried out in different contexts where cristobalite is used as raw or byproduct material in industrial production processes. Four different case studies (gold micro-casting, raw materials for artificial stone production, stone workshops, dental alginates production) were investigated by means of in-depth XRD, SEM, TEM, and spectroscopic investigations, evidencing both relevant specificity for each production process and some common features among these different occupational settings. The results suggest that also the toxicological effects of cristobalite should be sought in the organisation of the surface structural terminations (i.e. the nearly free silanols that act as toxicological primer for quartz), in close relationship with the diffused structural defectivity observed in all industrially produced/modified cristobalite materials.

## An insight to the Fenton reaction of amphibole asbestos

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Keywords: asbestos, fibres, HO radicals.

In this work the ability of amphibole asbestos (UICC crocidolite, UICC amosite, and tremolite) to generate HO radicals by Fenton reaction over time (i.e., catalytic activity) was investigated. The amount of HO radicals was measured by Electron Paramagnetic Resonance (EPR), during sample incubation, up to 15 days, in a buffered solution at pH 7.4 and in presence of H<sub>2</sub>O<sub>2</sub>. Moreover, the radical production of each sample was investigated on fibres pre-leached in a mimicked Gamble's solution (MGS) at pH 4.5, and on thermally treated fibres to highlight possible correlations among fibre surface chemical composition, surface Fe oxidation state and chemical reactivity. Surface chemical modifications of the samples were monitored by X-ray Photoelectron Spectroscopy (XPS).

Results showed no differences in the HO• radical generation between pristine and MGS pre-incubated fibres for all amphibole asbestos. However, the catalytic activity of the samples resulted markedly different, increasing over time for crocidolite fibres, decreasing for asbestos tremolite and being constant for amosite. The modulation of the catalytic activity was possibly related to the fibre dissolution kinetics during interaction with H<sub>2</sub>O<sub>2</sub>. In particular, the enhanced radical production of crocidolite may be due to its faster dissolution with respect to the other amphibole asbestos, leading to the occurrence of new Fe(II) centres on the surface from the bulk, as indicated by XPS analysis. It must be pointed out that the observed increase in radical production was not simultaneous with that of surface Fe(II). This may indicate that the HO radicals generated are not only a function of the total surface Fe(II) centres and that some low-coordinated ions may yield radical generation. The thermally oxidised samples showed a reduced chemical reactivity. Besides, catalytic activity of pristine tremolite fibres converges towards that of the oxidized sample suggesting that no new Fe centres are exposed from the bulk to the surface during fibre interaction with H<sub>2</sub>O<sub>2</sub>.

## Identification and quantification of Ni occurrence in serpentinites from the Valmalenco mining area (Sondrio, Central Alps, Northern Italy)

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Keywords: nickel, hazardous minerals, electron microscopy.

Valmalenco is an important mining area in Sondrio (Central Alps, Italy) with serpentinites occurring as schistose (or “slaty”, “Serpentinoscisto”) and massive (“Serpentino Massiccio”) varieties. Serpentine is a *green stone* composed mainly of one or more serpentine group minerals (namely antigorite, lizardite, and chrysotile, with ideal chemical formula  $Mg_3(OH)_4Si_2O_5$ ). Common phases in Valmalenco serpentinites are antigorite, olivine, clinopyroxene, chlorite, magnetite, minor chromite, Fe–Ni alloys, Fe–Ni sulphides, and Ti-clinohumite, together with other accessory minerals.

Generally, serpentinites has always been used as building stone worldwide. Unfortunately, there are three main environmental issues related to their mining and processing (e.g. Cavallo, 2022): i) the associated presence of NOA (naturally occurring asbestos); ii) the production and management of huge mining tailings; iii) the presence of Ni, Cr, Co, and other metals (up to 2000 mgkg<sup>-1</sup> in soils) in both serpentinite products and quarry/mine tailings that can be released into the environment with potential health risk (Shaheen et al., 2022). Focusing on the latter, quantification of Ni content and its assignment to mineral phases is necessary to assess its toxicity and carcinogenicity potential, as required by the current national regulations. It is important, e.g., to assess and quantify the presence of bunsenite, NiO, and liebenbergite, Ni<sub>2</sub>SiO<sub>4</sub>, two regulated and known carcinogen.

In this work, we devised an analytical protocol for the qualitative and quantitative determination of Ni in serpentinites using a suite of experimental techniques, i.e. X-ray powder diffraction, electron microscopy, thermogravimetric analysis coupled with evolved gasses determination, electron probe micro-analyser, and spectroscopies. More specifically, this study focused on the Italian Valmalenco “massive” serpentinite, from quarries of “Verde Vittoria” and “Verde Giada” as case studies. Besides the paramount importance of the toxicity and carcinogenicity potential assessment in classifying the hazardous waste, our results will help to elucidate metal uptake mechanisms used by plants growing on serpentinitic substrates, by identifying the bioavailability of the Ni species (e.g., Amin et al., 2023).

Results from combined XRD, SEM, and EPMA revealed the presence of several Ni phases, i.e. pentlandite, awaruite, and heazlewoodite. The Ni contribution of these phases in the sample is in the order of 500-1000 mgkg<sup>-1</sup>. More interestingly, a widespread distribution of Ni traces was found in the rock-forming minerals, namely antigorite, olivine, and pyroxenes. The contribution of these phases, due to their high weight fractions in the sample, is about 1000 mgkg<sup>-1</sup> of Ni. These results are in the same order of magnitude of those reported in the previous literature from ICP measurements on bulk serpentinites from the same mining district. It is noteworthy that no bunsenite, nor liebenbergite were detected.

Amin M.A., Haider G., Rizwan M., Schofield H.K., Qayyum M.F., Zia-ur-Rehman M. & Ali S. (2023) - Different feedstocks of biochar affected the bioavailability and uptake of heavy metals by wheat (*Triticum aestivum* L.) plants grown in metal contaminated soil. *Environmental Research*, 217, 114845. <https://doi.org/10.1016/j.envres.2022.114845>.

Cavallo A. (2022) - “Serpentino della Valmalenco” (Central Alps, Northern Italy): A green dimension stone with outstanding properties. *Res. Policy*, 75, 102467. <https://doi.org/10.1016/j.resourpol.2021.102467>.

Shaheen S.M., Chen H.Y., Song H., Rinklebe J. & Hseu Z.Y. (2022) - Release and mobilization of Ni, Co, and Cr under dynamic redox changes in a geogenic contaminated soil: Assessing the potential risk in serpentine paddy environments. *Science of The Total Environment*, 850, 158087. <https://doi.org/10.1016/j.scitotenv.2022.158087>.

## **A cliff-beach characterization of asbestos cement material discovered in coastal zone of Marechiaro Bay (TA)**

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*Keywords:* asbestos, coastal zones.

Asbestos is a generic term referring to different types of naturally mineral fibers (Virta, 2002). Great sound and heat insulation, robustness, cheapness, fireproofing, highly resistant to water, electricity and chemicals are few of the several properties which make asbestos unique for building materials. Due to these properties, the use of asbestos in construction grew from the 1930s until the end of the 1980s, leading to the construction of several factories in Italy and making it an almost ubiquitous material. Soon after the approval of the L. 257 (1992), the costs of disposing of asbestos-containing materials (ACM) rose rapidly and, also due to the lack of adequate state financial intervention, huge amounts of ACM were illegally dumped. In particular, in Italy coastal zones were found several dumping sites of asbestos constructions and demolition wastes. In this study, an extensive coastal cliff area (Marechiaro bay, Mar Grande, Taranto, southern Italy) consisting of remains from the demolition of buildings (including ACM) is described. The relationships between the erosional processes of the cliff, the alongshore transport and the rapid formation of a sandy beach consisting mainly of man-made materials, are described in detail. An interdisciplinary approach (remote sensing, sedimentological, stratigraphic, mineralogical and geophysical analysis) was used for this purpose. Although it is well known the presence (not only in Italy) of numerous coastal sites with environmental problems very similar to those of the Bay of Marechiaro, this study is the first example of in-depth analysis in this field.

Virta R. (2002) - Encyclopedia of chemical technology. Kirk-Othmer, pp. 319. <https://doi.org/10.1002/0471238961.0119020510151209.a01.pub3>.



## From Field Analysis to Nanostructural Investigation: A Multidisciplinary Approach to Describe Natural Occurrence of Asbestos in View of Hazard Assessment

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Keywords: fibrous antigorite, hazard assessment, NOA hazard.

The environmental impact of natural occurrences of asbestos (NOA) and asbestos-like minerals is a growing concern for environmental protection agencies. The lack of shared sampling and analytical procedures hinders effectively addressing this issue. The definition of a common approach to investigate the hazard posed by NOA must take advantage of a multidisciplinary approach that encompasses geology, mineralogy, chemistry, and toxicology. The applicability of a highly adaptive approach is demonstrated here on a natural occurrence of antigorite from a site in Val Varena, Italy. Antigorite is, together with chrysotile asbestos, one of the serpentine mineral polymorphs and it is an excellent candidate for investigating the asbestos-like properties of minerals as its toxicological profile is still under debate. The present study reports the detailed mineralo-chemical characterization of a fibrous antigorite sample coming from a serpentinite body by means of a set of multi-analytical approaches. SEM images confirmed the elongated fibrous habit (asbestos-like) of the antigorite sample, it was supported by TEM observation which revealed prismatic to fibrous antigorite crystals. XRPD indicated that the prevailing superstructure periodicity corresponds to  $m = 17$  antigorite polysome.

The chemical formula was obtained by integrating EMPA data with Mossbauer spectroscopy data, resulting in  $(\text{Mg}_{2.622}\text{Fe}^{2+}_{0.083}\text{Fe}^{3+}_{0.037}\text{Al}_{0.047}\text{Mn}_{0.006})_{\Sigma=2.795}(\text{Si}_{1.973}\text{Al}_{0.027})_{\Sigma=2.000}\text{O}_{5.000}(\text{OH})_{3.647}$ . The formula was normalized based on 8.647 oxygen atoms (Kunze, 1961).

Moreover, an advanced study of the dissolution kinetics was carried out by incubation at 37°C in a modified Gamble's solution (MGS, pH = 4.5) up to 1 week. Results of ICP-OES analyses, following the antigorite sample incubation, show that the release of Mg, Si, and Al progressively increases with sample incubation time. In the first stage of dissolution, a preferential release of Mg with respect to Si is observed, in agreement with Madelung site energy (Schott et al., 1981). Moreover, for longer incubation times a nearly congruent dissolution takes place. Through spin trapping technique associated with Electron Paramagnetic Resonance (EPR) was observed that antigorite was reactive in both carboxyl and hydroxyl radical generation. Moreover, the potency of antigorite to catalyse  $\cdot\text{OH}$  slightly increased with incubation in MGS, from 0 (pristine) to 168 h. This may be due to the fibre leaching promoting coordinative unsaturation of the surface Fe centres as proposed in previous work on amphibole surface reactivity (Andreozzi et al., 2017). The congruent and low solubility in an acidic simulated body fluid, together with the toxicity-relevant surface reactivity signalled a possible bio-activity similar or even greater to that of the chrysotile asbestos. Overall, the NOA site was reported to contain veins of asbestos-like antigorite and should be regarded as source of potentially toxic fibres during hazard assessment procedure.

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## PRIN 2017 Fibres - A Multidisciplinary Mineralogical, Crystal-Chemical and Biological Project. What have we learned after four years of research?

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Keywords: mineral fibres, asbestos, toxicity.

This contribution discusses the major results accomplished within the multidisciplinary project PRIN (PROGETTI DI RICERCA DI RILEVANTE INTERESSE NAZIONALE) 2017 "FIBRES: a multidisciplinary mineralogical, crystal-chemical and biological project to amend the paradigm of toxicity and cancerogenicity of mineral fibres" by the six different Research Units of the Universities of Ancona, Genova, Modena, Rome, Pisa-Parma, and Urbino. The general goal of the project was to increase the knowledge of the mechanisms by which mineral fibres (Ballirano et al., 2017; Gualtieri, 2017), with special attention to asbestos and fibrous erionite, prompt adverse effects *in vivo*, linking the fibres' crystal-chemical-physical parameters to their toxicity/carcinogenicity potential and recasting the existing mechanistic 'fibre toxicity paradigms' (Gualtieri, 2018). The findings of the project have implications that are beyond the advance of the knowledge in the world of mineralogy/crystallography and constitute a significant progress in the understanding of the biological activity of mineral fibres *in vivo* (Gualtieri, 2023) with impact on health, social, economic and legal issues.

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## Natural Asbestos fibers in decorative plasters used for artificial stones in Rationalist Architecture in Rural Villages between the XIX and XX centuries

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*Keywords:* natural asbestos fibers, artificial stone, petro-morphological characterization.

The use of artificial stone was particularly widespread at the end of the 19<sup>th</sup> century, following the discovery of Portland cement in Great Britain, when it was widely used as a structural building material, masonry material and decorative architectural element. To avoid the grey and dull appearance of cement, craftsmen began to manipulate mortar mixtures by adding mineral particles and pigments to create a material that resembled a particular natural stone. This imitation stone could be used as a layer of plaster on facades or as bricks in walls and were developed to replace more expensive quarried natural stones such as marble, sandstone and limestone when these were not available locally (Pecchioni et al., 2005). Asbestos is a general commercial-industrial term used to describe a group of naturally occurring silicate minerals of fibrous or asbestiform habit with exceptional properties (high tensile strength, flexibility, chemical and heat resistance). Asbestos minerals are generally present in ophiolitic rocks, and used as aggregates for road construction, railway ballast, concrete and other applications. These minerals are particularly hazardous to public health because fibres can be released into the air during the degradation of aggregates in service and inhaled into the lungs, causing serious health problems (Punturo et al., 2019).

The main purpose of this work was to characterise the building materials used in a historic building in Codigoro, a small town near Ferrara in north-east Italy. This building was constructed according to the Italian Rationalist rules for monumental architecture and is an example of Rationalist architecture found in rural villages, using innovative materials and decorations, including artificial stone. Petrographic, mineralogical and chemical characterisation of samples of artificial stone and concrete were carried out using transmitted light optical microscopy, scanning electron microscopy - energy dispersive spectroscopy and X-ray diffraction analyses. The results revealed chemical and biological degradation in almost all the artificial stones studied and allowed the identification of the presence of calcite, iron oxychloride complexes and asbestos lizardites used as fillers in two of the samples analysed. In addition, asbestiform habit minerals were observed in the fillers of some of these materials.

The aim of this study was to describe a general investigation methodology used to study the artificial stone facades of the Ex Casa del Fascio of Codigoro, whose architecture is particularly representative of rationalist architecture in rural villages. The results highlight the relevance of compatible and appropriate conservation measures that should be monitored during all restoration interventions in order to minimise fragmentation and transformation into elements harmful to human health and the environment after degradation. (Marrocchino et al., 2020).

Marrocchino E., Lattao V., Eftekhari N., Conte A.M., Franceschini S., Pepi S., Rizzo M. & Vaccaro C. (2020) - Rationalist architecture in rural villages: petro-morphological characterization of natural asbestos fibers in decorative plasters used for artificial stones. *Episodes*, 43, 893-908. <https://doi.org/10.18814/epiiugs/2020/0200s08>.

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## Identification of asbestiform mineral particles and cleavage fragments in the lung: regulated and unregulated amphiboles

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*Keywords:* cleavage fragment, asbestos, lung.

Identification of asbestiform mineral particles and cleavage fragments in the lung: regulated and unregulated amphiboles.

The CoFePMAi feasibility study, funded by ANSES, aimed to determine whether it is possible to detect exposures to elongated mineral particles of interest including non-asbestiform cleavage fragment (EMPi) in workers from the mining, quarrying, construction and public works sectors, as well as farmers, based on biometrology results on lung samples. Significant retentions of non-asbestiform EMPi or ferruginous bodies formed on cleavage fragments for workers with respiratory diseases may be an indication of the potential health hazard of these particles.

In this study, a group of 20 subjects with bronchopulmonary cancer and 5 subjects with other lung diseases were selected. All subjects had worked in one of the sectors mentioned above and had a concentration of asbestos bodies detected by optical microscopy greater than 1000 AB/g of dry lung.

An analysis protocol was developed using the biometrology preparation method of LAFP and the methods of Durmortier & De Vuyst (1988) and Dodson et al. (1983). This protocol allows differentiation between fibers from asbestiform minerals and those from cleavage fragments, with precise mineralogical identification of EMPi. The filter on which the particles are collected undergoes treatment with oxalic acid at 50°C to partially dissolve the ferroprotein coating that surrounds the EMPi, in order to release particle sections large enough for chemical analysis, quantitative electron diffraction, and visual observations during analytical Transmission Electron Microscope analysis. The visual observations, combined with a new flowchart, allowed the characterization of cleavage fragments and particles from asbestiform minerals. The flowchart was tested on 100 particles by five analysts after being trained in its use, and validation was based on the Cohen Kappa statistical test, which showed substantial agreement between participants.

44 asbestos bodies (AB) of amosite, 3 AB of crocidolite, 1 AB of ferro-actinolite, and 6 non-asbestiform ferruginous bodies of grunerite were detected and characterized. In this feasibility study, interest was also focused on all amphibole particles present: coated or uncoated, from cleavage fragments or asbestiform minerals, and regulated or unregulated. 376 amphibole particles were detected in total. In each family of amphibole (amosite/grunerite, crocidolite/riebeckite, tremolite, anthophyllite, actinolite, ferroactinolite, edenite, magnesio-hornblende, magnesio-ferri-hornblende), cleavage fragments were detected with a total of 123 fragments for 250 particles from asbestiform minerals, with only 3 particles unable to be determined.

The method should be continued for patients with respiratory pathologies who are typically exposed to non-asbestiform PMAi in order to characterize the nature of ferruginous bodies.

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## **Mineralogical and petrographic characterization of fibrous amphiboles in the blueschists of the Diamante-Terranova Unit (Calabrian-Peloritan Orogen, southern Italy)**

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*Keywords:* blueschists, Diamante-Terranova Unit, fibrous amphiboles.

Since the Neolithic to the Middle Ages and in modern times, blueschists were used for numerous purposes mainly as ornamental stone and as building stone for construction. In northern Calabria, the blueschists belonging to the Diamante-Terranova Unit are well exposed along the Diamante beach. Mineralogical and petrographic analyses by Optical Microscopy, Scanning Electron Microscopy and X-Ray Powder Diffraction show that the blueschists with HP-LT index mineral assemblage recorded metamorphic events in blueschists facies in the Diamante-Terranova Unit represented by glaucophane + epidote + lawsonite + white mica, while that one referring to of greenschists facies metamorphism is given by chlorite + albite + quartz + colourless amphibole (actinolite). The latter would represent an overprint under greenschist facies conditions, in which a decrease in the physical conditions of temperature and pressure (depth) is recorded during the metamorphic process. The geochemical data obtained by X-Ray Fluorescence indicate that the blueschists of the Diamante-Terranova Unit derive from basic rocks and in particular from basalts s.l. with a composition compatible with that one of tholeiitic basalts and show an affinity with mid-oceanic ridge basalt (MORB); therefore, they formed in correspondence with the oceanic ridges. Results show that all of the samples belonging to blueschist facies contain either sodium- rich fibrous amphibole and calcium- rich fibrous amphibole with fibrous habit and/or prismatic, acicular crystals in aggregates. This work focuses on the mineralogical and petrographic characterization of Magnesio-riebeckite and of actinolite mineral phases in order to improve the knowledge of these minerals in the studied area, and to contribute to information for reconstructing the geological and tectonic history; at the same time, results have environmental implications because it is well known that the release of fibres into the environment is dangerous for human health.



## From hazard to pioneering georesource: exploring the new role of asbestos and potentially harmful minerals in the 21st century

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*Keywords:* asbestos containing materials, secondary raw materials, sustainable solutions.

As it is known, it has been widely assessed that asbestos minerals (regulated and not) present in geological matrices represent a cause of danger to health (IARC, 1987), as they are potential environmental pollutants. As far as European Union, Asbestos is considered a highly dangerous, cancer- and malignant mesothelioma-causing substance (Alpert, 2020) that is still present in many of buildings and is responsible for many avoidable deaths in the EU (<https://www.eea.europa.eu/publications/environmental-burden-of-cancer/asbestos>). Although today All use of asbestos has been banned in the EU since 2005, and several Member States such as Italy had adopted asbestos bans well before then, the environmental or occupational exposure of the population to Asbestos Containing Materials (ACM) represents an environmental problem that is still unresolved. In addition to natural occurrences (i.e. geological outcrops), human activities such as agriculture, excavation, and/or building restoration can accelerate/trigger the processes of release of fibrous minerals into the environment and expose workers and citizens to risks (e.g. Bellomo et al., 2018; Marrocchino et al., 2020). Now-a-day, ACM and Asbestos-containing wastes (ACW) represent a global concern considering the accumulation of millions of tons of products encountered in building, boat and road applications. ACW are typically stored in landfill resulting in unsustainable land use and maintaining the toxicity of waste. In this context, the knowledge related to the minero-petrographic, petrophysical and geochemical aspects related to the presence of asbestos and asbestiform minerals in geomaterials is of paramount importance, and “classical” investigation techniques may be integrated by newer ones in order to constitute a starting substrate based on detailed knowledge, that move towards the European targets such as launching a study to identify asbestos waste management practices and new treatment technologies. Indeed, With Europe’s climate change targets, 35 million buildings are expected to be renovated by 2030, and many workers risk being exposed to asbestos ([https://www.europarl.europa.eu/doceo/document/TA-9-2021-0427\\_EN.html](https://www.europarl.europa.eu/doceo/document/TA-9-2021-0427_EN.html)). Finally, our contribution explores innovative solutions and technologies that may permit asbestos, after proper treatment, to be considered in a new light, ie from a neglected geomaterial to a precious resource of metals and minerals of industrial interest.

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IARC (1987) - <https://incem.org/documents/iarc/suppl7/asbestos.html>.

Marrocchino E., Lattaò V., Eftekhari N., Conte A.M., Franceschini S., Pepi S. & Vaccaro C. (2020) - Rationalist architecture in rural villages: petro-morphological characterization of natural asbestos fibers in decorative plasters used for artificial stones. *Episodes Journal of International Geoscience*, 43(3), 893-908.



## Namibia Marbles: Insights about occurrences of tremolite exhibiting various habits

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Keywords: Namibia Marbles, asbestos tremolite, health issues.

This contribution reports the results of a multi-analytical investigation, which was carried out on White Rhino Marbles exploited in the Karibib area (Namibia) and marketed in several countries as dimension stone.

The study focused on fabric-related and microstructural features of marbles, in order to highlight the occurrence and for imaging the geometry of the mineralogical assemblage, with particular regard to amphibole minerals present in the yellow nematoblastic levels that cross-cut the rock. From the petrological viewpoint, the Neoproterozoic White Rhino Marbles are characterized by a mineralogical assemblage testifying the absence of any terrigenous fraction in their protolith, since the paragenesis is given by calcite + tremolite ± dolomite. Calcite and minor dolomite grains, which are the constituent of the granoblastic levels, are the most abundant portions of the marble rocks exploited. No secondary minerals formed at expenses of primary minerals have been observed, proving that no weathering process has been affecting the studied marbles (Punturo et al., 2019).

Likely, during the metamorphic event, the high-silica (e.g., diatomaceous) levels reacted with the Mg-rich carbonates, giving rise to amphibole tremolite  $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ .

The detailed microstructural and morphological analyses carried out with optical microscopy, Scanning Electron Microscopy and Synchrotron radiation X-ray computed microtomography (Punturo et al., 2020) highlighted that, despite non-asbestos tremolite exhibiting acicular habitus is the most common mineral phase that was found, it is worth noting that asbestos tremolite fibers were also detected.

Indeed, new investigation highlighted that tremolite fibers, resembling the asbestiform habitus (WHO, 1986), occurred as fibrous aggregates with radial arrangement, prone to split into thinner fibers and ultimately into fibrils, often formed after cleavage fragments. Despite its occurring habitus, tremolite appeared as straight and stiff crystals (i.e., needles and fibers). Moreover, 3D imaging also showed the tight interlock between the nematoblastic microdomains (i.e., tremolite-rich) and the granoblastic portions (i.e., carbonate-rich) and their contact geometry.

Within this frame, the asbestos hazard related to the occurrence of fibrous tremolite veins that cross-cut the studied marbles arises when either natural weathering processes and human activities such as exploitation of dimension blocks and subsequent use as building stones may trigger fibers dispersion into the environment as breathable airborne. Therefore, from the one hand it is necessary that mining companies adopt monitoring surveys, in situ tests, as well as safety measures for workers and prevention practices (Bellomo et al., 2018); from the other hand, under the non-occupational point of view, it is important to assess the extent of exposure to those airborne particles, whose morphology may resemble asbestos, for population who live close to the quarry as well as to family members of workers.

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## Serpentinization and chrysotile vein development: some remarks about the metamorphic process and health issues

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*Keywords:* serpentinization, chrysotile veins, ophiolite units, Calabria (Italy).

As it is known, serpentinites are water-rich metamorphic rocks that are produced by low-grade metamorphism or hydrothermal alteration of ultramafic igneous rocks. The serpentinization of ultramafic rocks, whose hydration causes olivine and pyroxenes to be transformed into serpentine, is a widespread process, present in most ophiolite massifs and belts (Guillot & Hattori, 2013).

The serpentinization reactions that take place are controlled by the transport of fluid, which itself depends on volume change during the reaction. Element transfer can strongly modify the magnitude and sign of volume change. Unfortunately, one of the three serpentine polymorphs and the main one retrieved within the veins formed and developed within serpentinization is chrysotile, which crystallizes with a fibrous shape, and for this reason, it has been classified by the International Agency for Research on Cancer (IARC, 1987) as being carcinogenic to humans (Group 1) and many countries have banned its use.

This presentation aims to contribute to the knowledge of the serpentinization process, which partially or totally alters the physical, mechanical, and chemical properties of ultramafic protoliths, which can therefore exhibit various microstructural features associated with abundant veining development, and various generations of veins filled with serpentine minerals (Bloise et al., 2019). To this aim, we have focused on a serpentinite vein network filled with fibrous chrysotile, which forms during the serpentinization process which has been observed within the serpentinite rocks of the Mount Reventino-Gimigliano Ophiolite Units; these were previously characterized under the geochemical, petrographic and mineralogical viewpoints (e.g. Punturo et al., 2015). Our investigation included the geometrical features of the veins such as volume fraction, size, and orientation as well as the distribution of chemical composition in veins and matrix (Bloise et al., 2019; 2020).

Finally, by considering: a) the health concerns related to Natural Occurrences of Asbestos within ophiolite rocks, and b) the use of serpentinite rocks as dimension stones for Cultural Heritage, our approach can be successfully used for conducting detailed research on NOA-related minerals and their release into the environment after breakage and weathering of host ophiolite rocks, shedding new light on a serious health threat to the population who live in ophiolite-defined geological contexts.

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## Assessment of Naturally Occurring Asbestos in dismissed quarries: State of the Art and new perspectives for sustainable solutions

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*Keywords:* asbestos minerals, dismissed quarries, Southern Italy.

As established by the International Agency for Research on Cancer (IARC) in 2012, asbestos is a carcinogen substance, and the effect resulting from exposure to asbestos fibers that lead to the development of malignant mesothelioma, lung cancer, or asbestosis are well-documented. For this reason, the environmental exposure to Naturally Occurring Asbestos (NOA) as a component of source rock and derived soils poses a potential health risk to the population living close to NOA-bearing outcrops. Such exposure may be due to weathering, erosion, landslide, or human activities such as mining and construction, which can potentially release dust containing asbestos fibers. The presence of NOA is widespread in rocks, sediments, and soils all around the world from the United States (e.g., California), to Australia (e.g., New South Wales), to Europe (e.g., France – the Armorican Massif, the Central Massif, the Western Alps, the Pyrenees, and Corsica; Italy – the Alps and Apennine ridge). In southern Italy (i.e., Basilicata, Calabria, and Sicily) asbestos minerals from ophiolite outcrops (e.g. Bloise et al., 2020 and references therein) as well as from volcanic context (e.g. Pinizzotto et al., 2018 and references therein) have been studied using different analytical methods such as Scanning Electron Microscope (SEM), X-ray Powder Diffraction (XRPD), micro X-ray Fluorescence ( $\mu$ -XRF) and Inductively Coupled Plasma mass spectrometry (ICP-MS), to perform morphological observations, mineral-chemical characterization and to derive concentrations in terms of major, minor, and trace elements with the aim of evaluating how the Potentially Toxic Elements (i.e., Fe, Cr, Ni, Zn, Mn, Co and Rare Earth Elements) contribute to asbestos-related diseases. With this contribution, we point out the advantages and disadvantages of the techniques adopted to date for assessing the presence of NOA in dismissed quarries, opening new perspectives on sustainable solutions that can be implemented to mitigate potential exposure risk to asbestos fibers and exploring possible new perspectives in considering asbestos waste as a possible georesource.

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## **Serpentinites of the Pollino ophiolite massif (Southern Italy) as a sink for atmospheric CO<sub>2</sub>: Asbestos evolving from a health risk to an Earth resource to trap greenhouse gas**

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*Keywords:* serpentinite, carbonation for CO<sub>2</sub> sequestration, Pollino Massif.

Serpentinized peridotites are an important component of oceanic basement. During regional metamorphism, peridotites become readily serpentinized over a wide range of P-T-fluid conditions, and serpentinites are important as a sink for water, carbon, sulfur, chlorine, boron, arsenic, and nitrogen. This study focuses on the serpentinites of the Frido Unit in the Liguride Complex of the Pollino Massif (southern Apennines, Italy), derived from lherzolitic protoliths and formed under high pressure/low temperature (HP/LT), blueschist-facies conditions. These HP/LT serpentinites currently occur in natural outcrops and in active and abandoned quarries. They are composed mainly of serpentine, amphibole minerals, phyllosilicates, Cr-spinel, clinoclone, dolomite, Mg-calcite and quartz, and are hosted in talc-rich bodies and quartz and carbonate-rich veins. Carbonate-rich veins in serpentinites are a common feature of rocks of weathered fossil oceanic lithosphere. The studied serpentinites of the Pollino Massif include fracture surfaces, filled with fibers of several types of asbestos minerals (chrysotile, tremolite, edenite). These fibers can be released into the ambient environment (air, water, and soil) and inhalation of them could cause pathological effects as malignant mesothelioma and lung cancer. In recent years, societal and scientific interest in studying serpentinites has been shifted such that they are now considered not only as a health risk factor, but also as a resource and opportunity for CO<sub>2</sub> sequestration. In the presence of a CO<sub>2</sub>-rich fluid at low temperatures, the serpentine group minerals are transformed, through an exothermic reaction, into stable carbonate minerals such as magnesite (MgCO<sub>3</sub>) and dolomite [MgCa(CO<sub>3</sub>)<sub>2</sub>]. The significance of this reaction is that its manifestations can be easily disposed of as a solid Earth material inert in the Pollino Massif area, and that it also introduces a new perspective to the discussion of the potential reduction of greenhouse gas emissions into the atmosphere. Serpentinites exposed in ophiolites could serve as a sink by trapping CO<sub>2</sub> emissions originated from the combustion of fossil fuels.

## Serpentinite quarries at the Calabria-Basilicata boundary (Southern Apennine, Italy): A case study of petrography, geochemistry and mineralogy towards sustainable economy

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Keywords: serpentinite rocks, Pollino Massif, Pietrapica quarry.

Due to their aesthetic features and to their mechanical properties such as tensile strength, flexibility, high thermal stability, serpentinite rocks are extensively used, as building and ornamental stones and better known as Greenstone. Asbestos-bearing serpentinite rocks in the Pollino Massif (Calabria and Basilicata regions, Italy) occur at the scale of the outcrop as well as in several active and abandoned quarries,.. Quarry residues interact with the natural environment because they contain not only asbestos minerals but also high quantities of heavy metals (such as Ni, Co, Cr), which can contaminate soil and water and be harmful to human health (Bloise et al., 2019; Dichicco et al., 2019; Punturo et al., 2019; Rizzo et al., 2021). In this work, we present petrographic, mineralogical and geochemical data of the studied serpentinite rocks collected the Pietrapica quarry, located at the Calabria-Lucanian boundary, near San Severino Lucano and Episcopia settlements (Basilicata region, Southern Italy).

Serpentinites show an marked deformation and record a protracted history of high strain and fluid-rock interactions. Moreover, they are almost always intensely tectonized with several slip surface and pseudo-badlands morphology. The serpentinites-hosted talc-rich bodies associated with quartz and carbonate veins.

Serpentinites consist of serpentine, tremolite-actinolite, chlorite, magnetite and other Cr-spinels, with minor amounts of calcite, dolomite, clay minerals, and talc. The chemical composition of the analysed samples is dominated by major oxides SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub> and MgO, while the most abundant trace elements are Cr and Ni. Raman spectroscopy showed the main serpentine species which are lizardite, antigorite, chrysotile and polygonal serpentine. The X-ray powder diffraction analysis allowed clearly the identification of carbonate minerals, serpentine and amphibole minerals, that are the dominant phases, followed by 2:1 phyllosilicate. Electron microprobe analyses revealed that carbonates are represented in carbonate veins by calcite and in quartz-carbonate veins by dolomite, respectively; the analysed amphiboles revealed the occurrence of Ca-amphiboles and Mg-Fe-Mn amphiboles and, for the first time, the occurrence of edenite. Chlorite crystals are generally Fe-rich. Clinopyroxene is characterized by homogeneous compositions rich in the diopside end-member with high content of Fe and Cr, while talc shows high Fe-content and minor amounts of Al; Ca and Ni. The waste deriving from serpentinites quarries represent a potential source of critical elements such as Cr, Ni, Co since they can be valorised and reused after proper treatment, becoming geomaterials of industrial interest for the sustainable economy according to the latest European policy.

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## Radioactivity in building materials

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Keywords: radioactivity, granite, building materials.

All building materials have a small but not negligible amount of natural radioactivity; since they come from the earth's crust, this radioactivity is due to the radioactive families of Uranium (U-238), Thorium (Th-232), and Potassium (K-40), in varying concentrations depending on the type and origin of the original rocks.

Some granites and some tuffs can sometimes record significant concentrations of radioisotopes, while in marbles and carbonate stones radioactivity is rarely present unless they are settled in lagoon environments (i.e., Lecce, Italy limestones). Also building products fabricated with naturally occurring radioactive materials (NORM) can exhibit residual radioactivity, such as in various types of sand, ceramics, or cements.

The radioactive content in the materials used to build is therefore of a certain importance because it can significantly affect the annual effective dose equivalent absorbed due to the long residence time of people inside the buildings.

In Italy the reference regulatory device in the field of work activities involving the presence of natural sources is Legislative Decree 230/95 (including subsequent amendments and additions), while the radioactive content of construction materials is regulated by the Legislative Decree 101/2020.

In order to avoid excessive alarms or, on the contrary, to underestimate the problem, a cognitive investigation was carried out on the radioactivity content in ornamental and structural building materials, in order to possibly identify critical radioactivity concentration. The natural stones analyzed are granite rocks sampled in Sardinia (Ornamental Stones District of Gallura).

The analyses were done in the ENEA's Environmental Traceability and Radiometry Laboratory specialized in low and very low activity concentration of radioisotopes in the environment. The gamma spectrometry analyses were carried out on the samples reduced to grains, to which, following the EC guidelines, the criteria on the criticality of the materials were applied, calculating three parameters: the activity concentration index (I), the gamma absorbed dose rate (Da) and the annual effective dose (He). The results indicate low concentrations of Uranium and Thorium and therefore compliance with the legislation limits concerning the radio-exposure from minerals, so that they can be used for ornamental purpose in buildings.



**Digitized Inerting Process in a Protective Atmosphere in a Continuous Line Industrial Plant for the Inertization of Silicates and Asbestos Materials, for recycling in the Powder Metallurgy Industry, in the Aerospace, Arms and Defense Industry for technologies and military equipment, from industrial electronics to the goldsmith industry as well as for the production of refractory material - From hazardous asbestos containing wastes (ACW) to new secondary raw material through a new sustainable inertization process: A multimethodological mineralogical study**

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*Keywords:* asbestos, inertization, waste.

This is a digitalized industrial plant in a continuous line, composed by a low temperature furnace and a high temperature protective atmosphere furnace, connected by a conveyor belt where anthropomorphic robots are used in the loading-unloading of asbestos materials and quality control with devices used in NASA space programs. This invention allows the inertization of asbestos fibers for the recycling of Secondary Raw Material in Powder Metallurgy, for the production of new highly refractory and hard metal alloys, with applications in the field of air and land transport, electrical and electronic engineering, missile engineering, nuclear, aerospace, biomedical, nanotechnologies, for military applications and technologies in defense systems and armaments, precious metals and for the production of refractory material.

## Petrographic and mineralogical analysis of natural asbestos fibres in road pavements

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Keywords: asbestos fibres, petrographic analysis, asphalt.

Naturally Occurring Asbestos (NOA) may be present in the aggregate used as filler in asphalt in road pavements. As indicated by Leocat. 2020, the issue of NOA in building materials has been revealed during roadworks in 2013 in France. In fact, road coating aggregates are made of specific rock gravels that can contain Naturally Occurring Asbestos (NOA), which is mainly actinolite.

As these pavements are subject to wear and tear from vehicle traffic, aging asbestos-containing materials can cause problems for human health and the surrounding environment. Dust generated by the degradation of asphalt surfaces can disperse the minerals contained in road surfacing, exposing an increasing number of people and animals to asbestos fibres.

In recent years, more attention has been paid to naturally occurring asbestos (NOA) because the highest incidence of lung cancer has been observed in environments (Campopiano et al., 2022) characterised by rocks and soils rich in tremolite, which is characteristic of asbestos minerals.

The purpose of this study is to characterise asphalt samples taken from a section of a motorway in the Lombardy region (northern Italy) for the purpose of characterising asphalts used in road surfacing. The surfaces of each sample were analysed using a portable energy-dispersive X-ray fluorescence (ED-XRF) instrument. Fragments of each sample were prepared for X-ray powder diffraction (XRPD) and scanning electron microscope (SEM-EDS) analysis. During the XRPD and SEM-EDS analyses, the presence of asbestos fibres was unexpectedly observed in some samples (Marrocchino et al., 2020).

This evaluation, performed using a metrological approach based on petrographic and mineralogical analyses, should be a useful tool in order to implement the procedure to define the best treatment strategies for waste management with sustainable costs in fulfilment of Council Directive 67/548/EEC (1967) and EC Regulation 1272/2008 (2008).

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## **S25.**

### **A world at risk: evaluation of the hazard associated to volcanic eruptions, natural radioactivity and land instabilities**

#### *CONVENERS AND CHAIRPERSONS*

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## Reconstructing the recent eruptive history of Hasandağ volcano by tephrostratigraphic correlations along the Belbaşanı Valley, Central Anatolia, Turkey

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**Keywords:** Central Anatolian Volcanic Province (CAVP), Hasandağ, tephrostratigraphy.

Central Anatolian Volcanic Province (CAVP) is a post-collisional continental arc related to the subduction of the African plate beneath the Anatolian block. It has been the source of multiple and large volcanic eruptions since Miocene (including the famous Cappadocian ignimbrites). CAVP comprises several volcanic fields, numerous calderas and stratovolcanoes. One of the largest is Hasandağ: a Quaternary stratovolcano that has produced a huge range of explosive eruptive products, including caldera-related ignimbrites (Aydar & Gourgaud, 1998), block-and-ash flows (Friedrichs et al., 2020), and pumice-and-ash fall deposits (Kuzucuoğlu et al., 2020). Due to only a few studies have been focused on the geological evolution of this volcano, the aim of our research is to build a more complete Hasandağ tephrostratigraphy for a better reconstruction of its volcanic history.

Here we present the stratigraphic correlations of two large pyroclastic deposits (or ignimbrites) that outcrop along the Belbaşanı valley, a depression located between the Quaternary Keçiboyduran and Hasandağ Stratovolcanoes. Previous works have considered all the pyroclastic sequence visible through the valley as a unique eruptive deposit. However, there is a clear discontinuity in the middle of the pyroclastic sequence, suggesting that they are the result of two different large explosive eruptions with a period of quiescence between them. Differences in glass chemistry (major and trace elements) and geochronological dating (Ar/Ar and U/Th), confirm they are two different ignimbrites.

The lowermost deposit (the Yenipınar ignimbrite) starts with a short pumice fall (~2m) deposited on top of a thick colluvium deposit lahar-type. The uppermost part of Yenipınar ignimbrite is a sequence of dense and dilute pyroclastic flows (highly energetic PDCs), which are exposed continuously along the road of north Belbaşanı valley, having a minimum thickness of 5m. A thick paleosoil on top of Yenipınar ignimbrite is visible in some points, and an angular disconformity by erosion in other points. In a quarry near the upper part of the valley, a thick pumice fallout deposit (~8m) is deposited on top of this paleosoil. The pumice fall is the base of the Belbaşanı Ignimbrite, which moves gradually to a sequence of dilute PDCs and denser and rich in lithics pyroclastic flows at the upper part of the sequence (total thickness of PDCs ~ 12m). The Belbaşanı Ignimbrite is very widespread towards the north, having a thick coignimbritic lag breccia within, and hummocks at the İhlara valley. This unit can be the result of a caldera collapse.

**Acknowledgements:** This work is part of the Rengin Özsoy PhD thesis, funded by a scholarship from La Sapienza – University of Rome and the PÜSKÜRÜM project (a Marie Curie Action, Grant n° 101024337).

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## Uncovering cryoconite: the radioactive legacy of glaciers

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Keywords: environmental radioactivity, cryoconite, glaciers.

The term cryoconite refers to the sediment that accumulates on the melting surface of glaciers. Although first observed in Greenland in the 19<sup>th</sup> century, it has since been found on glaciers all over the world, from the Arctic to the Antarctic, as well as on Alpine glaciers spread on the mountains of Earth. For nearly a century, cryoconite was considered a glaciological curiosity with limited scientific relevance. However, over the last two decades, it has gained recognition as a hotspot for multidisciplinary research in Earth and environmental sciences. This is because cryoconite not only influences the mass balance of glaciers due to its dark color, but it is also rich in microbial life and plays an essential role in cycling elements and compounds in glacial environments, including pollutants. Among the latter, radionuclides play an important role. Notably, cryoconite has some of the highest reported activity concentrations of radionuclides in surface environments, second only to areas where nuclear tests and accidents occurred. Fallout radionuclides, both natural and artificial, are responsible for the radioactivity in cryoconite. <sup>210</sup>Pb and <sup>137</sup>Cs are the most abundant radionuclides in cryoconite, with activities often exceeding 10,000 Bq kg<sup>-1</sup>. Other radionuclides such as <sup>7</sup>Be, plutonium, and americium isotopes are also present, albeit at lower concentrations, yet still one or two orders of magnitude higher than in typical environmental matrices used for monitoring environmental radioactivity (e.g. mosses and lichens). To understand why cryoconite is so radioactive, it is necessary to consider its peculiar composition, the complexity of the supraglacial environment, the release of fallout radionuclides from retreating glaciers and the role of meltwater in mobilizing them. We discuss here a mechanism to explain the accumulation of radioactivity in cryoconite, highlighting what we have understood so far, what we need to investigate further, and the potential impacts of this new research line.

## A new perspective in radon risk assessment

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*Keywords:* natural radioactivity, geogenic radon potential, indoor radon, radon risk.

Radon (<sup>222</sup>Rn) is a radioactive gas considered the major source of ionizing radiation exposure for the population and has well demonstrated detrimental effects on human health (WHO, 2009). In particular, radon gas represents a serious hazard when it accumulates in indoor environments (Indoor Radon) such as in residential houses and workplaces.

Exposure to indoor radon is a serious problem that has prompted Europe to establish legislation (Basic Safety Standards Directive 2013/59/EURATOM) which, on the one hand, fixes some national reference levels with the aim of reducing Indoor Radon Concentration (IRC) exposure; on the other hand, urges the public administrations to define the so-called Radon Priority Areas (RPAs). An optimal hazard indicator is represented by the Geogenic Radon Potential (GRP) conceptualised as “what Earth delivers in terms of radon” from the geogenic sources (e.g. radionuclides content, faults and fractures) towards the atmosphere (Bossew et al., 2020). This parameter represents the Rn potentially available to enter within buildings and it is considered the most important spatial predictor of the IRC; mapping the GRP is a fundamental step to understand the potential risk over an area. The Rn risk is defined as the product of three factors: hazard (the GRP), vulnerability (type and characteristics of the buildings) and exposure (amount of population). Since Given a standardized approach for risk mapping and RPAs individuation is missing, in this study we propose a first procedure for mapping the risk in order to individuate these areas as required by the current legislation. The selected study area is located in the Pusteria Valley (Bolzano province, eastern Italy) and it is well-known from a geological and structural point of view; it is characterised by a wide non-seismically active fault zone showing a very high gas permeability (Benà et al., 2022). In particular, we have applied a machine learning technique (i.e. Forest Regression) to construct a high resolution (50 m\*50 m) GRP map (hazard) of the study area considering several proxy variables related to the Rn sources (e.g., radionuclide content in rocks) and to the Tectonically Enhanced Radon (TER) quantity. Furthermore, we have assessed the risk combining the GRP map (hazard), the location type (vulnerability) and the density of population (exposure) in order to individuate the RPAs. Preliminary results show that areas characterised by high Rn risk are located in correspondence to high GRP. These areas also show a location type corresponding to the residential areas and/or housing unit therefore characterised by a high density of population. This work represents the first attempt in Italy to map the Rn risk as a tool to define the RPAs.

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## Application of landslides susceptibility models by using GIS analyses

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*Keywords:* landslide susceptibility mapping, GIS applications, Southern Italy.

The investigation and mapping of mass movements in a regional planning of the landscape is one of the main objectives in the preservation of both human safety and anthropic infrastructures. The comprehension of the landscape vulnerability is strictly linked to climatic change which is actually the dominant process acting in the landscape. Generally, the evaluation of the landslide susceptibility is faced using a deterministic approach through physical modeling of the process. Several open-source landslide susceptibility model applications are available on the website showing different degrees of difficulty, from mono-dimensional to bi- and three-dimensional developments. In this work, a fast and multiparametric approach for the production of landslide susceptibility maps using open-source GIS applications was proposed, starting from the identification of the factors triggering the process. With the aim to identify the slope stability related to debris flow and rock fall processes in the high Agri valley, four slope stability models have been carried out. The selected models which are available online are as follows: i) shallow slope stability model (SHALSTAB)(Montgomery & Dietrich 1994), ii) soil stability index mapping model (SINMAP)(Pack et al., 2005), iii) semi-empirical debris flows model (FLOW-R)(Horton et al., 2013), and iv) predictive rock fall tool (QPROTO)(Castelli et al., 2021). The calibration of models was realized by using of geotechnical parameters related to different landslide types such as falls, slides, and flows. The data have been extracted by field surveys and laboratory tests. The application of several susceptibility models in the same area allowed for the increase of the robustness of the final map of susceptibility. A better recognition of the predisposing and triggering factors to mass movements have been made thus to select the more reliable method of application devoted to the achievement of the objective. Finally, the maps of susceptibility generated by each method have been overlapped by using the GIS application thus to detect the best input parameters for the analyzed methods of application.

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## Gamma-ray spectrometry to predict the indoor radon concentration

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Keywords: gamma spectrometry, NORMS, Geogenic radon.

Radon ( $^{222}\text{Rn}$ ), produced by the radioactive decay of uranium ( $^{238}\text{U}$ ) occurring as a trace element in most rocks, soils and water, is the most significant natural source of human exposure to ionising radiations. Despite the variability of the subsoil and dwelling characteristics, the amount of radon generated in the ground is expected to be correlated to that occurring indoors. In radon mitigation studies, it is logical to identify affected dwellings by direct measuring indoor radon levels. Where indoor measurements are few or irregularly distributed and where no dwellings exist, proxies can help identify radon-prone areas. The ground-specific activity of  $^{238}\text{U}$ , determined employing gamma-ray spectrometry, can provide a semi-quantitative evaluation of the indoor radon, and can be used as a predictive tool to identify high-hazard areas. We tested this methodology in the Alpine geological units of western Liguria (Italy), characterised by rocks spanning from sedimentary to metasedimentary and metavolcanic. The largest average specific activity of  $^{238}\text{U}$  (96 Bq/kg) was found in the acid metamorphic rocks. In the metasedimentary rocks, the mean specific activities of  $^{238}\text{U}$  were observed in quartz and mica schists (53-60 Bq/kg). In sedimentary lithotypes, specific activities were generally lower than 40 Bq/kg. We found that the number of buildings with  $^{222}\text{Rn}$  exceeding the critical level of 200 Bq/m<sup>3</sup> increases where the ground specific activity of  $^{238}\text{U}$  is larger. A comparison between  $^{238}\text{U}$  specific activity and the indoor  $^{222}\text{Rn}$  concentration measured on the same geological formations showed a linear correlation, which was used to map the expected indoor radon concentrations. Despite the limitations and uncertainties, mainly related to the uneven data coverage and the complex interaction between the building and the bedrock, the predictions are consistent with indoor radon records. Most of the detectors that recorded  $^{222}\text{Rn}$  concentrations exceeding the critical level were in sites with expected indoor radon >200 Bq/m<sup>3</sup>.

## From the Geogenic Radon Potential map to the Radon Priority Areas of the Italian territory

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Keywords: geogenic radon, machine learning, radon risk map.

Radon generation from rock and soil, as well as its migration towards the surface along geological faults, are natural processes that can enhance radon infiltration into dwellings, causing a health risk. The combined analysis of these two processes and the construction of spatial models, including the contribution of different proxies of the geological radon source (GRS) (e.g., geology, radionuclide content) and of the geological radon migration (GRM) pathways (e.g., faults) in the subsoil, can be used to construct a geogenic radon potential (GRP) map as a tool to predict the susceptibility of an area to increased indoor radon concentration for geogenic reasons. To date several direct and indirect models (e.g., deterministic and probabilistic) have been used to generate GRP maps for a certain region. In this research, we present a bottom-up analysis that includes the integration of many predictors to create a GRP map of the entire Italian area using a supervised machine learning technique in ArcGIS based on the Forest Regression algorithm. A database of about 35000 soil gas radon concentrations was divided into training and test data, and a conceptual model with ten predictors was constructed. The model can then be used to estimate soil gas Rn concentrations at unknown locations of a 1x1km regular grid with the same predictors. The model incorporated the following predictors: uranium content of bedrock (Nogarotto et al., 2017) and soil (FOREGS <http://weppi.gtk.fi/publ/foregsatlas/>), Available Water Content (Ballabio et al., 2016), Fault Density map constructed by using a new fault dataset developed combining fault distribution from national and regional dataset (Ciotoli et al., 2020), Heat Flow map (Cataldi et al., 1995), Karst Areas (KA) extracted from the map of the World Karst Areas (<https://www.whymap.org>), Gamma Radiation map constructed by using data of the kerma intensity measurement stations obtained from the Fire Fighters Corp (C.N.VV.F.), Solar Radiation dataset downloaded from WorldClim website (<http://worldclim.org>), and the Italian Digital Terrain Model 20m from SINANET (<http://www.sinanet.isprambiente.it>). DTM was also used to derive the map of the Slope and the Aspect. A combination of statistical metrics was used to validate susceptibility model and to define the top variable importance in the model. The final model shows a significant  $p=0$  and an  $R^2=0.830$ . SHAP graph shows the importance of the predictors in the model; in particular the main key influencing factors for GRP are: U content, gamma radiation, fault density and DTM. All these predictors are positively correlated with the presence of high soil Rn concentrations. The combination of the GRP map with the census sections (ISTAT database) and the population density provided the final risk map. The map will be useful to national and regional administrations to identify the Radon Priority Areas (RPA) as required by the European Directive 2013/59/EURATOM (art. 103).

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## Preliminary data from the permanent radon monitoring network in western Sicily

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Keywords: radon, Sicily, monitoring.

Radon is mobilized in the earth's crust mainly by processes associated with fluid migration. Due to its short half-life (the main isotope is 3.82 days), its mobility in the soil by diffusion is limited, and other fluids (CO<sub>2</sub>, CH<sub>2</sub> or N<sub>2</sub>) are the main carriers of this gas. Numerous evidence in the recent scientific literature suggest that the transport of fluids could play an important role in the stress changes associated with the preparatory phases of an earthquake, and therefore, in some seismotectonic contexts, radon could represent a useful marker of seismogenic processes also on a short term (Piersanti et al., 2016).

In recent months, a permanent network for monitoring radon emissions from the soil has been implemented in western Sicily. The projects in which this activity is framed are the IRON (Italian Radon Monitoring Network; Cannelli et al., 2018) and PON-GRINT research projects, coordinated by the staff of the National Institute of Geophysics and Volcanology (INGV). The development of the radon network was carried out in collaboration with the Department of Earth and Sea Sciences of the University of Palermo.

Sicily, together with the area of the central Apennines, is the area where the most monitoring stations are concentrated. The IRON network was therefore created with the aim of extensively monitoring the emission of radon in Italy and, among the main objectives, there is certainly also that of exploring the possible relationship with seismicity, in consideration of the high seismic hazard of the territory Italian.

Like most of the IRON sites, the radon monitoring units installed in Sicily are co-located in the sites of the National Seismic Network (RSN). This choice as well as strategically responding to the objective of multi-parameterisation of the RSN stations is also tactically aimed at optimizing the installation phase and subsequent maintenance operations. The installation of the first 14 control units took place in the months of June - September 2022.

The monitoring devices are equipped with a surface barrier semiconductor detector, sensitive to the alpha particles emitted by the decay of <sup>222</sup>Rn and its offspring with short half-life alpha emitters: <sup>218</sup>Po and <sup>214</sup>Po. The selection for counting only the alpha particles with energy corresponding to the decay of <sup>218</sup>Po is entrusted to the electronics, thus providing a prompt response (up to speed in 15 minutes); from the instrumental sensitivity obtainable during the calibration in terms of pulses/hour for each Bq/mc it is possible to trace the radon concentration. In detail, the "AER-C" (with IOT transmission) and "AER-Plus" (transmission via LTE router) models were used, both produced by "Algade" (<http://www.algade.com/>). For each site, a pair of sensors with a different type of transmission is installed. All the data recorded by the IRON stations (including the new PON-GRINT stations installed in Sicily), together with the installation details, the technical characteristics of the instruments and the calibration and correction parameters of the raw measurements necessary for pre- and post-processing time series are stored in a relational database (IRON-DB) specially designed and built internally in MySQL/postgreSQL language. IRON-DB is hosted on a virtual server platform managed by the IT services of INGV with access, currently reserved, which allows the consultation and use of all the data collected, as well as information on the instrumentation and the different types of installations. The database uses detailed protocols for archiving downloaded data ensuring their security and flexibility in terms of database architecture and error checking. Soon, to ensure the dissemination of data, a dedicated web interface will be developed and made available for their consultation.

We present the time series of the radon flux from all stations. Together with radon, the climatic variables are measured, namely: air temperature, atmospheric pressure, and relative humidity. The joint observation is necessary to filter any environmental effects or the periodic variations of the radon signal. We show some preliminary statistical analysis and the spatial distribution of the radon flux across the network.

## The Late Pleistocene volcanic activity at Campi Flegrei: new tephrostratigraphic and tephrochronological evidence

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*Keywords:* Campi Flegrei, tephrostratigraphy, tephrochronology.

Campi Flegrei (CF) caldera, located west of the urban area of Naples (southern Italy), is among the most productive volcanoes of the Mediterranean area. Its volcanic history comprises so far two well-known caldera-forming eruptions (e.g., Campanian Ignimbrite, CI, ~40 ka; Neapolitan Yellow Tuff, NYT, ~14 ka). Furthermore, recent studies correlated a well-known widespread distal ash layer, the so-called Y-3, with a poorly exposed proximal CF pyroclastic unit (Masseria del Monte Tuff, 29 ka), allowing a re-assessment of the magnitude of this eruption, now recognized as the third large-magnitude (VEI 6) eruption at CF. The discovery of this large eruption reduces drastically the recurrence intervals of large-magnitude events at CF and has major implications for volcanic hazard assessment. While the most powerful Late Pleistocene (e.g., post-NYT and partially post-CI) eruptions at CF have been the subject of extensive investigations, less is known about its earliest activity. We provide new tephrostratigraphic and tephrochronologic constraints of Late Pleistocene eruptions from CF (~110-90 ka) based on new compositional (EMPA and LA-ICP-MS) and <sup>40</sup>Ar/<sup>39</sup>Ar data of tephra layers from a marine sediment core from the central Tyrrhenian Sea. Our study provides new correlations of tephra layers and thus new insights on the Late Pleistocene volcanic activity at CF. These new findings are pivotal for a reassessment of recurrence times of the CF explosive activity, allowing to define future eruptive scenarios and for an improved volcanic hazard assessment in the Neapolitan area, which is much needed to understand the behavior of the CF caldera with a long-term perspective.

## **Dynamics and hazard of phreatic explosions at Vulcano island (Aeolian archipelago, Italy)**

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*Keywords:* phreatic eruption dynamics, volcano hazards, 3D numerical modelling.

Phreatic events may represent the typical precursors of magmatic eruptions of variable intensity, but they can also occur as single or multiple episodes punctuating the activity of volcanoes characterized by the presence of important hydrothermal systems. Despite the general low intensity of phreatic explosions, with respect to magmatic/phreatomagmatic activity, these events can represent important sources of hazards especially in highly inhabited volcanic areas or at volcanoes with a strong tourist vocation. The recent unrest started in September 2021 at La Fossa volcano (Vulcano Island, Italy) called attention to the possibility of occurrence and to the expected dynamics of phreatic explosions for the reactivation of the volcanic system. The occurrence of phreatic activity at La Fossa volcano has been sparsely documented, and only the important activity of the Breccia di Commenda sequence (1230 CE) has been studied in detail to date. Mainly based on historical and sedimentological evidence, we present here a multidisciplinary study focused on a sequence of small-scale (less than  $10^5$  m<sup>3</sup> erupted products) phreatic explosions occurred in the XIX century, preceding by decades the 1888-90 magmatic event. Field data clearly demonstrate the occurrence of pyroclastic density currents and ballistic showers potentially able to affect the currently inhabited area, despite the relatively small magnitude of the event. Thanks to three-dimensional, multiphase-flow eruption modelling, we discuss the possible reconstruction of eruption dynamics (as a single or multiple explosive events), the role of crater geometry (particularly, the influence of inclined vents) and the interaction with the volcano topography. Numerical simulations allow us to map the different hazardous phenomena, and in particular the areas potentially affected by pyroclastic currents and ballistic fallout. The developed model, calibrated on this event, can be used for an assessment of phreatic eruption hazards in the framework of the current hydrothermal unrest at Vulcano.



## Dissolved radon levels from the unresting Campi Flegrei caldera compared to concentrations in waters from other volcanic areas in Southern Italy using a RAD7 radon detector

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Keywords: radon, RAD7, Italian volcanic belt.

The present study concerns with <sup>222</sup>Rn measurements performed on several different waters mostly from the Campi Flegrei (CF) caldera, an active volcanic-geothermal field located NW of Naples in the Campanian Plain (Southern Italy). The study was conducted in the frame of Pianeta Dinamico project funded by INGV and aimed at improving volcanic and active system monitoring and surveillance.

At CF, as well as in geothermal and/or volcanic areas, monitoring the Rn content can be useful i) to identify hydrological circulation and preferential fluids pathways and ii) to discriminate amount variations associated with hydrothermal phenomena and particularly with gas emissions (mainly CO<sub>2</sub>, if we do not consider water vapour in emissions with temperatures close to boiling point) that are supposed to carrier Rn far from its source.

We focused on 26 waters samples, from wells, lakes, pools and springs (one submerged) almost all used for fluid geochemistry monitoring collected two times per years from October 2021 and measured for physical parameters, major ions geochemistry and radon content. Moreover, 6 waters were sampled at a shorter time interval for a much control on radon content susceptible of variability due its inert, volatile and unstable behaviour.

In addition, always from the Campanian Plain, were sampled and analyzed <sup>222</sup>Rn concentrations in: 23 cold waters from the quiescent Mount Somma-Vesuvius volcano, located SE of Naples at the intersection of two regional NW–SE and NE–SW tectonic fault systems; 12 waters north of the CF up to the extinct Roccamonfina volcano; and only one thermal water of Ischia island, a volcanically active resurgent caldera located at the NW corner of the Bay of Naples. 3 thermal waters, were instead collected from Vulcano island, in the Aeolian Arc archipelago, during the 2021 hydrothermal unrest episode. Almost all these additionally considered waters were from wells, except for two Vulcano samples, one from a pool and one from a submarine spring.

The CF caldera reaches the highest concentration of Rn varying from  $0.03 \pm 0.02$  to ca.  $1887 \pm 13$  Bq/L; but except the geothermal wells of the thermal bath “*Stufe di Nerone*” located at North of CF area, all the others have radon levels below 60 Bq/L. Somma-Vesuvius reach concentrations up to  $24 \pm 1$  Bq/L, north to the CF maximum is reached in the Roccamonfina area with levels of  $71 \pm 7$  Bq/L, while Vulcano island attains the lowest detected concentrations, less than  $2.4 \pm 1.0$  Bq/L. Ischia is at  $54 \pm 2$  Bq/L. The water salinity appears to don't affect the calculated <sup>222</sup>Rn content. All the <sup>222</sup>Rn concentrations were measured by RAD7 connected to Big Bottle RAD H<sub>2</sub>O and DRTYSTIK accessories, and calculated using Capture, the RAD7 default program.

The Rn amounts considered in this work aimed at a better understanding of the radon behavior and origin from different volcanic settings.

## Reconstructing the Holocene volcanic history of Erciyes stratovolcano, Central Anatolia (Turkey): the Karagüllü, Perikartin and Dikkartin explosive eruptions

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**Keywords:** Central Anatolian Volcanic Province (CAVP), Erciyes Stratovolcano, tephrochronology.

Mount Erciyes is the largest stratovolcano in the Central Anatolian Volcanic Province (CAVP), with its 3917 m and ~ 45 km in diameter. Erciyes has a long volcanic activity since late Neogene, with effusive and explosive cycles (Şen et al., 2003). The more recent products of this activity are the pyroclastic deposits of Karagüllü, Perikartin and Dikkartin. They have been erupted explosively during the Holocene from separated craters, which are distributed both in the north and south flanks of Erciyes. Karagüllü, Perikartin and Dikkartin deposits comprise a tuff cone with a lava dome/flow emplaced within at the end of the eruption/s. These lavas/dome partially destroyed the cones and generated pyroclastic density currents (PDCs) down flow the flanks of Erciyes. However, until today there is no detailed volcano-stratigraphic work to find the contacts between these three pyroclastic deposits and reconstruct the volcanic history of the related eruption/s.

Although there are some published geochronological analyses (e.g. cosmogenic by Sarikaya et al., 2019; and U/Th-He by Friedrichs et al., 2020), the yielded ages are not precise enough to discriminate if these three volcanic products are the result of one, two or three different eruptions. Here we present a tephrostratigraphic study (including glass chemistry) to better characterize each pyroclastic deposit and the stratigraphic contacts between them.

The first results indicate that Perikartin is younger than Karagüllü deposit (two different eruptions). Stratigraphically, Perikartin deposit is above a thick paleosoil developed on top of a 3-m thick reworked material that has been accumulated above the Karagüllü pyroclastic unit (in Hacilar site, northern flank of Erciyes). Major and trace elements composition show clear differences between these two eruptive products. Unfortunately, there is no stratigraphic contact between Dikkartin pyroclastic unit (erupted through a southern flank vent) and the other two Karagüllü and/or Perikartin (northern flank vents). In addition, the chemical composition of Dikkartin and Perikartin deposits are exactly the same (both major and trace elements), and if considering that only one distal tephra with this composition has been found in several sedimentary records (S1 tephra in Mediterranean Sea, Dead Sea, Caves in Egypt or paleolakes in Lebanon and Arabia; e.g. Hamman et al., 2010), rise the hypothesis that these two deposits are part of the same eruptive event (syneruptive deposits), but from different craters (one in the northern and one in the southern flank). Further studies of this ongoing research, which is funded by the PÜSKÜRÜM project (a Marie Curie Action, Grant n° 101024337) and the EXCITE-TNA project (HORIZON 2020), are focused in petrological analyses on minerals (e.g. crystals of plagioclase and hornblende) and on radiogenic dating (<sup>14</sup>C and Ar/Ar) in order to find more evidences that could support the proposed volcanic history, which is by two different Erciyes explosive eruptions during the Holocene: first the Karagüllü deposit and after the syneruptive Perikartin and Dikkartin deposits during the same eruption.

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## Paleomagnetic dating of prehistoric flank eruptions from the SE lower slopes of Etna volcano

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Keywords: Etna, paleomagnetic dating, flank eruptions.

The volcanic hazard assessment is of fundamental importance for the densely inhabited lower slopes of active basaltic volcanoes such as Monte Etna (Sicily, Italy). Indeed, the Etna volcano, despite its eruptive activity mainly concentrated at the summit craters, was also characterized in the past by large, less frequent and more destructive eccentric eruptions (e.g., AD 1669). The chronological framework of the 2750-year-long historical period of the Etna activity is fairly well known. Conversely, the timing of the prehistoric flank eruptions is still poorly constrained, being supported by only stratigraphic evidence and a few Ra and paleomagnetic ages. The paleomagnetism is a dating tool whose accuracy is difficult to achieve using other radiometric techniques in volcanics of the last ca. 14 ka, making it necessary for the chronological reconstruction of Holocene basaltic flank eruptions and for related hazard implications. Here, we report on the paleomagnetic dating of fifteen Holocene flank eruptions characterized by scoria cones and major lava flows distributed over the SE Etna lower slopes. They were produced by the S eruptive rift, the most historically active among the three main rifts of Etna. We paleomagnetically investigated 44 sites (440 oriented cores) and compared flow-mean paleomagnetic directions to the SCHA.DIF.4k geomagnetic regional model (for one eruption) and the SHA.DIF.14k global model (for the other eruptions). Our results indicate that many possible time windows can be obtained for a single eruption. In four cases, the paleomagnetic ages do not significantly shorten the input time window, either extending up to ~12 ka BC (Camporotondo Etneo and Blandano eruptions) or spanning the 6 ka BC – AD 750 (Dagala) and the 1520–122 BC (Monte Gorna) intervals. For the other eruptions, input time spans are significantly reduced by paleomagnetic dating. In particular, the lava flows stack of Pisano, Passopomo, Mangano, Monte Arcimis, and Cancellieri yield progressively younger ages from around 6–5.5 ka BC (Pisano) to ca. 400–150 yr BC (Cancellieri). Moreover, Monte Trigona, Tremestieri Etneo, and Mascalucia eruptions appear having occurred in a narrow time interval (between 3.4 ka BC and 2 ka BC). Furthermore, the dating of the Monte San Leo lava flow confirms its old emplacement age: 8.7–5.4 ka BC. Finally, several paleomagnetic ages from 3.5 ka BC to 1.6 ka BC have been obtained for Monte Serra eruption, whereas the underlying Trecastagni flow yields a narrow 3666–3545 yr BC time window. The new data yield a significant improvement in the chronology of Holocene eruptive activity, thus providing a better evaluation of the flank eruptions hazard at Etna volcano.

## On the long-term multi-source probabilistic hazard assessment: an example from Neapolitan volcanoes

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*Keywords:* volcanic hazard assessment, multi-sources, numerica modelling.

Nowadays, modelling of tephra fallout hazard is coupled with probabilistic analysis that considers the natural variability of the volcanic phenomena in terms of eruption probability, eruption sizes, vent position and meteorological conditions. As for earthquakes and tsunamis, historical catalogs of volcanic eruptions are usually incomplete, and thus it is usually adopted a computational hazard scheme, based on the combination of probabilistic source models and empirical or numerical models of propagation of the hazardous phenomena. In this framework, a prototypal methodology to carry out the long-term tephra fallout hazard assessment in Southern Italy is shown, considering the active Neapolitan volcanoes: Somma-Vesuvius, Campi Flegrei, and Ischia, that showed a very well-known past explosive behavior.

To explore the intrinsic variability of the investigated volcanic phenomena, a probabilistic approach by defining a set of different eruption size classes for each volcano (Small, Medium, and Large) is applied using the Fall3D numerical model to create a synthetic dataset of tephra ground loads composed by a total of 10500 simulations (1500 for each eruption size class) that consider a meteorological variability over the last 30 years. In each simulation the eruptive source parameters (e.g., eruption duration, mass of the fallout, total grain size distribution) were randomly sampled from published data distributions.

The model output in terms of tephra ground load were processed within a new workflow for large-scale, high-resolution volcanic hazard assessment relying on a Bayesian procedure, to provide the mean annual frequency with which the tephra load at the ground exceeds given critical thresholds at a target site within a 50-years exposure time. The main results were expressed in terms of absolute mean hazard maps considering different levels of aggregation, from the impact of each volcanic source and eruption size class to the quantification of the total hazard. Basically, the greater tephra load thresholds are exceeded with longer averaged return times, and that, the SSE regions are mainly affected by the tephra fallout hazard which is greater in the proximity of the Neapolitan area. Trough hazard disaggregation, the greatest contribution to the hazard results due to the eruptions from Somma-Vesuvius.

This study provides, for the first time, a multi-volcano probabilistic hazard assessment posed by tephra fallout, comparable with those used for seismic phenomena and other natural disasters. This methodology can be applied to any other volcanic areas or over different exposure times allowing to account for the eruptive history of the target volcanoes that, when available, could include the occurrence of less frequent large eruptions representing critical elements for risk evaluations.

## **Eruptive dynamics and hazards associated to pyroclastic density currents from the Las Derrumbadas rhyolitic twin domes (Puebla, Mexico)**

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*Keywords:* lava domes, eruptive dynamics, volcanic hazards.

The eruptive style of monogenetic domes has been poorly documented so far. It is nevertheless important to study them in order to establish their volcanic hazards, assess risks, and mitigate their impact on society. Las Derrumbadas rhyolitic twin domes in the Serdán-Oriental basin, eastern sector of the Trans-Mexican Volcanic Belt, were formed by a single volcanic eruption 2000 years ago, being the youngest of these volcanoes in Mexico (Chédeville et al., 2020; Guilbaud et al., 2022). In this work, we present results of the study of pyroclastic density current (PDC) deposits associated to the domes, in order to understand their eruptive dynamics and related hazards. Methods included stratigraphy, field-work, granulometry and componentry.

We found that the domes are associated to mainly two types of PDC sequences which have distinct characteristics that denote different eruptive styles and processes. The first type lies stratigraphically at the bottom of the eruptive sequence. It mainly outcrops to the northeast of the domes, although similar deposits were also found to the southwest. These deposits are massive, lithic-rich and indurated at the base, and cross-stratified, rich in rhyolitic clasts, and loose at their top. Distally, they also contain accretionary lapilli. This PDC sequence is interpreted as evidence for violent and destructive, phreatomagmatic activity at the beginning of the eruption, which resulted from the interaction of the magma with a shallow water table hosted in the basement limestone. The second type of sequence lies stratigraphically above debris avalanche deposits. It was found mostly to the east of the domes, but similar deposits were observed to the west. These PDC deposits are moderately indurated and extremely rich in rhyolitic clasts, with a pumice and lithic-rich layer at the base in one site. They present cross and parallel stratification, sand-waves in proximal sites, and accretionally lapilli in the finest-grained layers. They are interpreted as products of the collapse of unstable frontal parts of the growing dome, which may have been preceded, in places, by sector collapse and the emission of a lateral explosion that would be fatal to surrounding life. We conclude that the Las Derrumbadas PDC deposits have high scientific value as they reveal violent eruptive processes associated with the formation of monogenetic silicic domes, which should be taken into account in hazard assessments.

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## Functional recovery of the provincial road n° 22 at Km 9+000 - Historical analysis of previous problems, evaluation of construction errors and planning of landslide risk resolution

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*Keywords:* landslide hazard, road safety.

The Province of Southern Sardinia has planned various public work interventions to make safety and reduce the danger from gravitational phenomena on various road sections under its jurisdiction. Given the large extension of the road heritage, (almost 1300 km), the planning and design of short and medium-term interventions is subject to continuous evolution, according to the necessary priorities and the emergence of new problems and previous criticalities. Among the latest financed interventions, finished designing and contracting out in March 2023, there is that concerning the “historic” unstable area insistent on the provincial road n° 22 at Km 09+000, located in the Municipality of Escalaplano, a border area between the territory of Sarcidano and Gerrei, at a distance of 2 kilometers from the town, in the Province of South Sardinia, south-eastern Sardinia.

The area is subject to situations of instability that insist on the provincial road n° 22, with the presence of particularly dangerous landslides in progress, which have made a indispensable and decisive intervention for a length of 35 meters, for the safety of the road section marked from a development with a “halfway up” profile.

Previous intervention was carried out by means of a surface restoration of the damaged road surface, with the laying of a “rigid concrete pavement” which however obviously did not give the expected results as with the subsequent gravitational movements of the substrate they manifested very serious cracks on the roadway, for which it was necessary to proceed with traffic regulation with the interdiction of the lane towards the valley.

In order to be able to proceed with the definitive stabilization of the area, between the end of 2022 and the beginning of 2023, a survey was carried out on all the previous data, which was followed by an accurate geological, geomorphological and preventive lithotechnical study aimed at drafting a first geological model insistent on the area. Subsequently we proceeded with the planning, design and execution of targeted geognostic investigations, direct and indirect, through surveys, in situ tests, sampling and laboratory analyses, seismic refraction survey and MASW. The latter were completed in February 2023, for which the definitive geological and geotechnical modeling of the area was carried out, the results of which were as follows:

- from the study of historical aerial photos it has been highlighted that the road section was subject to rectification of the previous layout, in the mid-70s;
- the type of active landslide movement is similar to a rotational slip, given by various relative movements, to be identified both in the stratigraphic passages between the base conglomerates and the detrital alteration blanket, and between the latter and the embankment placed in place with the rectification of the previous route during the construction of the road during the “70s”;
- additional kinematic systems in place are induced by the variations in permeability between and in the stratigraphies present;
- the profiles of the indirect surveys, correlated to the geognostic surveys, identify at variable altitudes between 5 and 15 meters from pc stony rock after having crossed thickened terrigenous lithologies for about 2-3 meters passing through solid and semi-stone soils;
- the main hypothesis on the causes of instability is linked to deformation geometries with generalized settlement and slippage activated by the drainage of the sub-surface water outflow, in correspondence with which the lack of support at the base of the road embankment is noted

Following an appropriate evaluation of the executable interventions, it was agreed to proceed with a functional recovery of the road section through the consolidation by means of a suitably sized micro-pile bulkhead, having the function of containing the land subject to the historical rotational movements that immediately afflicted the constructed section in the year “70”. The intervention will start at the end of 2023, and once carried out it will be subject to a cadenced phase of “post operam” checks and monitoring, in order to verify the effectiveness and functionality of the intervention, or, if it will have been able to solve definitively the “historic” stability problems of the area.



## Preliminary results of a susceptibility analysis of a Ligurian (Italy) coastal area

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*Keywords:* hazard, landslide, susceptibility.

This study aims to develop preliminary landslide susceptibility maps for various types of landslides (rockfall/topple, rotational/translational slides, complex landslides and rapid flows) in the Liguria region's coastal area in Northern Italy. The maximum entropy model, MaxEnt (Phillips et al., 2006) and the inventory of Italian landslides, IFFI (Inventario dei Fenomeni Franosi Italiani <https://idrogeo.isprambiente.it/app/iffi>) are being used to assess landslide susceptibility. A total of 12 environmental variables, including DTM, geological map, CORINE land cover and topographic map of the region, are being analysed. The accuracy of the models is being evaluated using ROC (receiver operating characteristic) curves and AUC (area under the curve). The study area covers the coastal zone of the region, extending from the coast to 2 km inland, and landslide occurrences have been divided randomly into training and testing sets. The results obtained so far show good performance for all models, although this is dependent on the type of landslide considered. Finally, susceptibility maps will be created for each type of landslide and combined into a final map to provide a comprehensive overview of the landslide hazard at the regional level. This methodology could potentially be applied to other regions to assess landslide susceptibility. Further research is needed to refine the models and validate the results.

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## Study of the origin of soil $^{222}\text{Rn}$ and $^{220}\text{Rn}$ activities in Taylor Valley, Antarctica

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Keywords: permafrost, radon, Antarctica.

The stability of the polar regions is under threat from global climate warming, which could have wide-ranging effects. Recent studies on Arctic permafrost reveal that these areas store nearly twice the amount of carbon currently found in the atmosphere. Consequently, thawing permafrost has the potential to exacerbate the warming impact, effectively doubling the direct anthropogenic effects caused by fossil fuel combustion, agricultural practices, and land use changes. Moreover, thawing permafrost can intensify the transport of radon ( $^{222}\text{Rn}$ ) due to increased soil fluid saturation and permeability. Investigating the activity levels of  $^{222}\text{Rn}$  and  $^{220}\text{Rn}$  in polar soils serves as a crucial starting point to understand gas migration processes associated with permafrost thawing. While numerous studies have been conducted in the Arctic, there is limited data available from the Southern Hemisphere. To bridge this gap, the “SENECA” project, a collaboration between Italy and New Zealand, aims to provide the first assessments of gas concentrations and emissions from permafrost and/or thawed shallow layers in Antarctica’s Taylor Valley. This valley is particularly suitable for permafrost investigations as it is one of the few regions in Antarctica not covered by ice. Field measurements from our study reveal extremely low levels of  $^{222}\text{Rn}$  and higher levels of  $^{220}\text{Rn}$ , indicating a shallow source. Normally, measured  $^{222}\text{Rn}$  activity values are influenced by soil radionuclide content, soil temperature, porosity, and water content. By comparing in-situ  $^{222}\text{Rn}$  values with laboratory analyses of collected soil samples, we have identified higher levels of  $^{222}\text{Rn}$  than what is naturally produced by the exposed sediments. These findings demonstrate the presence of preferential gas pathways through the permafrost originating from a deeper source. This study represents the first of its kind conducted in Antarctica and significantly contributes to our understanding of permafrost thawing processes and their environmental implications. Additionally, this dataset serves as an important reference for future measurements aimed at tracking the progress of Antarctic permafrost melting.

## Identification of active and capable faults (FAC) using geochemical ( $^{222}\text{Rn}$ , $^{220}\text{Rn}$ and $\text{CO}_2$ ) and geophysical (ERT, GPR) investigations: Case study of the Rieti Basin (Lazio Region, Italy)

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*Keywords:* radon, geochemical survey, geophysical investigation.

The “Active and Capable Faults” are tectonic structures with a significant potential for displacement at or near the Earth’s surface and/or that have been active in the last 40K years in an area which occurred earthquakes larger than 5.5. Knowing the most likely position of the FACs can help reduce the impact of future earthquakes on existing buildings/infrastructures and, consequently, perform a Risk Mitigation in areas with high seismogenic potential. In order to study and detect FACs, with the consequent area of activity, a multidisciplinary approach was applied integrating structural geology, geophysics and geochemistry in one of the most active sector of the Apennines, the Rieti Basin (Central Italy).

The strategy used was based on a series of profiles performed along the edges of the sedimentary basin, to identify the position of the fault systems by indirect and direct investigations.  $^{222}\text{Rn}$ ,  $^{220}\text{Rn}$  and  $\text{CO}_2$  concentrations, Ground Penetration Radar (GPR) and Electrical Resistivity Tomography (ERT) profiles were performed to investigate the soil gas spatial distribution, their migration mechanisms and to mark off permeability belts possibly corresponding to buried faults.

234 measurements were performed along several profiles, highlighted average values of 49 kBq/m<sup>3</sup> of  $^{220}\text{Rn}$  and 26 kBq/m<sup>3</sup> of  $^{222}\text{Rn}$ . The highest values are located close to the fault planes highlighted by ERT surveys and overlapping with anomalous values of other gas (e.g.,  $\text{CO}_2$  and  $\text{CH}_4$ ) acting as a carrier gas for radon along preferential leakage pathways. Obtained results show a good correlation between geophysical and geochemical data, shedding light on the fluid circulation in inter-seismic period. The soil gas technique applied in this study has demonstrated to be useful in a geological environment characterized by buried faults in alluvial plains.

The indoor radon hazard can affect the air quality in public and private buildings, and therefore the human health, even in non-volcanic areas, such as the Rieti plain, characterized by active extensional tectonics.  $^{222}\text{Rn}$  can also upraise through permeable faults and fractures, the so-called tectonically enhanced geogenic radon and enter buildings located in the surrounding area of these tectonic structures. It is necessary to take into account this type of contribution and plan the monitoring of Indoor Radon in dwellings located near tectonically active areas.

Overall, high anomalous values were detected, especially of  $^{222}\text{Rn}$  and  $\text{CO}_2$  concentrations and sometimes methane fluxes, highlighting the presence of an advective migration mechanism.

The presence of  $^{220}\text{Rn}$  and  $^{222}\text{Rn}$  in a tectonic environment in the immediate proximity of active faults, as the ones studied in the framework of FACs project, gives a represents an important contribution in such multidisciplinary approach. Indeed, this multidisciplinary approach applied to the study of FAC can also be replicated in other locations and in different geodynamic environments.

**S26.**

**Exploring geoscience communication**

*CONVERERS AND CHAIRPERSONS*

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## **Impacts of regenerative agricultural practices on soil health and carbon sequestration as a driver of rural eco-entrepreneurship towards the creation of a Living Lab in Southern Italy: the case study of FARMS4CLIMATE project**

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*Keywords:* ecosystem services, regenerative agricultural practices, Living Lab.

The dominant farming systems widely spread over the past years, relying on synthetic inputs and mismanagement of agricultural practices, led to a decrease in soil organic carbon (SOC) and contributed to the degradation process of agricultural land, that also threatened the semi-arid Mediterranean regions. At the same time, a growing global human population, which is expected to increase in the next years, is demanding more food, exerting a significant pressure on soils to increase their productivity. Changing the agricultural system is essential to make agriculture no more a cause of decline, but an activity that can improve ecosystems health and quality, such as by creating carbon stocks in the soil, performing functions and providing services with the aim of achieving a condition of long-term sustainability.

The study aims to facilitate the creation and development of Community Based Organization (CBO) that can drive economic growth by fostering agro-ecological C farming. Digital enablers will be developed to make C farming operational for smallholders and stakeholders empowered through programs designed to promote eco-entrepreneurship. Within the CBO, Living Labs will be a tool to co-design rural innovation focused on training and transfer activities, particularly targeted at rural communities and the farming sector. Trainings will be exploited to find solutions, evaluate their benefits and encourage the adoption of digitization tools in order to extend the value chain of traditional agricultural areas in the Mediterranean. A strategy will be developed to assure the optimal visibility and communication of the project activities and objectives and effective dissemination and knowledge-transfer to relevant stakeholders.

Different experimental orchard sites (apricot, peach and yellow-fleshed kiwifruit) were identified in the Mediterranean area and chosen to evaluate the effects of regenerative agricultural practices on SOC and agroecosystem health. A set of sustainable orchard management practices (i.e. no-tillage or minimum tillage of the soil, cover crop, mulching of pruning residues and application of organic amendments) was adopted and its potential benefits and related functions involving the enhancement of greenhouse gases relationships, through carbon storage, the increase of soil fertility, microbial community and biodiversity, water holding capacity and consequent water reservoir in soil, crop resiliency, plant biomass and productivity were assessed in a long-term study. In the experimental orchard sites fertilisation management was based on plant demand and periodical monitoring of soil nitrate content and other macro- and micro-nutrients availability in the soil allowing to reduce mineral fertilizers inputs and consequent environmental pollution and enhance nutrient use efficiency. Optimized irrigation strategy supported by continuous monitoring of weather conditions and soil moisture by tools and sensors was developed to satisfy actual plant water requirements, reducing water losses and increasing water use efficiency. The analysis focuses the attention on both the pivotal role of soil carbon stock on soil structure, water storage capacity, nutrient availability, biodiversity and on carbon sequestration potentials in fruit tree orchards increased by sustainable field practices. Promoting the adoption of increasing SOC management practices in fruit tree orchards could enhance the provision of ecosystem services (ES) and support the development of environmentally friendly actions aimed at the conservation and improvement of soil capital resource. In conclusion the study aims to demonstrate and transfers that the transition towards a sustainable agriculture, which ensures an appropriate land management, can effectively increase the mean annual carbon stocks and maintain the capacity of soils to sustain steady quali-quantitative yield productions over the years for the present and future generations, ensuring global food and climate security.

## Towards the use of Citizen Science for land consumption monitoring

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Land consumption, meant as the variation from natural to artificial land cover, represents a threat to ecological functions and to soil ecosystem services provided (ISPRA, 2014). Furthermore, it is one of the land transformation dynamics capable of altering the ability of a territory to respond positively to the risks associated with climate change (ISPRA, 2022). In Italy the synergistic activity of the SNPA (National System for the Protection of the Environment), consisting of ISPRA (Higher Institute for Environmental Protection and Research) and the regional and provincial agencies for the protection of the environment (ARPA and APPA) supply an yearly updated monitoring of land consumption, through the publication of the report “Consumo di suolo, dinamiche territoriali e servizi ecosistemici” (Soil consumption, territorial dynamics and ecosystem services), providing an updated picture of the transformation processes that cause the loss of soil and its related functions. The methodology used for data collection, done by open-source GIS, is based on photointerpretation of satellite data and orthophotos for the detection of land cover changes due to the phenomenon. Considering the importance of the phenomenon, which is also the subject of national and European policy goals e.g., the “No-net-land-take” by 2050 (European Commission, 2016), the outcome of the monitoring requires multi-levels cross-checking, engaging all the territorial governance subjects and stakeholders. In this perspective, as part of the latest monitoring activities, a WebGIS platform has been introduced, allowing the local administrative officials to consult the ISPRA-SNPA data, giving their own contribution to the monitoring activities, thanks to their expert knowledge of the territory. The initiative, opening to the voluntary engagement of stakeholders as data collectors, could represent a first step towards the application of Citizen Science principles in the collection of land consumption data (Sui et al., 2013).

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## Climate change, effects and strategies in the drawings of elementary school students

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*Keywords:* children drawings, climate change, statistical analysis.

Starting in 2005, the Istituto Nazionale di Geofisica e Vulcanologia (INGV), projected the creation of calendars designed for schools and realized with drawings from a contest for primary school children. Each year, schools enthusiastically participate by sending in pupil's drawings on themes selected as part of the Earth science subjects. Involving primary school children in this project, on the one hand can bring them closer to science and to the natural world and on the other hand give the opportunity to investigate their perspective on the Earth, science, the environment and sustainable behavior.

We performed a preliminary analysis of the children perceived image of the Planet Earth, its sustainability and its future over the drawings collected for the 2009 calendar: "The Earth of tomorrow is in my hands today", the 2010 calendar: "Precious Earth" and the 2021-2022 calendar: "A future sized for the Planet". Drawings were coded and values stored in three different data sheets. A similar classification scheme was designed in order to be able to synthetically describe the sets of images and analyze it. A coarse-grained, quantitative analysis were conducted in order to test and tune the classification scheme, as well as to infer some considerations.

We present and compare the results of the datasets set apart by twelve years, highlighting differences, similarities, convergences. Furthermore, the results provide us a direct and unconventional approach to point out how we convey science - a strategic topic for a suitable future of the humanity - to the players of the world of tomorrow.

## Vesuvius, from risk to resource? The show for the past and future Grand Tour

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Keywords: Mt. Vesuvius, theater, music.

When it comes to disseminating topics related to natural hazards, interdisciplinary is the most efficient approach, if then the leading actor is Mt. Vesuvius, due to its 2000 years of history and the exceptional quantity and quality of the information available, it is mandatory to use this approach.

In the face of natural phenomena, especially the ones responsible for human losses, it is natural to wonder about the causes and whether they can be foreseeable. The first step is to transform the culture of emergency into a culture of prevention and risk mitigation. To do so, the key tool is to implement risk education in all social strata in order to overcome the cultural barriers that consider the volcano only as a burden because of the problems it creates, and not as a resource in the name of security and prosperity.

In this context, we created the show “*Dottò, ma quando scoppia il Vesuvio – il Nuovo Grand Tour*” (i.e.: “*Doc, when does Vesuvius burst? – The New Grand Tour*”) to stage all the ingredients that the Vesuvius machine has been able to produce and preserve over time until today.

For the first time, thanks to this theatrical performance the public can learn about the eruptive history of Mt. Vesuvius and fully understand the functioning of the volcano traveling through time. This itinerant story is possible thanks to the bonding, sometimes even amusing, established between the two protagonists, the “Doc” and the “Maestro”. In the meanwhile, a video showing appealing images flows in the background, accompanied by the live performance of moving musical pieces.

The show is not limited to the description of the volcano eruptive activity that has occurred over the centuries but is also focused on the cultural growth of the vesuvian area, from the phenomenon of the Grand Tour up to modern times, highlighting the many technological discoveries that were displayed in the Neapolitan living rooms over time. The “journey story” not only includes the last eruptive event of 1944 in Naples annihilated by barbarities of the II World War but also the period following the economic boom when, through the new regulatory plan, the foundations to complete the wicked urban expansion in the Phlegrean Fields and vesuvian areas were thrown. This choice will determine the uncontrolled expansion of the urban fabric of Naples, bringing the volcanic risk threshold to today’s growing and unacceptable level.

In the final part of the show, an idea for the solution to the volcanic risk is proposed, highlighting how Mt. Vesuvius can be a powerful economic resource for territorial growth. While it is necessary to work on a program to decongestion at-risk areas, it is also fundamental to modernize the tourist offer, connecting with means of transportation at low environmental impact, the Mt. Vesuvius to all the areas of Campania region. This would trigger a new Grand Tour that could improve tourist programs with a renewed cultural power.

## Combining Geophysics, Sound Engineering and Multimedia Art for improving Communication and Education in Geosciences

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*Keywords:* seismic, music, art.

Communicating complex technical subjects in geosciences can represent a critical challenge especially when the message is addressed to non-technical audiences. In many circumstances, appropriate communication requires innovative approaches to convey complex topics and related issues. Art and music can be used to bridge the gap between scientific and humanistic cultures, and support geologists and geophysicists in this difficult communication task. Modern digital music techniques and sound engineering tools can be particularly useful for that purpose. In fact, music is a natural and familiar domain to everybody and, at the same time, the physics of sound is similar to that of seismology (Dell'Aversana, 2013; 2014). Converting geophysical data into sounds (Dell'Aversana et al., 2016) has numerous applications, from educational purposes to improvements in interpretation. Successful attempts have been made in the hydrocarbon industry, where seismic SEG-Y files have been transformed into MIDI (Musical Instrument Digital Interface) files - the most commonly used format in digital music. These files can be played using "sequencer" software that decodes the MIDI messages into sounds, resulting in "geophysical music" associated with geological systems/features such as hydrocarbon reservoirs and faults. These "geophysical sounds" can be combined efficiently with texts, images, movies, and other media to create multimedia files that improve communication and representation of complex phenomena in geosciences. The use of multimedia also combined with Deep Learning techniques, allows for a better analysis/understanding of Earth phenomena and geological systems such as volcanic eruptions, earthquakes, and hydrocarbon reservoirs, by analyzing and presenting information from different points of view and with variable levels of accuracy. Deep Neural Networks allow extracting and analyzing a wide suite of multimedia attributes from the original geophysical data. These features are used for fast and accurate data classification and for supporting the entire interpretation process. Finally, these multimedia products can be combined with other types of representations to create artistic effects, merging Earth disciplines, music, and art for improved communication and education. We have widely applied this hybrid approach in various real case histories and examples, where technological and artistic aspects are discussed in detail.

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## **The CORE project APP: Teacher's training**

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*Keywords:* teachers, training, risk communication.

The devastating effects of recent natural and man-made phenomena have once again highlighted the gaps in European society's level of disaster preparedness, emphasising the importance of increasing risk awareness and the level of resilience of communities.

The EU-funded CORE project, while identifying and implementing best practices and knowledge by learning from seven past cases (earthquake, tsunamis, flash floods, forest fires, industrial accidents, terrorist attacks and pandemic), devotes great attention to education in schools, making the younger generation a kind of 'sentinels of prevention'. In the project aims, young people are both creators and users of a modern and inclusive APP. A competition involving high schools with technical skills as well as socio-economic backgrounds is being organised around Europe. The first part of the competition requires teachers to receive a bespoke training on risk and risk perception, which also delivers background knowledge on the CORE project, case study phenomenology, guidelines on how to be prepared before an event occurs, how to act during an event and how to increase resilience after the event. The second part concerns content app development and implementation. The competition takes place on two possible lines:

- Content development
- Development of the APP for institutes
- The winners of the competition will present the APP during the final project meeting scheduled for July 2024.

*Acknowledgments:* This work has been supported by CORE ("sCience and human factor for Resilient sociEty") project, funded from the European Union's Horizon 2020 - research and innovation program under grant agreement No 101021746.

## Different examples of serious games to educate risk perception

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Keywords: RiskComm, SeismicRisk, ScienceCapital.

In a geologically interesting land like Italy, and in particular Campania, educating and informing about the concept of risk in general, and specifically seismic risk, is of fundamental importance.

The possibilities of seismic risk mitigation, in fact, depend not only on the scientific community but also on how well-prepared and informed society is about the risk itself. Therefore, training the local population to increase disaster risk preparedness and resilience within our region is crucial.

During the COVID-19 pandemic, we developed, using serious games, two didactic experiences, one dedicated to seismic risk (ALARM) and the other dedicated to climate change (Finding Gaia), targeting secondary school students, their families, and science enthusiasts. Both experiences are characterised by an approach that is virtual and inclusive, allowing participation to people with motor disabilities, and fully interactive, through a series of quizzes, puzzles, and tasks of different difficulty, to include experts/enthusiasts and exploit not only top-down but also peer-to-peer learning.

In 2022, with the reopening to the public of schools and universities, we developed a more intense course, based on the science capital framework, to be delivered before the Escape Room.

The Science Capital framework, developed by Prof. Louise Archer et al. (Archer et al., 2016), refers to a person's science-related resources, such as science-related understanding, knowledge, attitudes, activities, and social contacts. It also offers a key to defining how everyone's store of scientific knowledge is enriched and influenced by their habits, family, and network of contacts. Understanding this context and its dynamics helps us to enhance the resources available for scientific culture, with a view to building a competent and inclusive educational community.

An evaluation phase was carried out to assess the learning experience and the effectiveness of the science communication technique.

This work has been supported by CORE ("sCience and human factor for Resilient sociEty") project, funded by the European Union's Horizon 2020 - research and innovation program under grant agreement No 101021746.

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## SADP - Southern Alberta Dinosaur Project (Canada)

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Keywords: science communication, SADP, fieldwork.

The Southern Alberta Dinosaur Project (SADP) is a field-based enterprise of the Royal Ontario Museum (ROM). This long-term project was previously established with the partnership of the Cleveland Museum of Natural History and the Royal Tyrrell Museum, with a focus on the Milk River region of Southern Alberta, Canada near the border with Montana (USA). The rocks exposed in this area represent some of the oldest dinosaur-bearing sedimentary units in Alberta, and have the potential to reveal new dinosaur species, contributing to our knowledge of this relatively obscure time in the evolution of Late Cretaceous dinosaurs.

The Southern Alberta Dinosaur Project (SADP) aims to perform a complete paleontological survey of this area, with the goals of: compiling a detailed biostratigraphic framework for this region that can be compared directly to the better known and well-dated units of the close Dinosaur Provincial Park locality; to document the poorly known dinosaur fauna of the lower half of the Belly River Group and the Milk River Formation.

This project started over 10 years ago and has benefitted in the last 2 years of the collaboration of the Alma Mater Studiorum of Bologna and of our association. This new partnership was created mainly to support the fieldwork of Earth Science undergraduate students volunteering in this area, who are given the opportunity to gain direct field experience in paleontological prospecting, excavation, and musealization of specimens for these north American museum collections.

The contribution of APPI (Italian Paleontological Paleoartistic Association) aims to bridge this field and research activities with the general public. As a science communication association, APPI has >15 years of experience with this kind of activities in our country. The collaboration with the ROM in the SADP represents our first international partnership with the aim to establish a long-lasting network between these leading research institutions, university students and the general public. Our working group includes not only scientists but scientific communicators and paleoartists as well. Students, supported by Appi with travel grants thus have the opportunity not only to carry out field research activities but also to experiment in the process of popularizing research outcomes, producing palaeo-artistic material, written articles, website and social media contents.

Our final goal is to make the paleontological research activity accessible to a wider audience, from schoolchildren to young students, enabling them to independently perform fundamental research and acquire key communication skills.

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## **Awareness to land degradation phenomena on Earth surface: chronicles from Basilicata (Southern Italy)**

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*Keywords:* land degradation, sustainability, escape room.

It is becoming increasingly important for geoscientists to communicate their key research findings to a wider audience, both to raise awareness of involving citizens in scientific research (Citizen Science) and to gain direct benefits for the health of the Earth through their active involvement.

Appropriate communication requires the means and techniques used to be tailored to audience size and competence.

This work stems from activities realized by the IMAA-CNR (Institute of Methodologies for Environmental Analysis–National Research Council of Italy) in the framework of the European project named SuperScienceMe: REsearch is your R-Evolution - European Researchers' Night, aimed at reaching out to the general public in the regions of Calabria and Basilicata (southern Italy), with a special focus on the young generations.

The goal was to bring the 17- to 18- year-old students from Agri Valley (Basilicata) closer to the research frontiers, and at the same time to provide them with the basic knowledge and methodological tools to understand the phenomenon of land degradation in a holistic way involving different disciplines: remote sensing, mineralogy, geochemistry, and geophysics.

The activities began with classroom lectures to provide students with an overview of the land degradation processes and the basic physical principles of the various disciplines involved and continued with field investigations. A final visit to the IMAA-CNR laboratories helped to highlight the key role of using a multidisciplinary approach to address complex issues such as land degradation.

To conclude the experience, the students were asked to devise an escape room, based on storytelling, technical-scientific puzzles and quizzes encompassing all the disciplines involved.

Part of the activities involved the administration of a questionnaire to understand the student's level of awareness regarding the main environmental issues on the international agenda (climate change, desertification, sustainable use of resources), with a specific focus on the impacts in the local context (Basilicata).

The results showed a partial awareness of land degradation processes and impacts, which gradually increased as the activities developed. Despite a widespread lack of knowledge and awareness of certain issues, this experience has shown that the use of less conventional and standardised educational tools has great potential in stimulating the environmental and scientific sensitivity of high school students, particularly with regard to a more comprehensive perception of the wide concept of environmental sustainability. Another advantage of the illustrated approach is that it can be easily exported to other groups of citizens.

## Geodiversity assessment in the Beigua UNESCO Global Geopark (Liguria, Italy): valuing geoheritage for education, tourism, and community engagement

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Keywords: geosite, geoconservation, geosystem services.

The Beigua Geopark extends over 42 376 hectares, and it comprises the provinces of Genova and Savona, including eleven municipalities. In 2005, it was acknowledged as member of the European Geopark Network (EGN) for its unique geological features and for the conservation, enhancement, and territorial development actions. Moreover, since 2015, it has been one of the eleven Italian geoparks included in the in the prestigious list of UNESCO Global Geoparks (UGGp).

The Beigua UGGp is mostly composed of metamorphosed ophiolites and their sedimentary cover, with minor occurrences of metamorphosed rocks of continental crust (gneiss and sedimentary carbonate successions). All the lithologies are capped by limited outcrops of clastic sedimentary rocks and Quaternary sediments. The Beigua UGGp meta-ophiolite (i.e., Voltri Massif Auct.) is among the remnants of the Tethyan ophiolites in the Mediterranean area, and one of the main ophiolitic complexes of the Italian Alps–Apennine system. The most distinctive feature of the Beigua UGGp is its geodiversity, which includes a large variety of geological environments, landscapes, rocks, minerals, fossils, and soils. The geodiversity of a territory is strictly integrated with people, their environment, and their culture, through interactions between biodiversity, agricultural soils, productive activities, and evolutionary phenomena with the surrounding environment, considered in its totality (Stanley, 2001). To represent the remarkable geodiversity of the Beigua UGGp, fifty-four geosites have been recognized in geopark territory, twelve of which already included in the National Inventory of ISPRA.

The goal of this work was to bring out, with a scientific approach, the value of geodiversity and geological heritage in the Beigua UGGp by i) assessing the geodiversity- and geoheritage-values and their potential impact on the local communities, ii) enhancing uniqueness and territoriality of local productions to promote sustainable development, and iii) engaging the local communities in geoconservation strategies and valorization actions.

The preliminary results comprise: i) the qualitative and quantitative assessment, based on Brilha's method obtained from ten selected geosites (Brilha, 2016; Marescotti et al., 2022); ii) the mineralogical, lithological, and geochemical characterization of geosites rocks and soils for the determination of the natural background as well as for the identification of potential markers of territoriality; iii) the realization of a three-steps model to assess the perception and the value of geodiversity to be applied to tourism, education and local products. The three-step model comprises i) the selection of a focus group with stakeholders, ii) the drafting of a national-scale survey, and iii) the planning of a field experiment based on the survey's results.

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## The many voices of Vesuvius. Anthropology of risk communication

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*Keywords:* misinformation, anthropology, risk.

The volcano Vesuvius, in southern Italy, is one of the best known in the world: it is both much studied and monitored, and much narrated and mediated. Its “success” also makes it a “protagonist” of contemporary communication, since it always attracts a large audience, but at the same time makes it subject to misinformation and disinformation, which, as a 2013 World Economic Forum study put it, is “one of the main risks for modern society”. This proposal intends to contribute to collective reflection by outlining the context in which the current communication of the Vesuvius risk unfolds, which, in terms of the media, can be framed in three types of information 1) the communication held by national television and newspapers, which tends to be more institutional, in the sense that official news is mainly communicated, expert knowledge is interviewed from within scientific research and civil protection institutes; 2) the information disseminated by local newspapers and websites, which is more uninhibited, because it uses a less rigorous and more sensationalist language, to the point that sometimes the director of the Vesuvius Observatory had to issue a press release explaining the groundlessness of certain fears or alarms; 3) the so-called ‘counter-information’ of anonymous websites or websites with a very short average life span because they open and close for the time needed to accumulate a high number of clicks, which are vehicles for news that is often catastrophic, exaggerated, apocalyptic, not infrequently conspiratorial.

Focusing on the ‘bad information’ concerning Vesuvius, one can see numerous variants of it: the hoax (the news-fake), the fake-news (bufala, in Italian, which aims to counteract any unveiling, aiming at ambiguity, at the swamp between the true and the false), the provocation (the false provocation), the absurd-but-credible news, the product of fiction, the anti-news created to make people laugh and not to misinform. To all this must be added further forms of manipulation and adulteration of messages, often stemming from simple sloppiness, oversimplification and superficiality. In any case, these are all ways of polluting information, just as harmful as other forms of pollution of our ecosystem (Manfredi, 2015).

Obviously, all this has social repercussions because the mass media contribute to the construction of a ‘local filter’ that relates personal and global threats, the micro and the macro perspective, so we can say that it is precisely this attention by the press that contributes to the social construction of risk (Wallman, 2001). In other words, the media communication of risk relates, on the one hand, the different meanings of the actions of social groups and, on the other hand, general and abstract categories.

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## **Disclosure of geological sciences through the geosites: the example of Geoscuola project in Basilicata**

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*Keywords:* disclosure, GeoScuola, Basilicata.

GeoScuola is an educational project aiming at promoting Geoscience among students of first degree – secondary school in the Basilicata region. The initiative, promoted by ExtraGEO, spin off of Basilicata University, in collaboration with Shell E&P Italy, official sponsor, has been proposed since 2014 and reached the sixth edition. The project involved 20 schools and 2000 students up today. Teaching activities, generally carried out between March and May, are divided into 5 frontal lessons and 1 final field trip in the national and international geosites of Sasso di Castalda (PZ), Castelmezzano (PZ) or Rionero in Vulture (PZ). The teaching program encompasses the main topics of Geoscience (origin of solar system, plate tectonics, rocks recognition, volcanoes and earthquake, energy overview and geological heritage) while classroom activities benefit from multimedia tools and advanced technologies. During lectures, laboratory and interactive approaches are adopted, with innovative teaching methods such as cooperative learning, flipped classroom, mind mapping and problem posing. In this paper we present the experience of 6 editions of GeoScuola, analyzing methodologies and feedback. We also demonstrate how the school can become a dynamic system, capable of evolving together with the territory and acting for protection, enhancement and promotion of geological heritage.

## **The contamination of quantitative approaches with qualitative methods as a communication strategy for geoscience. Practices from field work in human geography**

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*Keywords:* fieldwork, qualitative methodologies, contamination.

New methods to research and fieldwork are necessary to help non-technical audiences to approach the representations of place, space and territory more readily. Whilst the debate between protagonists of qualitative and quantitative methodologies can become somewhat partisan, it is evidence that the two approaches should be used to contaminate and complete one another. Indeed, physical geography themes often favor a more scientific (and quantitative) approach, whereas more people-centered fieldwork and research often require a balance of qualitative and quantitative methods.

This work aims to show how qualitative methods can be used for pragmatic reasons in situations where formal and quantified fieldwork and research is not possible: it will present some of the results achieved by coupling the quantitative approach of the spatial analysis with the qualitative methodology of human geography, in particular studying the economic development of inner areas, the social impacts of Covid-19 pandemic and the increased social risk connected with land degradation in the agricultural regions of Southern Italy (Matarazzo et al., 2022a, b; Matarazzo et al., in press).

Most quantitative fieldwork uses a strict 'route to enquiry' approach, whereas qualitative research can involve a more 'fluid' or recursive strategy. In this latter approach the hypotheses and questions may be manipulated and expanded, as the research process evolves. In the wide field of geography, there are a number of key methods in the fieldwork and research toolkit that are used to gather qualitative information:

Observation (of people and places), for example making field notes either by hand or by using a dictaphone, sketches, video and photographic evidence. This type of work is sometimes called 'ethnographic' fieldwork and research.

Informal and in-depth interviews, for example a more in-depth discussion with a group of people about a particular issue in the local area. In-depth interviews are much longer than their questionnaire counterparts. This can also include *focus groups*.

Textual analysis including printed matter, websites and other relevant audio-visual material. This can help uncover the identity of a place and its people.

Sequential and recursive approaches to fieldwork and research.

Perhaps the critical skill in quantitative fieldwork is not the mechanical act of observation, recording and analysis, but moreover appreciation that something or some data is significant and noteworthy. Qualitative approaches represent a different way to achieve a different kind of understanding, one that appeals to non-technical audiences who find satisfaction in the recognition of what is going on at a more intimate or personal level. Fieldwork therefore becomes a very powerful tool for self-understanding and communication of geoscience. The results from qualitative research are often more understandable to people who are not statistically trained and can reveal more insightful geographical thinking than purely numerical outcomes.

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Matarazzo N., Coluzzi R., Imbrenda V., Lanfredi M. & Russo Krauss D. (2022) - La «perifericità» della Basilicata quale fattore positivo in tempo di epidemia. In: Casti E., Riggio A. (eds), Atlante del Covid-19. Geografie del contagio in Italia, Roma, Associazione dei Geografi Italiani, 319-338.

Matarazzo N., Imbrenda V., Coluzzi R., Samela C., Pace L. & Lanfredi M. (in press) - L'industrializzazione dell'agricoltura nella Piana del Sele: remote sensing e geografia. Bollettino dell'Associazione Italiana di Cartografia.

## Comics as a new tool to communicate science: an example from the University of Perugia

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*Keywords:* comics, mineral exhibition, dissemination.

Science communication strategies are of paramount importance to efficiently disseminate research results. One of the main targets of University outreach programs is to overcome academic boundaries and reach a wider audience. Different approaches and new languages can be used to explore which one is more effective for different targets (primary school students, secondary school students, generic public etc.).

Comics in recent years had a new golden age, Manga or Zerocalcare are very successful among teenagers for example. Recently Leo Ortolani published the Space Trilogy in collaboration with ESA and ASI, an example of how comics can be a powerful tool to disseminate science. Since 10 years the publications of Comics&Science, a CNR project, aim to communicate science to a wide audience outside Academy.

Here we present two projects that use comics as a new tool in scientific dissemination.

We have started LabComUnipg, a laboratory to monitor and implement the communication of scientific knowledge of the University of Perugia. LabComUnipg is an interdisciplinary lab that intends to combine scientific points of view from all the scientific disciplines from hard sciences (geology, mathematics, agronomy) to social sciences (political sciences, history etc). The project stems from the need to question the self-referentiality, sometimes excessive, of scientific research, because we believe that greater social and cultural dissemination of research results can help to strengthen public debate and inform and guide policies.

As pilot project we targeted students of Umbrian secondary schools that will be involved in the project by using comics as methodology. They will be guided to produce a comic on the scientific arguments discussed in class with researchers.

The second example is the exhibition “Il Mondo A Colori: Uno Sguardo Su Arte, Pigmenti E Minerali” set up at the Museo Archeologico Nazionale dell’Umbria. In the exhibition minerals are shown together with archeological material aiming to illustrate how pigments used by artists during centuries are made from minerals and how we know this. A special volume of Comics&Science, “The Colour Issue”, was produced as part of the exhibition project, Walter Leoni and Filippo Paparelli translated the topic of the exhibition in a comic using Leonardo and Peruginetto characters. These characters were also used as tag throughout the exhibition.



## Trust in experts and authorities as influencing factors of communities' risk perception

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*Keywords:* trust in authorities and experts, risk perception, disasters preparedness.

When a disaster occurs, in its aftermath authorities issue directives and researchers give their scientific suggestions on how to behave in order to lower the probabilities of cascading effects. Messages spread out by policy makers and scientific community get positive effects, only if they are trusted by citizens. Trust in both authorities and experts has a key role, as it influences not only risk perception but it very relevant also for disasters preparedness (Algan et al., 2021; Bronfman et al., 2016)

By considering past disasters analysis a lot can be learnt in terms of what worked and what not after the event hit a region.

Within the framework of the European project entitled “*sCience and human factOr for Resilient society*” (H2020 CORE) trust in authorities and experts is considered essential to understand in what measure it influences individuals' risk perception (Wachinger et al., 2012). The activity is focused on a in depth bibliographic research where some hypothesis will be tested thanks an online survey in which socio-economic indicators will be considered as “descriptive factors”. Simple and tested questions will be asked to test people's risk perception, their preparedness with respect to some hazardous events and their trust in both authorities and scientists. The aim of the survey is twofold: on one hand, it permits to consider the effects on citizens' behaviors in presence of different hazards, that is earthquakes, tsunami, wildfire, industrial accident, terrorist attack, flash flood and COVID-19 pandemic; on the other one, it allows to underline best practices adopted by institutions during emergencies in different countries by also investigating the role of fake news.

Survey results will feed policymakers (at EU and national levels) & scientific community guidelines, in order they can understand which the winning strategies are to be trusted by populations.

This work has been supported by CORE (“*sCience and human factor for Resilient sociEty*”) project, funded from the European Union's Horizon 2020 - research and innovation program under grant agreement No 101021746.

Algan Y., Cohen D., Davoine E., Foucault M., & Stantcheva S. (2021) - Trust in scientists in times of pandemic: Panel evidence from 12 countries. *Proceedings of the National Academy of Sciences*, 118(40), e2108576118. <https://doi.org/10.1073/pnas.2108576118>.

Bronfman N.C., Cisternas P.C., López-Vázquez E. & Cifuentes L.A. (2016) - Trust and risk perception of natural hazards: implications for risk preparedness in Chile. *Natural hazards*, 81, 307-327. <https://doi.org/10.1007/s11069-015-2080-4>

Wachinger G., Renn O., Begg C. & Kuhlicke C. (2013) - The risk perception paradox—implications for governance and communication of natural hazards. *Risk analysis*, 33(6), 1049-1065. <https://doi.org/10.1111/j.1539-6924.2012.01942.x>.

## **Dedicated storytelling to introduce pre-scholar children to the seismic risk: Giuseppa e Tremotto the dragon**

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*Keywords:* seismic risk, storytelling, Kamishibai.

How can we explain seismic risk to pre-scholar children? Or earthquake dynamics? Educational material and activities available both online and on literature are limited to engage pre-scholar children (3-5 years) on geophysics concept. Since infants and children are not yet aware of the dangers and must therefore be protected from potential injuries, teachers would be one of the primary addressees of prevention interventions. Adequate and detailed information on seismic risk is required to plan and implement appropriate prevention interventions. Italy is a seismic country being in the merging zone of African and Euro-Asiatic plates and several destructive earthquakes occurred in the last few decades. For this reason, it is important to educate children about seismic risk and make them aware of simple behaviors and expedients that can save their life. During August 2016, a Mw 6.2 earthquake occurred at Amatrice (Central Italy) and was felt in a ray of more than 200 Km far from the epicenter. After this catastrophic event, a new method to approach earthquake has been developed and tested at a kindergarten with the collaboration of teachers willing to educate their young students to deal with natural risks and teach how properly behave.

In a technological era where children are used to play/interact with tablets, smartphones and computers, the developed method consists in a storytelling narrated using a “kamishibai” (imagine theatre) with manually sliding paper imagines. This old technique, used by Japanese wandering storyteller, is very incisive because the kamishibai produces by itself a scenography that creates a strong involvement between the teller and the listeners.

The story is about the young girl Giuseppa that meets Tremotto the dragon whose jumps cause earthquakes. Inside the story, there is a nursery rhyme explaining what to do when the dragon jumps and so the school shakes. The story telling has just the purpose to catch children attention while the nursery rhyme helps to teach, entertaining, the right behaviors to adopt during an earthquake. After a break during which children can create/color their own dragon, there is a game having the aim to draw up the life-saving actions. The game is developed by means of a magnetic blackboard divided in two parts (true and false), magnets of the story characters acting (in the right or wrong way) during an earthquake. One by one, children pick a magnet from a bag and put it on the right/wrong side of the blackboard. After the first test, the “Giuseppa and Tremotto the dragon” method has been carried out in several kindergartens and public engagement events always obtaining a positive outcome. In particular, teachers and parents love Giuseppa story because activities are proposed in a playful but, at the same time, seriously way especially when life-saving actions are showed communicating the importance of what children are learning.

**S27.**

**Geoscience at School**

*CONVENERS AND CHAIRPERSONS*

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**The dissemination of Geosciences for the enhancement and protection of the historical and cultural heritage, through educational workshops and geological itineraries:  
The Basilica of St. Paul Outside the Walls in Rome**

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*Keywords:* geological heritage, cultural heritage, Agenda 2030 sustainable goals.

In order to implement environmental protection measures and guarantee our Country sustainable development, in accordance with the objectives set out in the UN 2030 Agenda, it is necessary that all citizens are sensitized and involved, especially the new generations. It's fundamental let them know the territory in which we live, a country rich in resources, but sometimes vulnerable. Hence the dissemination of Geosciences through didactic-laboratory paths of Alternation School-Work (today PCTO - Paths for Transversal Skills and Orientation) and geological itineraries in the city of Rome, that the Department of Sciences - Geology Section of Roma Tre University has addressed mainly to students of the high schools of the capital, to understand, comprehensively but simply, the geological history of our city, its transformations over time, resources, but also risk factors. Among the resources, an important place is occupied by lithoid materials, which have guaranteed over time, thanks to increasingly advanced mining techniques and the expansion of application fields, the development of a great civilization, materials now “masked” by intense urbanization, but which however find expression in the rich historical-architectural heritage, together with the ancient marbles imported to Rome, especially between the second century B.C. and the 4th AD., from quarries of the Mediterranean basin, as evidence of the economic and social development of Rome. The realization, together with students of the E.Q. Visconti High School in Rome, of a geological itinerary among the heterogeneous lithoid resources of the Basilica of St. Paul Outside the Walls in Rome, has allowed to highlight how through Geosciences and the study of the “marbles” used there, it is possible to reconstruct the historical-artistic evolution of a monument, the economic and social context in which it is inserted, and last but not least the modifications of the landscape with which this is in continuous relationship, raising awareness of a protection of our architectural and landscape heritage.

## **The historical geological collections of the “Ennio Quirino Visconti” Higher School at the Roman Collegium: a hidden geological jewel in Rome, from the XVII century to nowadays**

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*Keywords:* geological heritage, cultural heritage, Agenda 2030 sustainable goals.

The geological collections, hosted in the Liceo Classico Statale “E. Q. Visconti” in Rome, from the “wonders” of Jesuit Father Athanasius Kircher to the nineteenth-century collections and the present-day “Wunder Musaeum”, will be presented in this presentation. These collections represent a rich and “hidden” geological jewel preserved in the heart of Rome, made up of thousands of minerals, rocks, fossils and teaching tools, acquired through a long and fascinating story. A historical-scientific heritage that the “Geomuseum” project, developed between the geologists of the University of Roma Tre and teachers of the higher School, has made possible in order to enhance it and make it accessible to the general public and the students, for educational purposes and for awareness towards sustainable development, as a goal indicated in the UN 2030 Agenda.

## **Sustainable city virtual game: how to engage students in sustainable lifestyles**

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*Keywords:* Agenda 2030, educational games, virtual worlds.

The Sustainable City Game (S-City Game) is a game created to approach the United Nation Agenda 2030 and Sustainability topics. A cardboard version, already tested, has been translated as a digital version, for on-line school activities. This educational game aims to increase students' awareness about a more sustainable lifestyle, encouraging them to take action towards a responsible management of planet resources. The S-City virtual game has been created in a virtual world based on the 3D Opensimulator platform that can be accessed by teachers and students as avatars. Virtual worlds can offer new possibilities for education, teaching and learning formats and it was evident especially during COVID-19 pandemic, when most Italian schools adopted distance learning (Allison & Miller, 2012; Littleton, 2008). In fact, S-City digital game, histed in the Techland virtual world, allows students to investigate, in an active way, topics like water saving, carbon footprint, ecological rucksack, circular economy and waste reduction, starting from daily routine actions, like eating and dressing. The game is planned to be played by K6-K10 level students. A multidisciplinary approach is used, with inputs from several disciplines, to have a holistic vision of the Sustainable Development Goals (SDGs). The game has been tested both with teachers and students, and the results are very satisfying in terms of involvement of students as well as teachers' interest. Students and teachers declared that it is an effective and engaging educational tool to vehicle the key principles of Sustainability and good practices in everyday life. This gaming approach allows students to acquire knowledge (Paras, 2005) and key competences of sustainable behaviours and active citizenship for eco-friendly lifestyles and to develop problem-solving attitude and digital skills.

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Littleton F. & Bayne S. (2008) - Virtual worlds in education. The Higher Education Academy Subject Centre for Education, Newsletter No. 10. <http://escalate.ac.uk/4453>.

Paras B. (2005) - Game, Motivation, and Effective Learning: An Integrated Model for Educational Game Design. DiGRA Conference: Changing Views: Worlds in Play, International Conference.



## **Joining the Barcelona manifesto for the teaching of Geosciences: an EGU initiative to emphasize the relevance of Geoscience education for the building of citizenship**

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*Keywords:* geoscience education, citizenship, Barcelona Manifesto.

Geosciences - together with Physics, Chemistry, Biology and Mathematics - make up the core of the basic sciences. Apart from the university degrees, in which future professionals are trained, the relevance of their contents for the building of citizenship is currently not enough recognized by the policy makers and the educational authorities. Geosciences offer the opportunity to:

- Describe, analyse and interpret the present and the past of the Earth and, by extension, of other planets
- Acquire an integrated vision of Nature as well as to forecast its future
- Understand the deep interactions and interdependencies among the terrestrial subsystems
- Provide interpretation of materials and processes and their evolution throughout history.

Geosciences play a primary role in aspects of social, economic or environmental relevance that are basic for all citizens, like:

- 
- Geological resources (minerals, rocks, water, soils, hydrocarbons, etc.) and the impact of human activity on their efficient and sustainable exploitation.
- Climate change and global warming
- Natural hazards (earthquakes, volcanic eruptions, tsunamis, floods, landslides, etc.)
- The need to know, value and preserve the geological heritage as a witness of the processes that have shaped the planet and the evolution of life in the past
- The 17 Sustainable Development Objectives promoted by the United Nations, in such relevant aspects as sustainable agriculture, water, energy, oceans, ecology, climate change, heritage preservation, disaster reduction...

It is therefore essential to:

- Ensure in every country an appropriate presence of the geosciences in the school curricula
- Define key principles for geoscience literacy as reference for curricular designs, recognizing the singularity of field and laboratory work that characterize geosciences
- Encourage the vocations to take university studies in the different geoscientific careers that ensure the need of professionals in that our societies demand.
- Demand the inclusion of Geoscience subjects in university degrees and masters in which such training is relevant to reach an appropriate vision of our planet and its dynamics
- Set mechanisms that ensure the scientific and didactic competence of teachers dealing with geoscientific contents at pre-university levels.

For these reasons, as organizers of the session GEOSCIENCES AT SCHOOL, we decided to join this EGU initiative, inviting educators, entities, associations, organizations to share these reflexions and join this manifesto. We also encourage everyone to disseminate it among citizens and, especially, to share it with the policy makers and educational authorities.

## Science@school: the example of the GIFT workshops

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Keywords: geoscience, school.

Geoscience Information for Teachers (GIFT) workshops are teacher enhancement workshops organized by the EGU (European Geosciences Union) Education Committee and held in conjunction with the EGU annual General Assembly. The programme focuses on a different general theme each year (<https://www.egu.eu/education/gift/workshops/>). Past themes have included, for example, 'Energy and Sustainable Development', 'The Carbon Cycle', 'Mineral Resources', 'The Solar System and beyond' and 'The Mediterranean'. The 2023 topic, on the 20<sup>th</sup> anniversary of GIFT, was 'The key role of geosciences for the global challenge of sustainable development: the Agenda 2030'.

These workshops combine scientific presentations on current research in Earth and Space Sciences, given by prominent scientists attending EGU General Assemblies, with hands-on, inquiry-based activities that can be used by the teachers in their classrooms to explain related scientific principles or topics. Participating teachers are also invited to present their own classroom activities to their colleagues, regardless of the scientific topic. The main objective of these workshops is to communicate first-hand scientific information to teachers in primary and secondary schools, significantly shortening the time between discovery and textbook.

The GIFT workshop provides the teachers with materials that can be directly incorporated into their classroom, as well as those of their colleagues at home institutions. In addition, the full immersion of science teachers in a truly scientific context (EGU General Assembly) and the direct contact with leading geoscientists stimulate curiosity towards research that the teachers can transmit to their pupils. The value of bringing teachers from many nations together includes the potential for networking and collaborations, the sharing of experiences and an awareness of science education as it is presented in other countries. Since 2003, the EGU GIFT workshops have brought together more than 1500 teachers on site and 190 virtual participants from 58 countries worldwide. At all previous EGU-GIFT workshops teachers mingled with others from outside their own country and informally interacted with the scientists, providing a venue for rich dialogue for all participants. The dialogues often included ideas about learning, the presentation of science content and the curriculum. For their scientific content, the GIFT workshops are of high societal value.

## **“Antropocene: alla scoperta delle rocce 2.0”: a multidisciplinary laboratory about plastic rocks formation**

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*Keywords:* plastic rocks, environment, Anthropocene.

The formation and evolution of sedimentary rocks are closely related to the interaction between climatic aspects, type of eroded material, and deposition environment, which are all influenced by human behavior and activities. In the current Anthropocene epoch, plastics are one of the most common materials deposited in active sedimentary environments, that settle and compete with the rest of the sediment, threatening the entire marine and terrestrial ecosystem. Currently, many of these plastic agglomerates and sediments have attracted the attention of the scientific community, and several nomenclatural classifications have been proposed (De la Torre et al., 2021). The focus on environmental issues, particularly in marine environments, has become a widespread topic with importance in both the scientific and social communities, such that numerous social projects and thematic events are widespread worldwide. On the occasion of the “Festival della Scienza di Verona 2021”, the scientific communication group “La Sagra della Scienza” presented a documentary film that traced the genesis and evolution of different types of rocks (magmatic, clastic, carbonatic) along with the plastic rocks. The video was addressed with a multidisciplinary online laboratory aimed at raising children’s awareness regarding the damages caused by the incorrect disposal of plastics. The interactive activity gave emphasis on the longevity of the different plastic compounds in the various sedimentary environments, on the good practices for the disposal of existing plastics and possible alternatives to replace them.

De la Torre G.E., Dioses-Salinas D.C., Pizarro-Ortega C.I. & Santillán L. (2021) - New plastic formations in the Anthropocene. *Science of The Total Environment*, 754, 142216. <https://doi.org/10.1016/j.scitotenv.2020.142216>.

## **The LAB2GO project: enhancement and sharing of Earth Science laboratory practice in secondary schools**

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*Keywords:* geoscience hands-on activities, school laboratory enhancement, school laboratory sharing.

The LAB2GO project was firstly launched in 2016 by Sapienza University of Rome in collaboration with the Italian National Institute of Nuclear Physics (INFN) to promote laboratory practice at secondary schools. LAB2GO is a PCTO (Percorsi per le Competenze Trasversali e l'Orientamento) project originally financed by the Italian Ministry of University and Research through the PLS (Piano Lauree Scientifiche) program. The project has the twofold aim of valorising the school laboratory infrastructures and science museums, and training secondary school teachers in laboratory practices by setting up experimental kits and events open to the school community. The project also provides for the documentation of the implemented laboratory experiences, promoting their dissemination among a network of schools built-up through a Wiki platform.

Teaching Earth Science in schools is often neglected or poorly cared, often due to the lack of an appropriate geoscience background among teachers. Therefore, the Department of Earth Science of Sapienza has enthusiastically participated in the LAB2GO project since 2017 with an Earth Science program that offers two laboratory practices paths. The first path, “*Rocks: from microscope to urban buildings*”, includes inventorying school rock collections, selecting rock samples, producing thin sections to be observed under a simple USB optical microscope modified with the addition of two polarizing filters, and a field-trip in the Rome city centre to recognize the rocks used to build some of the most impressive monuments. The second path, “*Earthquakes from deep dynamics to site effects*”, includes the introduction to earthquake physics and site effects, the set-up of experimental kits such as the *spring-slider* for the dynamic simulation of earthquakes, and the *seismo-box*, to reproduce the resonance effects on buildings under seismic shaking at variable frequency, and a field-trip in the Rome city centre to observe and understand the localized earthquake effects on some of the most impressive monuments. The LAB2GO Earth Science program is attracting an ever-increasing number of students to the Earth Science disciplines. Nonetheless, to better promote the role of geoscientists in the society, for promoting sustainable development and resilient communities, the LAB2GO Earth Science program LAB2GO Earth Science program will be expanded with new topical experimental kits.

## **Integrating the Italian and Uzbek higher education system in Geosciences: the example of the preparatory year at the Branch of the University of Pisa in Tashkent (Uzbekistan)**

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*Keywords:* internationalization, sustainability, higher education.

The Branch of the University of Pisa in Tashkent was established in 2022 in accordance with the Agreement between the State Committee of the Republic of Uzbekistan on Geology and Mineral Resources, the University of Geological Sciences, Uzbekistan (UGS), and the University of Pisa (UniPi). The main tasks of the Branch are the integration of educational, scientific, and production processes, as well as the preparation of highly qualified specialists to develop the geosciences of Uzbekistan, combining exploration and mining processes with environmental sustainability.

The opening of a new bachelor's degree in Geology (L-34) (first-degree course) in a foreign country hinges on the internationalization process of UniPi. In these regards, this BSc course is the first organized by UniPi in a foreign branch, and the first in Geosciences delivered abroad by an Italian University. This BSc will prepare graduates with the skills of L-34 courses and a focus on georesources and environmental geology.

To harmonize the differences between the Higher Education (HE) curricula in the two countries (Italy and Uzbekistan), UGS and UniPi came to the agreement to adopt EU curriculum with some changes made for fitting it into local educational standards. One of them is to introduce a Preparatory Year (PY) to fulfill the Italian requirements for a minimum of 12 years of school to access to HE and satisfy the needs in the preparation of incoming students. The PY is a one-year course whose aim is to complete the preparation needed by students with only 11 years of schooling to enter a UniPi BSc program and includes several fields of study to achieve a solid background in science and an intensive course in English language to achieve a B2 level, necessary to attend the BSc courses in English. The first semester includes teaching of English, as well as basic math, physics, and chemistry taught in Russian. The second semester includes basic physics, chemistry, math, and a course of Introduction to Geosciences, fully taught in English. The peculiarity of this PY is the relevant role given to geoscience subjects. The contents of the Introduction to Geosciences course involve four main parts: i) the physics of the Earth: cartography and base astronomy; ii) the four spheres of the Earth: geosphere, hydrosphere, atmosphere, and anthroposphere; iii) the dynamic planet: plate tectonic and geological time; iv) the Anthropocene: the global changes and the use of natural resources. These contents refer to the Italian Ministry Guidelines for high school natural sciences curricula and to the International Geoscience Syllabus, prepared by International Geoscience Education Organization (IGEO) and the International Union of Geological Sciences Commission on Geoscience Education (IUGS-COGE) in 2014.

This project also represents an opportunity to test the teaching ability of the Italian University in a foreign and culturally distant context, exporting the educational model of our country.

## **Geosciences in natural sciences and in civic education in Italian upper secondary school: is interdisciplinarity a resource?**

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*Keywords:* geosciences, civic education, interdisciplinarity.

Since Geoscience is mainly taught, in Italian upper secondary school, within Natural Sciences together with Chemistry and Biology, an interdisciplinary approach (Klein, 1991) could be useful to make Geoscience teaching more effective. In addition, since September 2020, Civic Education has been introduced in Italian schools: this could be a new opportunity to develop interdisciplinary themes involving Geosciences.

To get an initial picture of Geoscience teaching and of the relationships with National Indications for Licei and the Guidelines for ITIS and Vocational Institutes, in January-February a survey was sent to Italian upper secondary schools. The survey was aimed at investigating three main points: (1) the amount of time dedicated to Geosciences during different school years and (2) how many hours were dedicated to the Geoscience topics within Civic Education; (3) the teachers' perceptions about interdisciplinary teaching of subjects pertaining to the Natural Sciences as a possible approach to foster learning in the Earth Sciences.

The survey was sent to 500 schools, selected to cover all the Italian regions and having more than 1000 students. We received answers from 249 teachers, largely from Liceo.

The survey showed that about half of the teachers are over 40 years old (from OECD data - 2018- the average age of teachers is around 49 years old) and in concordance with OECD data - 2018- a 70% turn out to be female. Approximately 68 % do not have a geology background, confirming a situation that does not differ from a previous survey carried out between January-March 2014 (Realdon et al., 2016).

The picture that emerged provides several points for reflection: (1) the time dedicated during the year to geosciences was found to be very small in some cases, especially in the second two-year period; (2) Civic Education is an opportunity to address Geoscience issues but in some cases it seems to be the only discipline to develop these topics; (3) most of the teachers interviewed expressed themselves favorably about the effectiveness of an interdisciplinary approach within Geosciences.

In conclusion, there still remains a criticality in the time dedicated to Geosciences, probably related to the initial background of teachers. Therefore it would be necessary to focus on teacher training, to overcome the inevitable initial knowledge and methodological deficiencies in the different disciplines pertaining to the teaching subject. Also worthy of attention is the teaching of Civic Education, which turns out to be a real resource in the education of future citizens regarding the importance of Geosciences for society.

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## “TRASH CAMP: an experiential learning path for Global Citizenship Education”

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Keywords: plastic pollution, circular economy, global citizenship education.

In 2019 we achieved the record production of 353 million tons of plastic waste, of which 9% was recycled, 19% incinerated, 50% disposed of in landfills, while the remaining 22% was abandoned in illegal landfills, burned in the open or dispersed in the environment (Geyer, 2017). Plastic is found everywhere and harms all forms of life, also contributing to the overexploitation of geo-resources such as oil and coal and influencing global warming. We are facing a global emergency and Environmental Education (Parejo, 2021) at school is essential to enable pupils to understand and deal with this situation. This work presents an interdisciplinary didactic path in the field of Civic Education to link the SDGs (Sustainable Development Goals) of Agenda 2030 to Geosciences and the topic of Circular Economy. Working with operational teaching methodologies of the STEAM disciplines such as inquiry based learning (Bybee, 2016), combined with cooperative and outdoor learning scenarios, we have proposed in 6 schools in the Marche region for a total of sixteen high school and 327 pupils involved a project that included the following activities: a) seminar I about plastic and its environmental impact; b) laboratory I, analysis of the plastic waste produced at home; c) seminar II, linear economy vs. circular economy model in which waste is a resource to be introduced into new production cycles (e.g. geomaterials and transformation of waste from construction, transformation of used oils into biofuels, recovery of elements contained in WEEE, waste from electrical and electronic equipment, etc.); d) laboratory II, production of bioplastics from food waste (coffee waste, expired milk, egg shells, bovine/porcine collagen); e) clean up of parks/school yards/beaches as an initiative of Global Citizenship Education (Pigozzi, 2006); f) production of short papers, where pupils, in groups, described to classmates and teachers insights into the topics dealt with. Through the evaluation of pre- and post-activity questionnaires administered to the students involved, we observed a significant increase in knowledge on Sustainable Development compared to the starting level and a greater awareness of the central role that individual citizens play in terms of reducing consumption and waste generation.

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Geyer R., Jambeck J.R. & Law K.L. (2017) - Production, use, and fate of all plastics ever made. *Science advances*, 3(7), e1700782, <https://doi.org/10.1126/sciadv.1700782>.

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Pigozzi M.J. (2006) - A UNESCO view of global citizenship education. *Educational Review*, 58(1), 1-4.

## MEMOSIL: a Path for Transversal Competences and Orientation (Italian PCTO) aimed at increasing seismic risk perception in high school students. Methodology, activities, and results

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Keywords: earthquake, risk perception, PCTO.

Risk perception entails the subjective assessment of the chance of a definite peril and how concerned the persons are with the effects. Risk perception influences people to take proper actions when dealing with natural hazards. People who perceive a high risk where they live are more likely to take adequate countermeasures and support institutional actions even if new efforts are needed (Plapp & Werner, 2006).

Studies focused on the Italian context show the need to increase people's perception of risk. For example, a recent study based on psychometric and cultural theory approaches evaluates the seismic risk perception through the analysis of about 5000 online tests (Crescimbene et al., 2014). The research reveals that most of Italians living in areas with high seismic hazard have a low or incorrect risk perception, thus suggesting the need for new communication strategies. Similarly, Marincioni et al. (2012) who investigate a sample of population involved in the 2009 L'Aquila earthquake (Mw 6.3) conclude that the residents of the town have a low-risk perception and no awareness of the structural performance of their own buildings. Therefore, increasing the perception of risk is a pressing need, especially among the younger generations.

The present work aims to discuss the activities coordinated and developed by ISPC-CNR within MEMOSIL (acronym for *MEMORie Sismiche Lucane*, Seismic Memories of Lucania), a *Percorso per le Competenze Trasversali e per l'Orientamento* (PCTO) (Pathway for Transversal Competences and Orientation) devoted to some high school students of IISGF.

MEMOSIL, which fits in the wake of other activities already developed by ISPC-CNR at IISGF (Gizzi et al., 2019), is aimed at increasing seismic risk perception in about 40 students of two fourth classes (school year 2022-2023) from both *Liceo Scientifico* ('Liceo' specializing in scientific studies) and *Liceo Classico* ('Liceo' specializing in classical studies).

From a teaching point of view, MEMOSIL involves a theory part complemented by a practical one to be carried out in the computer lab. Furthermore, the path also includes visits to two exhibitions on earthquakes.

Looking at the medium-long term impact, the activities are planned to:

1. increase students' perception of seismic risk; stimulate in the students the critical role of active and proactive citizens with respect to seismic risk mitigation issue;
2. support the development of skills and competences complementary to the curricular ones such as those in the field of Information and Communication Technology (ICT).

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Gizzi F.T., Biscione M., Danese M., Maggio A., Pecci A., Sileo M., Potenza M.R., Masini N., Ruggeri A., Sileo A. & Mercurio F. & School-Work Alternation (SWA) Working Group (WG) (2019) - Students Meet Cultural Heritage: An Experience within the Framework of the Italian School-Work Alternation (SWA) - From Outcomes to Outlooks. *Heritage*, 2(3), 1986-2016. <https://doi.org/10.3390/heritage2030120>.

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Plapp T. & Werner U. (2006) - Understanding Risk Perception from Natural Hazards: Examples from Germany. In: Vullet A.D. (ed) *Risk 21 - Coping with Risks due to Natural Hazards in the 21st Century*, Taylor and Francis Group, London, 101-107.

## Earth science teaching in Italian Upper secondary school: the floor to Natural Science teachers

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*Keywords:* earth science teaching, upper secondary school, teachers survey.

Earth science teaching in Italian upper secondary school was strongly affected by the change in guidelines that occurred in 2010 (MIUR, 2010). These guidelines re-distribution over 5 years of the different topics included in the Natural Science curricula (Chemistry, Biology, and Earth science) and strongly suggested an experimental and multidisciplinary approach.

Following this reform, Realdon et al. (2016) investigated how teachers implemented the new Earth Sciences curriculum but their results showed that theoretical teaching and the scarce use of laboratory were still prevailing. During the COVID outbreak and the remote learning experience, the teaching practices and activities in upper secondary school have been changed, with the relevant use of digital tools during the lessons (Yates et al., 2020). For this reason, we decided to perform a new survey to understand if this affected Earth science teaching. The survey has been first tested among Natural Science teachers from one upper secondary school (Liceo Manzoni, Caserta) and then distributed Nationwide to the school involved in Natural Science Games, thanks to the support of the Italian Association of Natural Science Teachers (ANISN). From the 1st to the 31st of March 2023 113 natural science teachers answered the questions. The survey was composed of 3 sections (Teachers' personal data, Didactical activity in Earth sciences, Critical issues in Earth science teaching) each one included distinct types of questions (multiple choices, net promoter(R), Likert Scale, short answer). The results of the survey showed that among the topics included in the natural science curricula, Earth science is less represented in terms of hours dedicated to lessons (5.8 hours compared to 7.1 and 7.4 for Chemistry and Biology). On the other hand, theoretical teaching is still one of the most didactical approaches represented, in fact almost 30% of interviewed declare to organize their classes as frontal lessons. The use of active methodological approaches (inquiry/project-based learning, flipped classroom, and gamification) is poorly represented, and the most used teaching material is still the textbook.

The results of this survey represent a useful starting point to rethink of Earth science teaching in the Italian Upper secondary school and support teachers in their didactical activity based on their needs.

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Realdon G., Paris E. & Invernizzi M.C. (2016) - Teaching Earth Sciences in Italian liceo high schools following the 2010 reform: a survey. *Rendiconti Online Società Geologica Italiana*, 40, 71-79.

Yates A., Starkey L., Egerton B. & Flueggen F. (2020) - High school students' experience of online learning during Covid-19: the influence of technology and pedagogy. *Technology, Pedagogy and Education*, 30, 59-73. <https://doi.org/10.1080/1475939X.2020.1854337>.

## **“Fire in the center of the Earth” - Exploring alternative geological ideas in entry-level high school students**

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*Keywords:* alternative ideas, meaningful learning, empirical research.

We present a quantitative study of responses to an anonymous survey of first-year high school students enrolled at a Liceo of the Ravenna province, Italy. This research captured student alternative ideas in geology and their perceived level of understanding of key geological concepts.

The survey was prior to the beginning of the Natural Science classes (end of September 2021). The survey is a modified and simplified version of the Geological Concept Inventory of Libarkin & Anderson (2005). It consists of 29 close ended questions organized into 6 modules. The whole process of reviewing the original Geological Concept Inventory questionnaire, including translation, terminological rephrasing and deletion and conversion of some questions was supervised by a High School teacher of Natural Sciences.

Overall, the results suggest that alternative geological ideas are common in the first-year high school students. Of the total responses ( $n=508$ ), more than 50% answered correctly to the “Geological Time” and “Internal Structure of the Earth” modules. The other four modules, “Rocks and Minerals”, “Plate Tectonics”, “Volcanoes” and “Earthquakes” were more difficult to grasp, with less than 50% of the respondents able to answer correctly. “Fire in the center of the Earth”, “plates floating over a layer of lava”, minerals and rocks that “grow” as living organisms are among the incorrect geological ideas that emerged from the respondents.

According to the bibliography, everyone begins to interpret the natural world from the first years of life, giving naïve explanations of natural phenomena (Treagust, 1988). Often, these naïve explanations, which we call alternative ideas, persist over time and can affect meaningful learning. In fact, based on the constructivist and cognitivist vision, the scholastic teaching of geosciences is mediated by these alternative ideas (Ausubel, 1968). In order to improve student acquisition of key geological concepts, instructors must explicitly address these alternative ideas (Libarkin & Anderson, 2005).

The results presented provide a snapshot of the pervasiveness of alternative ideas in geology and yield an interesting area of future research on how these ideas form.

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Treagust D.F. (1988) - Development and use of diagnostic tests to evaluate students’ misconceptions in science. *International Journal of Science Education*, 10, 159-169.

Ausubel D.P. (1968) - *Educational psychology: a cognitive view*. (New York, 1968).

## Effectiveness of fieldwork in Earth Sciences education

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*Keywords:* fieldwork, out-of-school learning, earth sciences education.

Degree courses in geosciences and natural sciences often include field activities and field trip since in Earth Sciences teaching these kinds of practical activities are considered essential for learning geology and for practicing professional geoscientist. Field activity and field trips consist in bringing students for one or more days in a place where they are actively involved in collecting and analyzing data using specific instruments and methods, under the supervision and support of professional researchers.

In this study we want to evaluate the effectiveness of fieldwork on a sample of 70 university students of the bachelor courses in Geological Sciences and Natural Sciences and Technology at the University of Pavia that took part to a field program in 2023 in the Como Lake area. In this qualitative and exploratory study, we started from the assumption that experiential learning is a methodology in which student's knowledge and skills are well developed (Wurdinger & Carlson, 2010) and we considered the fieldwork as an example of out-of-school learning (Schwan et al., 2014).

In order to evaluate the effectiveness of the fieldwork in Earth Science learning we asked students to reply two questionnaires, before and after the activity. In the first one, three closed questions were asked relating to pre-requisites or concepts that the teacher had already introduced in class during traditional lessons. In the second one, administered after the field activity, the previous questions were asked again as well as three new ones relating to new concepts introduced in the field and two open questions aimed at outlining a cognitive autobiography of the students. From a preliminary analysis of the collected data, it appears that in 85% of cases the students manage to fill the gaps in the prerequisites after the practical activity, almost all of the participants consider the activity in the field stimulating and useful for the acquisition of knowledge while only 1% of the participants after the field activity recorded a worsening in the verification of the prerequisites.

From this pilot project, it has been clear was clear that fieldwork encourage students to actively engage and collaborate with each other by building a community of subject geological practice. As stated by Streule & Craig (2016), the construction and effectiveness of communities of practice are important because, even after the studies, the professional geologist will find himself collaborating within such communities. In our opinion, the fieldwork designers should be aware of the social learning theory and ensure that the activities include some work within communities of practice. In doing so, we will produce subject graduates who will equally meet the requirements of industry and academia, as well as other graduate careers.

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Streule M.J. & Craig L.E. (2016) - Social Learning Theories—An Important Design Consideration for Geoscience Fieldwork. *Journal of Geoscience Education*, 64 (2), 101-107. <https://doi.org/10.5408/15-119.1>.

Wurdinger S.D. & Carlson J.A. (2010) - Teaching for Experiential Learning: Five Approaches That Work. *R&L Education*.

## Geologia 3D: explaining geological features in VR at school

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*Keywords:* VR, 3D geology, planetary exploration.

Technological development with software that allows the processing of different and large digital data has allowed the creation of three-dimensional terrain models that are the closest representation to reality.

In geology these models help a lot to visualize structures and rock successions and are also a very useful teaching tool.

Geologia 3D is part of the UdAScienza project funded by Ministero dell’Università e della Ricerca (MUR) under the program PANN 2020 to promote scientific dissemination ([https://udascienza.unich.it/?page\\_id=95](https://udascienza.unich.it/?page_id=95)).

In this project we selected some examples on Mars and Earth to visualise and explain geological features in VR environment.

This experience is fully immersive for the user and students attracted by the VR environment can learn some geological content by having fun.

We started from high-resolution 360-degree images of different landscapes and reproduce them using the software Unreal to get the setting suitable for virtual reality.

The journey starts from a view of our Solar System with brief information about each planet. All the images are real data acquired by various NASA and ESA missions. The user can interactively move through the Solar System and learn their main characteristics. For example, by selecting on Mars, the user can start an astonishing tour of the geological history of the planet, the richness of water in the past and main features observable on the surface. A narrator voice explains the main part of this story.

The journey can continue on the peculiar Gale crater, an impact crater where the NASA’s Curiosity rover is exploring the rock sequences. The user can see at 360 degree this landing site and visualize the geological description through pop-up windows to be opened with a laser pointer on highlighted targets.

We tried to express the geological concept using simple wording and practical examples to facilitate the comprehension.

We plan to enlarge the VR experience with 360-degree panoramas of other significant terrestrial sites where a simplified geological field activity can be achieved virtually.



## SEISMOMETER THEFT: discovering the guilty

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*Keywords:* Inclusive game, natural risks.

The product “Seismometer theft” was born because it would be a theft not to count among the many games produced by the INGV already existing, an educational game entirely based on geology especially in a country, Italy, with a unique geological heritage in the world.

We are convinced that geology can already belong to the small and precious heritage of every child, even more so if its value can be transmitted through discovery and ... play!!

Believing in a learning methodology based on discovery, the analysis, observation and sharing of peculiarities and characteristics of the geology of our country is our goal. The same approach was also taken for geography: the players “discover” the different cities and their location by a travel through Italy.

It would be, thus becoming aware of the orientation and the possibilities of movement offered by the different means of transport, with a real transposition of the network railway (but also naval and air).

SEISMOMETER THEFT is a party game for a minimum of two players and a maximum of four, while the recommended age is from 8 years ... up to traditional 99 years!

Purpose of the game:

A precious seismometer has been stolen and hidden in an undisclosed location. The Ministry of University and Research has discovered where it is, but will reveal the hiding place only to those who will prove to be a good detective!

1. to win you must return the seismometer to the place where it was stolen
2. first you have to retrieve the seismometer in the secret location by answering different seismometer questions
3. therefore, you must ask the Ministry to tell you where it is hidden, demonstrating to be a detective
4. to be an expert seismologist you must earn at least 5 Ministry Credits...
5. to win Credits you must recognize the geological characteristics of our country
6. to recognize geological features, you have to interpret clues and travel through Italy to reach the place where that characteristic is located
7. To earn new travel tickets you need to answer a question on the geographical area where you are...

...but pay attention to the final twist: if you are TREMORFAKE, the Fake Detective, you win the game as soon as you get hold of the stolen seismometer, without having to bring it back to its destination, performing a THEFT OF THE SEISMOMETER

## **Critical minerals and energy transition: an educational activity in a webXR virtual world and Opensimulator**

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*Keywords:* critical minerals, virtual worlds, energy transition.

“The large-scale deployment of renewable energies is expected to cause increase demand of critical mineral resources” (Viebahn, 2015), highlighting important aspects related to their carbon footprint, technical process problems (e.g. separation of rare earth elements; Koltun & Tharumarajah, 2014) and social and geopolitical concerns.

School should have the responsibility of raising students’ awareness on these issues, pointing on lights and shadows in the use of renewable energy and electric mobility.

The purpose of this work is to introduce students to the topics of renewable energy and the importance of critical elements in the transition to clean energy.

The educational activity was conducted in two different virtual platform: Opensimulator (Gregory et al., 2016) and FrameVR, a web immersive platform (Gómez et al., 2021).

In both platforms students accessed as avatars, exploring the content of the learning scenarios and working in teams of 3-4 students each to solve games, challenges and accomplish missions. The educational path of both virtual worlds was identical and consisted of 5 sections: 1) Fossil fuels and climate change; 2) Production of renewable energy; 3) Carbon footprint of energy production; 4) Critical elements necessary for energy and technology; 5) Electricity consumption.

The project involved 16 K8 degree students of a K6-K8 school in the center of Italy (Opensimulator) and 101 K 8-students of a K6-K8 school in the south of Italy, Students’ accessed the world from the computer laboratory, during the regular school time, under the supervision of their science teachers. The author was connected in remote, in sharing screen mode and by an avatar, to provide support if needed.

Teams, through a link in the world, accessed an online form (called the Mission Sheet) where they had to answer driving questions, looking for information in the multimedia presentations placed in the different sections and solving together online games (crossword puzzle, matching pairs, group assignment, simple order and so on). After 2 hours, at the end of the activity, the “Mission Sheet” was sent to the author. The Mission Sheet results show a good value of correct answers for both schools (respectively 73.9% in the Opensimulator platform and 73.5% in the FrameVR platform).

Pre-activity and post-activity questionnaires were delivered to the students, and a satisfaction survey was administered to students and teachers involved. The analysis of pre-activity and post-activity surveys reveal a significant increase of the mean total score (from 59.5% to 71.3% in the Opensimulator platform and from 58.5% to 71.8% in the FrameVR platform).

Moreover, the observation of the students’ behavior during the activity and the analysis of the satisfaction survey delivered to teachers and students show a great potential of these engaging platforms to approach sustainability topics for students in this age range. Teachers and students appreciate the gamification approach, although they pointed out that time to accomplish all the activities presented in the virtual world was too short.

Gómez V., Peñaranda K. & Figueroa P. (2021) - Lessons Learned from Requirements Gathering for Virtual Reality Simulators. *Virtual Reality & Intelligent Hardware*, 3(5), 407-422. <https://doi.org/10.1016/j.vrih.2021.09.002>.

Gregory S., Lee M., Dalgarno B. & Tynan B. (eds) (2016) - Learning in virtual worlds: research and applications. Athabasca University Press.

Koltun P. & Tharumarajah A. (2014) - Life Cycle Impact of Rare Earth Elements. *ISRN Metallurgy*. <https://doi.org/10.1155/2014/907536>.

Viebahn P., Soukup O., Samadi S., Teubler J., Wiesen K. & Ritthoff M. (2015) - Assessing the need for critical minerals to shift the German energy system towards a high proportion of renewables. *Renewable and Sustainable Energy Reviews*, 49, 655-671. <https://doi.org/10.1016/j.rser.2015.04.070>.

## A collaborative project on urban sustainability using Minecraft

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*Keywords:* urban sustainability, Minecraft, virtual worlds.

This work covers a synchronous collaborative project on urban sustainability experimented in Minecraft, a 3D virtual sandbox block-building-game with online multiplayer capability, with a group of K8 students, during the Covid-19 pandemic, as part of a broader project called Mineclass (Benassi, 2021).

Minecraft is suitable to be used in education because allows collaborative work, the improvement of digital skills, and creativity. Students can show in a tangible way the comprehension of the topics proposed (Cipollone et al., 2014). Most collaborative projects in Minecraft with underage students have been done in person or asynchronously, so very few synchronous projects have been carried out remotely, as the present work. The Agenda 2030 Sustainable Development Goal 11 -Sustainable cities and communities) is crucial to mitigate climate change because, by 2030, urban areas are projected to house 60% of people globally and most of the georesources and energy are used in cities (United Nation, 2018). In addition, Agenda 2030 recognizes the critical role of education as a catalyst for broader change (Sustainable Development Goal 4 - Quality Education). So Minecraft is a valuable digital environment where students can imagine solutions and systems to make city more resilient and sustainable.

The project required the students to use the following sustainability criteria to create a building / structure / service: suitable building materials, waste management, renewable energy, systems to save domestic water and energy, zero Km food, sustainable transportation.

The study divided 25 K8 students of a low secondary school of Nettuno, Italy, into the experimental and the control group. Alawajee, (2021) found that only the 19% of the paper reviewed used a control group. However, we preferred to perform a study more quantitative than others in the literature. The experimental group consisted of four teams of 3-4 K8 students who accessed Minecraft from home and independently organized the division of tasks and times to build a model of a sustainable city. The control group participated in a 2-hours video lesson in sharing screen mode focused on the same topics as the experimental group. The post activity test showed that the experimental group achieved a significant better mean test score.

The paper offers a new perspective that goes beyond the concept of the classroom as the only learning environment and opens up teaching methods other than the widespread use of online screen-sharing.

Alawajee O. (2021) - Minecraft in Education Benefits Learning and Social Engagement. *International Journal of Game-Based Learning*, 11(4), 20-56.

Benassi A (Ed.) (2021) - A scuola con Minecraft. Progettare un mondo a cubetti. Giunti Scuola.

Cipollone M., Schifter C. & Moffat R. (2014) - Minecraft as a creative tool: A case study". *International Journal of Game-Based Learning*, 4(2), 1-14.

United Nations, Department of Economic and Social Affairs, Population Division. (2018) - The World's Cities in 2018 - Data Booklet.

## **Unforeseen connections and new points of view to promote interest and passion for Earth Sciences**

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*Keywords:* unexpected connections.

This study is the result of an in-depth research work, including scientific texts and historical documents, which has led to surprising discoveries on the fundamental role that Earth sciences have had in determining historical events, in modifying social dynamics, in the impact on culture, as arts or literature..., far from the usual perception of this discipline.

In fact, everyone knows, teachers, scientists or simply enthusiasts of the discipline, the decisive role of Earth Sciences in the understanding of natural phenomena, in the knowledge of the dynamics and the evolution of the landscape, of natural risks and dangers, of environmental protection towards sustainable development, for the achievement of the SDGs, as well as the richness of themes, of intertwining that the Earth sciences have in various ways with all scientific disciplines. But years of teaching, practical activities and diversified and original laboratory experiences carried out personally in the various fields of Earth Sciences, to promote knowledge, interest and, when possible, passion for this fascinating discipline, have shown that, even when taught and transmitted with passion, it can remain undeniably boring: a complex and complicated discipline, which speaks of stones and catastrophes.

To overcome this reality, I tried to propose a different methodological approach, particularly effective based on the experiences carried out to date, providing a new point of view on traditionally curricular themes. Volcanoes, earthquakes, meteorites, but also climatic variations, events related to global dynamics, instantaneous or long-lasting, documented or hypothesized, but always supported by solid scientific bases available in international journals and publications, are observed not so much or not only for the catastrophic and dramatic consequences they have had on Earth, but for the unpredictable consequences that these geological events may have had on living beings, on humanity, its evolution, its history, its culture and which can therefore be interpreted as causes, unpredictable but indispensable, of events that, at first glance, they have nothing to do with the Earth sciences but which, instead, have made the history and culture of humanity.

In some cases, these events are known to many; but the innovative aspect of this research was to try, among the different types of events, and to find, some unifying principles, to build a functional timeline for a didactic and informative use of these catastrophic events, which allow to give the Earth sciences a different and somewhat unconventional reading.

Earth sciences become a founding node of different disciplines, particularly effective to open students' minds to interdisciplinarity, able to promote the growth of knowledge, development of skills, but also a stimulus to curiosity, a way to excite, and perhaps to orient towards a complex but unpredictable discipline and perhaps for this reason particularly fascinating.

## **From Geotourism and Geoeducation, to Geoheritage: the value of tangible and intangible heritage**

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*Keywords:* heritage, cultural tangible and intangible values.

This research aimed to explore the emerging challenges and the rapid evolution of awareness of the value of the geo-heritage of one's territory; particularly how this can evolve both in a value for geotourism and in effective educational paths.

An attempt has been made to demonstrate, through a few examples, that the construction of a sensitivity towards a tourism attentive to geological and geomorphological values, important because it leads to greater attention to the sites, their conservation and protection and ultimately to respect for the environment, requires, for their effective valorization, scientific knowledge, albeit at different levels of depth, of what is observed, of what is protected, and above all of what natural phenomena are the result.

It is easy to appreciate, observe, photograph, and keep the memory of a beautiful mountain, a landscape, or a particularly original geological or geomorphological aspect, often identifiable with a geosite. It is less easy to recognize that the same value for the purposes of geoconservation, and therefore of valorization, can be attributed to phenomena, perhaps less beautiful from an aesthetic and environmental point of view, with a lower visual impact, significant both from a geological point of view, but even more historical, cultural, anthropic, revealing unexpected connections and transversal cultural and intangible values between different cultural areas.

These sites, places, contexts can have a profound impact on human sensitivity and perception, transforming a geological place into a place of cultures, a geo-site into a geoheritage-site. This research has tried to deepen this aspect, proposing some cases, situated in an author's known context, and particularly appreciated by the author, precisely because of the wealth of stimuli they can provide to the interested tourist, but also to the student to whom we wish to convey the perception of richness and depth of an environmental context, rich in scientific contents but also in cultural values.

## The hydrological cycle in the field starting from a glacier: the experience with a secondary school of first level

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*Keywords:* hydrological cycle, mountain environment, Ventina glacier (Central Italian Alps).

The hydrological cycle is proposed to students, in a very simplified form, starting in the primary school. The topic should be also considered in the upper school levels in an increasingly complex way. However, this rarely happens, and simplifications often translate into misconceptions that remain and consolidate over time (Borghini et al., 2021). The main conceptual errors concern the cycle nature of the phenomenon and the poorly considered groundwaters. The present work is a part of a wider project aimed to “look at” the hydrological cycle on the field as an instrument to helpfully removing such misconceptions. Through field activities it is in fact possible to acquire more easily and effectively not only knowledge about the landscape processes and changes, but also skills and abilities that can be exported to other contexts (Pelfini et al., 2016). More in detail, we focus on the hydrological cycle starting from the water stored in glaciers, a natural asset disappearing due to global warming. In the present project, field activities have been carried out in May 2022 and 2023 at the Ventina Glacier (Valmalenco, Central Italian Alps). The field work is realized with a secondary school of first level located in Valtellina, with a specific teaching course on the Alpine environment with experiences on the field. Field observations are addressed to the different components of the hydrological cycle and on glacial processes and landforms along the Glaciological trail of the Ventina Glacier (Servizio Glaciologico Lombardo, 1992), looking also at the glacier responses to climate change (Pelfini & Smiraglia, 1994). During the field activities, the USGS diagram illustrating the hydrological cycle edited for schools is used as a base for students to highlight its components encountered along the trail. A worksheet entitled “Let’s brain-storming on the hydrological cycle in the mountain environment” guides students to recognize the elements related to the concepts of water flows and water archives, and on the changes that may occur in the hydrological cycle in mountain environments. Moreover, a topographic map represents the support for mapping the dated moraines and for calculating the glacier retreat. Other available data as a buried trunk dated through <sup>14</sup>C, are used to start a discussion about the main process responsible of the tree uprooting (glacial or gravity process) thus stimulating observation and reasoning skills.

Borghini A., Pieraccioni F., Bastiani L., Bonaccorsi E. & Gioncada A. (2021) - Which geoscience knowledge at the end of upper-secondary school? Results from an Italian survey. *Mediterranean Journal of Education*, 1(2), 249-261.

Pelfini M., Bollati I.M., Pellegrini L. & Zucali M. (2016) - Earth Sciences on the field: educational applications for the comprehension of landscape evolution. *Rend. Online Soc. Geol. It.*, 40, 56-66.

Pelfini M. & Smiraglia C. (1994) - Nuove ipotesi sulla massima espansione olocenica del Ghiacciaio della Ventina (Valtellina, Alpi Retiche). *Geog. Fis. Dinam. Quat.*, 17, 103-106.

Servizio Glaciologico Lombardo (1992) - Il sentiero glaciologico “Vittorio Sella” al Ghiacciaio della Ventina, Melograno Edizioni, 32 pp.



## Hypernarrative online Escape Room as a learning tool: experiences since pandemic to date

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**Keywords:** gamification in education, best practice dissemination, natural risks, climate changes.

To address the issues of natural hazards and environmental sustainability, two competitive hypernarrative Escape Rooms were created to be played online during special events, simultaneously involving several classes located all over Italy. The first one, “*Let’s free Salvina!*” - an Escape Room to run away from natural risks”, was designed for the 9th Planet Earth Week 2021: more than 900 students (about 300 from 14 classrooms of 5 Primary Schools in the first and 600 from 29 classrooms of 15 Middle Schools (ISCDE 2) in the second competition) played two different races. This Escape room grew out of the ‘Salvina’s adventures’ experience gained during the Pandemic concerning natural hazards, which enthusiastically involved thousands of students playing online (Piangiamore & Maramai, 2022). The second Escape, “*4S: Salvina and Samanta Save the Species*”, is dedicated to environmental issues and the mitigation of ‘global warming’, to promote sustainable behavior through the *PBL approach*. The students of a second grade secondary school class are the new game designers in an innovative participatory phase supported by teachers and INGV researchers. This Escape was played online during World Earth Day 2023, involving almost 800 students from 35 classrooms of 14 Middle Schools. This type of activity facilitates the development of all key competences and citizenship skills, stimulating discussion among peers and with adults and fostering critical thinking development. The activities are all designed on *inquiry-based learning* aimed at promoting behavioral change (*transformational learning*) respecting the environment. Both the Escapes have in common the use of a storytelling to develop engaging adventures, facing different situations from time to time, according to players’ choices and solutions. In “*Let’s free Salvina!*”, to survive in the event of an earthquake, tsunami, landslide, and flood, the involved teams have to use their knowledge in Civil Protection matters. Instead, in the “*4S*” Escape Room, students must use all their skills to preserve biodiversity in different settings to win. This experiment between School and Research presents a collaborative didactic approach, promoting education for sustainable development. The ambitious goal of *lifelong learning* triggers a process that fosters knowledge, awareness and best practices, both for facing natural risks and fighting climate change, in a *challenge-based learning* perspective too. To create both the interactive Escape rooms was used the no-code platform *Genially*, together with other free learning apps (*Quizziz*, *Word Wall*, *Flippity*). The digital Escape, created to support the teaching difficulties due to the Pandemic, has been revealed to be a useful learning tool even after the health emergency because it allows simultaneous interaction between many classes at distance, stimulating learning. In fact, the competition triggers students’ enthusiasm, facilitating the understanding of scientific issues.

Piangiamore G.L. & Maramai A. (2022) - Gaming and Resilience: Teaching by Playing Together — Online Educational Competition at School during the Pandemic. *Applied Science*, 12(23) 11931. <https://doi.org/10.3390/app122311931>.

## Science teaching for sustainability: the SSI approach

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Keywords: socio scientific issues (SSI), sustainability, evolution.

While the concept of sustainable development has been central in public discussion since the 1980s, in recent years the challenges to sustainability have become more urgent due to rapid environmental changes, putting the planet’s biological support systems at risk (United Nations, 2015). These challenges include global warming with increasing number of extreme weather events causing natural disasters, sea level rise and ocean acidification, environmental degradation, depletion of resources and scarcity-driven international migrations.

In the scenario of a rapidly changing world new approaches are needed for the education to sustainability. One of these approaches is based on Socio Scientific Issues (SSI).

SSI are ill-structured problems and dilemmas that are controversial in nature, with no clear-cut immediate solutions, require evidence-based considerations, and can be informed by various ideas and perspectives, such as economic, political, and ethical (Zeidler, 2014)

SSI based pedagogical approach uses personally relevant, controversial problems that require scientific reasoning, but include social aspects which need “*students to engage in dialogue, discussion, debate, and argumentation; Integrate implicit and/or explicit ethical components that require some degree of moral reasoning*” (Sá-Pinto et al., 2023).

In this conference we intend to present a teaching resource produced within the COST Action project EuroScitizen, aimed at the promotion of SSI-based approach for addressing the problems of sustainability from an evolutionary point of view.

This resource is an open-access e-book, entitled “Learning evolution through socioscientific issues” and results from the contribution of 34 authors and 29 reviewers from 15 different countries. The authors of this presentation were also involved as translators into Italian and, in one case (Realdon), also as a reviewer.

“Learning evolution through socioscientific issues” consists of two parts:

- chapters addressing theoretical and methodological issues involved in scientific literacy, the SSI educational approach and evolution education;

- chapters proposing examples of best practices showcasing the use of the SSI approach in formal and non-formal science teaching.

While the presented resource focuses on a set of examples related to evolution (biodiversity conservation, health issues, e.g., pandemics, antibiotic resistance, agriculture and pesticide resistance, ...) the SSI approach can profitably be exploited in other different contexts more specifically related to geosciences, such as the use of natural resources (water, minerals, fossil fuels), energy production, land management, waste disposal, mitigation of climate change, and many others, all connected in the framework of education for sustainability.

Sá-Pinto X., Beniermann A., Børsen T., Georgiou M., Jeffries A., Pessoa P., Sousa B. & Zeidler D.L. (Eds.) (2022) - Learning Evolution Through Socioscientific Issues. UA Editora, 219 pp. [https://ria.ua.pt/bitstream/10773/35673/3/Learning\\_evolution\\_through\\_SSI.pdf](https://ria.ua.pt/bitstream/10773/35673/3/Learning_evolution_through_SSI.pdf).

United Nations. (2015) - Transforming our world: The 2030 agenda for sustainable development | department of economic and social affairs. United Nations, <https://sustainabledevelopment.un.org/content/documents/21252030%20Agenda%20for%20Sustainable%20Development%20web.pdf>.

Zeidler D.L. (2014) - Socioscientific Issues as a Curriculum Emphasis: Theory, Research and Practice. In N. G. Lederman & S. K. Abell (Eds.), Handbook of Research on Science Education, Volume II, Routledge, 697- 726

## **Scienza Under 18 Isontina: a new approach to science communication in schools, for schools, with schools**

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*Keywords:* Scienza under 18 Isontina, science in school, science communication.

Scienza Under 18 Isontina is a cultural association established in 2010 in Friuli Venezia Giulia to implement a participatory and innovative way of doing and communicating science inside and outside the schools and to provide schools with opportunities for visibility, exchange and cultural growth.

Every year SU 18 Isontina organises various initiatives aimed at schools of all grades, the main one being the Festival “Science under 18 - the scientific knowledge of the school”, now in its 13<sup>th</sup> edition: a context in which students, from kindergarten to secondary school, exhibit their scientific activities in an interactive way (proposing exhibits, videos, posters, theatre performances, lectures, etc.). In this way they test their ability to communicate with visitors: students, teachers, families and general public (Bertini et al., 2011). The Festival is flanked by a student photography contest entitled “ Science Shots - The Beauty of an Image”, an opportunity to look closely, through a lens, at the world around us.

In addition to the annual Festival, SU18 Isontina organises public meetings and themed days on national and international events with a scientific and environmental theme (Pi Greco Day, M’Illumino di Meno, World Ocean Day) scientific training courses for teachers recognised by the Ministry of Education, educational workshops in schools and fieldwork activities on the nearby coastline.

Science Under 18 Isontina is part of the National Network Science Under 18, which counts nine territorial centres in various Italian regions, each of which organises an annual festival and other science communication initiatives for schools.

Participation in these initiatives contributes to improving students’ preparation, to approaching science with critical thinking, to tackling concrete problems with a correct methodological approach (Cigada et al., 2007), to enhancing the ability to apply the knowledge acquired at school to different fields and to developing interest in pursuing scientific studies, also with a view to future employment.

Bertini G., Franchini E., Samek Lodovici P., Vitali N. (Eds) (2011) - Attori del sapere - Un progetto di teatro, scienza, scuola. Scienza express, Milano, 284 pp.

Cigada F., D’Addato C., Danise P., Franchini E, Razzini R. (Eds) (2007) - Il sapere scientifico della scuola Con una ricerca sull’immaginario di scienziati, docenti e studenti. Franco Angeli, Milano.

## **The “School-Shake” project: growing seismologists for the future at the University of Perugia (Italy)**

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Occhipinti M.<sup>1</sup>, Ortenzi S.<sup>1</sup>, Pandolfi Balbi E.<sup>1</sup>, Parparousi E.M.<sup>1</sup>, Pasqualone L.<sup>1</sup>, Perugini D.<sup>1</sup>, Pisello A.<sup>1</sup>,  
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*Keywords:* earthquakes, seismology, orientation.

“School-Shake” is a project developed by researchers of University of Perugia, in the framework of the PLS program, to integrate and enhance the conventional outreach and orientation activities proposed to high-school (secondary) students. The project has implemented a seismic network within some selected secondary schools using low-cost professional seismometers RaspberryShake. The latter are based on the Raspberry Pi platform, a single-board computer developed in the United Kingdom by the Raspberry Pi Foundation since 2012. These tools are ideal for educational projects aimed at enhancing Earth Sciences in schools. Such instruments, suitable for earthquake detection and recording, can easily involve students and professors, by studying earthquakes in a rigorous way but using a ‘Learning by doing’ approach. We have currently installed a number of seven RaspberryShake stations in schools located in the Umbria, Marche and Lazio region and in different cities such as Perugia, Città di Castello, Fabriano, Assisi, Spoleto, Cascia and Rieti, in central Italy. A station is also located in the University of Perugia laboratory TerraLab Explorer (dedicated to orientation activities, <http://orientamento.fisgeo.unipg.it>). During the COVID19 pandemic, demonstration videos have been created and remote education activities have been provided for teachers and students, while during the last months some lectures and practical laboratories have been made fully in presence. The PCTOs were based on the introduction of the main concepts of seismology and some practical activities were carried out. Among them, we have introduced the young students to the calculation of the epicenter through the triangulation method (using the ShakeNet platform of the Raspberry Shake community) and we have made practical exercises on the calculation of the earthquake magnitude. The students were also trained to research historical and recent seismic events within the parametric catalog of Italian earthquakes and within online macroseismic databases made available by INGV. These seismometers recently recorded some moderate seismic events which struck the central Italian region (e.g. the Umbertide seismic sequence, 2023 March 9<sup>th</sup>, with two main events Mw 4.3 and 4.5), and the seismograms have been publicized via the Geologia UniPg social media (Facebook and Instagram), with the dual purpose of educating awareness of geological hazard and orienting students towards Earth Sciences disciplines. The “School-Shake” project is under continuous development and the network is expected to be further implemented as also nearby University began to install RaspberryShake stations (e.g. Marche Region) in order to collaborate increasing the knowledge on the seismological problems and contributing to grow fearless seismologists for the future!

## A new teaching approaches to promote significant geological learning: Human Paleogenetics

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Keywords: paleogenetics, deeptime, evolution.

The Nobel Prize in Physiology or Medicine was awarded to Svante Pääbo, honoring work that illuminates both the distant past and the genetic heritage of people living today. Paleogenomics has changed the study of human origins, because it allows us to look directly at the genome to infer relationships and assess population history. None of these developments would have been possible without next-generation sequencing (NGS) (Goodwin et al., 2016), which remains thus far the most transformative technology in the history of ancient DNA research. Fossils and morphology tell very important parts of the story of human evolution, but paleogenomic techniques have given scientists a new way to address important questions about humanity's origins, including where we came from, why some species went extinct, and what makes us uniquely human (Bornschein et al., 2023). The high school curricula do not include a substantial geology component because deal extensively with molecular biology and genetic (Roca et al., 2020). The insufficient geological training of high school teachers who are later expected to teach Earth science generates a certain degree of insecurity and fear about teaching geology. We explore innovative ideas and practices that can promote geologically significant learning. This project has a dual objective: first, we show how DNA sequencing technologies make it possible to understand the human origins; second, we explain modern human origins using the fossil records as well as reconstructions of evolutionary history based on the examination of patterns of genetic diversity within populations of living humans.

In our teaching structure, a biology teacher and a geologist with a solid background in scientific dissemination, design a didactic unit to fill the gap in geological knowledge.

In our activities, we integrate the information obtained from Hominin fossils, rocks, sediments, the internal structure of Earth and the process of fossilization to improve the understanding of evolutionary processes over the short and medium term (Macdougall). Furthermore, the present project also focuses on the concept of time. Using the International Chronostratigraphic Chart, we aimed to address the discussion that time is all around us and is the basis of how we record life on Earth. Through this didactic unit, the teachers have a critical role to play: encouraging their secondary students to develop geology knowledge.

Bornschein U., Zeberg H., Enard W., Hevers W. & Pääbo S. (2023) - Functional dissection of two amino acid substitutions unique to the human FOXP2 protein. *Scientific Reports*, 13(1), 3747.

Goodwin S., McPherson J.D. & McCombie W.R. (2016) - Coming of age: ten years of next-generation sequencing technologies. *Nat. Rev. Genet.* 17, 333-351.

Macdougall J. D., (1999), *Storia della Terra- Piccola Biblioteca Einaudi* Ns.pp. XII - 313

Roca N. & Garcia-Valles (2020) - M. Trainee Teacher Experience in Geoscience Education: Can We Do Better?. *Geoheritage* 12, 92. <https://doi.org/10.1007/s12371-020-00518-8>.

**S28.**

**Unveiling the evolution of the oceanic and continental  
lithosphere through the study of mantle rocks, primary melts  
and crustal sections**

*CONVENERS AND CHAIRPERSONS*

*Federico Casetta (University of Vienna)*

*Carlotta Ferrando (Università di Genova)*

*Arianna Secchiari (Università degli Studi di Milano Statale)*



## The oxidation state of iron in Mg-chromite inclusions from lithospheric diamonds: implications for the redox heterogeneities in the upper mantle

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*Keywords:* diamonds, spinel, synchrotron radiation.

The investigation of mineral inclusions trapped in lithospheric diamonds along with mantle xenoliths represents a valuable tool to directly access the deep Earth and improve our understanding of its chemistry and mineralogy. Inclusions allow to retrieve pressure ( $P$ ), temperature ( $T$ ), and oxygen fugacity ( $f_{O_2}$ ) occurred during diamond formation, as well as to constrain their source rock. Among all the mineral inclusions observed in lithospheric diamonds, those having a peridotitic mineral assemblage (i.e., P-type) show often the presence of Mg-chromite (e.g., Stachel and Harris, 2008). Such finding is the evidence that spinels can play a role in the diamond formation from a CO<sub>2</sub>-bearing fluid. However, to date, the knowledge of peridotitic mantle redox state is limited to spinel-bearing peridotite xenoliths based on Fe<sup>3+</sup> in spinel and oxy-thermobarometric estimates (Ballhaus et al., 1991). The mantle oxidation state retrieved by the chemistry of minerals inclusions remain less explored.

In this study, we focused on a suite diamonds from the Udachnaya kimberlitic pipe (Siberian craton) characterized by multiple opaque inclusions of Mg-chromites with sizes ranging between ~50 micron and ~200 micron. The selected diamonds were double polished to expose some dark inclusions. Few tiny transparent inclusions were also observed.

Measurements of the Fe<sup>3+</sup>/ΣFe were performed on both encapsulated and exposed inclusions using in situ synchrotron Mössbauer spectroscopy at ID 18 beamline of the ESRF (Grenoble, France) with a 615 μm<sup>2</sup> focused beam. Those inclusions exposed to the surface of the polished diamonds were also analyzed by scanning electron microscopy and electron microprobe for chemical and textural observations.

Our preliminary data show a large variability of Fe<sup>3+</sup>/ΣFe ratio with values ranging from 0.07 to 0.28. The measured Mg-chromites showed values of FeO between 12 and 17 (Wt%) and the Cr# measured around 0.87. These data will be integrated with those available in literature and results discussed in terms of redox-driven mechanisms of diamond formation in the lithospheric mantle.

Ballhaus C., Berry R.F. & Green D.H. (1991) - High pressure experimental calibration of the olivine-orthopyroxene-spinel oxygen geobarometer: implications for the oxidation state of the upper mantle. *Contributions to Mineralogy and Petrology*, 107, 27-40. <https://doi.org/10.1007/BF00311183>.

Stachel T. & Harris J.W. (2008) - The origin of cratonic diamonds—constraints from mineral inclusions. *Ore Geology Reviews*, 34(1-2), 5-32. <https://doi.org/10.1016/j.oregeorev.2007.05.002>.

## Multianalytical investigation of inclusions in a lithospheric diamond reveals possible metasomatism-driven mechanisms of formation

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*Keywords:* natural diamond, mineral inclusions, synchrotron radiation.

The knowledge of chemical and mineralogical heterogeneities in the deep Earth has improved and expanded over the last decade through the accurate analysis of minerals entrapped in (sub-)lithospheric diamonds. The possibility to investigate tiny inclusions has allowed the application of common oxy-thermobarometers combined with experimental studies to determine the pressures, temperatures and redox conditions for their encapsulation and/or diamond formation.

In this study, we focused on a lithospheric diamond from the area of Rio Soriso, Juina (Brazil), known for the abundance of extracted diamonds with inclusions representative of the Earth's lower and upper mantle (Hayman et al., 2005). The diamond was double-polished along [100], and shows 10 visible, colourless or greenish inclusions, with sizes ranging between ~20 microns and ~200 microns.

Synchrotron X-ray tomography and single-crystal diffraction techniques were employed to identify the inclusions entrapped in the diamond using data collected at the 13BM-D (GSECARS) beamline at the Advanced Photon Source (Argonne, US), equipped with a new Pilatus 1M CdTe detector. Furthermore, spectroscopic techniques such as Fourier transform infrared spectroscopy and Raman spectroscopy were also used. The texture and chemical composition (in terms of major and trace elements) of an exposed inclusion were analyzed by scanning electron microscopy, electron microprobe and laser ablation-inductively coupled plasma-mass spectrometry. Finally, the Fe oxidation state of selected inclusions was determined in situ by synchrotron Mössbauer spectroscopy at the ID 18 beamline of the European Synchrotron Radiation Facility (Grenoble, France) with a beam collimated to 6x15 μm<sup>2</sup>.

Our data identified the exposed inclusion as a diopside with a ~20% of ureyitic component. On the basis of six oxygen atoms, its mineralogical formula can be written as (Ca<sub>0.56</sub>Na<sub>0.27</sub>K<sub>0.02</sub>Fe<sup>2+</sup><sub>0.05</sub>Mg<sub>0.10</sub>) (Mg<sub>0.69</sub>Cr<sup>3+</sup><sub>0.19</sub>Al<sub>0.11</sub>Fe<sup>3+</sup><sub>0.01</sub>)Si<sub>2.00</sub>O<sub>6</sub>. It has a Fe<sup>3+</sup> content of 0.009 atoms per formula unit and a Cr<sub>2</sub>O<sub>3</sub> content of 6.21-6.41%. These preliminary results provide evidence of a wehrlitic environment where the investigated diamond might have formed. Based on the measured Fe<sup>3+</sup>/ΣFe of the trapped minerals, we propose a possible redox reaction through which syngenetic inclusions can be encapsulated in the upper mantle.

Hayman P., Kopylova M. & Kaminsky F. (2005) - Lower mantle diamonds from Rio Soriso (Juina area, Mato Grosso, Brazil). *Contributions to Mineralogy and Petrology*, 149(4), 430-445. <https://doi.org/10.1007/s00410-005-0657-8>.

## Raman spectroscopic study of omphacites at variable pressures: implications for elastic geobarometry

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Keywords: omphacites, Raman spectroscopy, elastic geobarometry.

The widespread occurrence of omphacitic clinopyroxenes (a solid solution of jadeite, augite and aegirine, with the general chemical formula  $(\text{Ca},\text{Na})(\text{Mg},\text{Fe}^{2+},\text{Al},\text{Fe}^{3+})\text{Si}_2\text{O}_6$ ) in several geological settings and rock-types (e.g. high pressure eclogites, mantle xenoliths etc.), make them ideal candidates to be exploited for Raman elastic geothermobarometry applications. Raman elastic geobarometry uses the deformation recorded by a mineral inclusion trapped in its host to retrieve the pressure and temperature conditions at which the inclusion has been entrapped (Angel et al., 2019), because Raman scattering is very sensitive to structural deformations in crystal structures developed upon heating or compression. Several host-inclusion systems have been studied so far, but clinopyroxene inclusions have not been thoroughly investigated yet. Therefore, the application of Raman elastic geobarometry to omphacites in various mineral hosts requires an accurate calibration of the Raman-peak positions against hydrostatic pressure.

However, the Raman-peak positions and their pressure evolution depend also on the chemical composition. Besides, natural omphacite crystals can show a significant degree of cationic ordering related to the crystallization temperature, which can also affect the elastic behaviour of omphacite. Therefore, we have started with the study of natural ordered ( $P2/n$ ) and experimentally disordered ( $C2/c$ ) crystals of omphacite coming from Münchberg Massif, Bavaria, Germany (peak conditions  $P > 2$  GPa,  $T = 600\text{-}650^\circ\text{C}$ ; O’Brien, 1997). On these samples, we carried out in situ high-pressure Raman spectroscopy measurements using a diamond anvil cell. As expected, the modes frequencies increase as pressure increases.

Since the study included omphacite crystals with different degrees of order, obtained with isothermal annealing experiments at different times, we were able to observe that progressive cationic disorder causes essentially a broadening of the peaks, whereas the changes in the Raman peak positions and FWHM are mostly due to pressure variations.

To better understand the elastic behaviour of the modes best suitable for elastic geobarometry, the Raman spectrum of a completely ordered omphacite of composition  $\text{Jd}_{50}\text{Di}_{50}$ , has been simulated at variable pressures with *ab initio* Hartree-Fock / Density Functional Theory simulations and compared with experimental spectra. The calculated data resulted to be in a good agreement with experiments and allowed us to understand changes in the pressure dependence of some modes.

Our results readily enabled us to calculate the entrapment pressure of omphacite inclusions still trapped in their host rocks by determining the Raman shifts of the main peaks along with changes in the cation order.

Angel R.J., Murri M., Mihailova B. & Alvaro M. (2019) - Stress, strain and Raman shifts. *Z Kristallogr Cryst Mater*, 234(2), 129-140. <https://doi.org/10.1515/zkri-2018-2112>.

O’Brien P.J. (1997) - Garnet zoning and reaction textures in overprinted eclogites, Bohemian Massif, European Variscides: A record of their thermal history during exhumation. *Lithos*, 41, 119-133. [https://doi.org/10.1016/S0024-4937\(97\)82008-7](https://doi.org/10.1016/S0024-4937(97)82008-7).

## Reactive melt percolation and impregnation processes through the Oman lithospheric mantle (Wadi Tayin Massif)

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*Keywords:* melt-rock interaction processes, lithospheric mantle, Oman ophiolite.

The Oman ophiolite extends 30.000 km<sup>2</sup> along the coast of Oman and exposes a complete stratigraphic sequence from mantle peridotite to oceanic gabbros and its volcano-sedimentary cover, providing direct access to several kilometres of the oceanic lithosphere. Decades of petrographic and geochemical studies on the crustal section of the Oman ophiolite have revealed (i) the complexity of melt generation and melt migration mechanisms and (ii) the presence of two different magmatic suites associated with the accretion of the Oman oceanic lithosphere (Godard et al., 2003). By contrast the mantle section has been poorly investigated, and the original setting and evolution of the Oman ophiolite are still currently debated between mid-ocean ridge and proto-arc geodynamic environments (Belgrano & Diamond, 2019).

Here we investigate the evolution of the upper mantle section exposed in the Wadi Tayin Massif in the southern part of the Oman ophiolite, where the oceanic accretion of the Oman lithosphere at a ridge environment is best preserved. A preliminary study of mantle harzburgites sampled from drill-cores of the OmanDP CM sites (Oman Drilling Project; Kelemen et al., 2020), revealed multiple melt percolation and melt-rock interaction events, which occurred at different depth from spinel- to plagioclase-facies conditions. Melt reactive porous flow at spinel-facies conditions caused partial dissolution of pyroxenes and crystallization of new olivine. Additionally, at shallower depths melt impregnation led to the crystallization of interstitial plagioclase (Plg) and various modal proportions of pyroxenes. Such processes are also recorded in peridotite samples collected by our team along the Wadi Nassif close to the CM Sites. Although the drill-cores offer a 1-D vertical continuity of the structures, field-based sampling is crucial for the definition of melt migration structures in a broader 3D environment. Combined petrographic observations on core and field samples revealed the occurrence of different melt impregnation structures, including (i) discrete layers of interstitial Plg ± Cpx, roughly parallel to mantle foliation, (ii) segregations of Plg + Opx ± Cpx within the host harzburgite, and (iii) diffuse melt impregnation forming Px-bearing troctolite pods and layers, characterized by rounded olivine included in poikilitic assemblage of Plg + Cpx + Opx. All the impregnation structures are crosscut by subsequent intrusion of discrete gabbroic dikelets. Geochemical investigations reveal An%(Plg)= 94 mol%, Mg#(Cpx)= 92 wt% contents in the impregnation structures, and An%(Plg)= 77 mol%, Mg#(Cpx)= 88 wt% in the gabbroic intrusions, thus pointing to parental melts with different magmatic affinities and/or degree of evolution.

Unravelling the chemical signature and origin of melts migrating through the upper mantle is crucial in constraining the complex geodynamic environment in which the Oman lithosphere evolved.

Belgrano T.M. & Diamond L.W. (2019) - Subduction-zone contributions to axial volcanism in the Oman–UAE ophiolite. *Lithosphere*, 11(3), 399-411. <https://doi.org/10.1130/L1045.1>.

Godard M., Dautria J.M. & Perrin M. (2003) - Geochemical variability of the Oman ophiolite lavas: Relationship with spatial distribution and paleomagnetic directions. *Geochemistry, Geophysics, Geosystems*, 4(6). <https://doi.org/10.1029/2002GC000452>.

Kelemen P.B., Matter J.M., Teagle D.A.H., Coggon J.A. & the Oman Drilling Project Science Team (2020) - Proceedings of the Oman Drilling Project: College Station, TX (International Ocean Discovery Program). <https://doi.org/10.14379/OmanDP.proc.2020>

## The lithospheric mantle beneath central Mongolia: constraints from spinel-bearing peridotite xenoliths and high pressure experiments

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*Keywords:* Mongolia, xenoliths, experiments.

It is well known that mantle xenoliths provide clues to understand the evolution of the lithosphere beneath regions where no samples were exposed by tectonic activity. When dealing with spinel peridotites, it is however difficult to accurately determine which lithospheric portions they come from, as there are currently no accurate geothermobarometric methods to estimate their depth of formation. Therefore, it is essential to characterize in the best possible way the few fragments found in different sampling campaigns in alkaline magmatic provinces.

One of the regions where the lithospheric mantle is still poorly investigated is the Central Asian Orogenic System, particularly the area of central Mongolia. Here, we focus on a suite of spinel-bearing mantle xenoliths from different volcanic structures in the Mongolian region of Mandakh-Mandal-Gobi. These xenoliths are hosted in alkaline lavas of 71 - 51 Ma and are mainly lherzolites, with minor amounts of harzburgites. Texture is generally protogranular with some samples showing reactions between melt and crystals. Composition of mineral phases are homogeneous within individual xenoliths, but vary among samples from different volcanic structures: samples from the Southern area have a more fertile mineral chemistry compared to samples of the Northern area.

Due the lack of a precise, accurate and well tested geobarometers for spinel peridotites, experiments are being performed with the aim to test the performance of the available methods (e.g., Ca exchange between olivine and clinopyroxene; Köhler & Brey, 1990) and possibly calibrate new reactions to determine the phase equilibrium pressure and temperature of natural samples more precisely. Experiments are conducted with a piston cylinder press at the Bayerisches Geoinstitut (BGI) of the University of Bayreuth. The P-T window spans from 10 to 20 kbar and from 1000 to 1200°C. Two starting compositions are being used: one made by a mixture of synthetic oxides, reflecting the mineral chemistry of one natural sample, the other by powdered hand-picked minerals of the same natural sample. All these data will help to achieve the following goals: i) to understand whether the xenoliths derive from just below the crust-mantle transition zone or rather represents fragments that have been sampled throughout the mantle section in which spinel peridotites are stable; these observations would help understanding the mechanisms that drive the fracturing and entrapment of mantle peridotites during deep-seated magmatism; ii) to understand the vertical and lateral variations in lithospheric structure and thermal state in a region that underwent collisional processes followed by extensive anorogenic-type magmatism.

Köhler T.P. & Brey G.P. (1990) - Calcium exchange between olivine and clinopyroxene calibrated as a geothermobarometer for natural peridotites from 2 to 60 kb with applications. *Geochim. Cosmochim. Acta*, 54, 2375-2388.



## The investigation of the oxidizing role played by the subduction-driven metasomatic fluids through the oxygen fugacity of mantle peridotites coupled with the mineral oxygen isotopes: case of the peridotite mantle xenoliths of Tallante (Betic Cordillera, Spain)

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Keywords: peridotite mantle xenoliths, oxygen fugacity, crustal recycling.

The study of oxidation state of peridotite mantle xenoliths allows to model the volatile speciation within the C-O-H system and estimate the oxidizing role of subduction-driven metasomatic fluids. Recent measurements of the oxygen isotopes (i.e.,  $^{18}\text{O}/^{16}\text{O}$  ratios) in rock-forming minerals from mantle xenoliths provide evidence for recycling of the continental crustal into the deep mantle (Dallai et al., 2019). However, no data exists that couple the estimates oxygen fugacity ( $f_{\text{O}_2}$ ) of mantle rocks through the determination of the  $\text{Fe}^{3+}/\Sigma\text{Fe}$  in coexisting spinels with the  $^{18}\text{O}/^{16}\text{O}$  ratios from the same upper mantle assemblage.

In this study, we investigated the  $\text{Fe}^{3+}/\Sigma\text{Fe}$  of coexisting spinel (spl), clinopyroxene (cpx) and orthopyroxene (opx) from three anhydrous lherzolites and a rare, veined peridotite xenolith from Tallante (Betic Cordillera, Spain) located within a post-collisional tectonic setting. The pressures and temperatures of equilibration of these rocks are 0.7-0.9 GPa and 830-1000°C. These rocks have been widely studied to the present (Bianchini et al., 2011; Avanzinelli et al., 2020) since the petrographic and geochemical data reveal the interaction between mantle and crustal-derived Si-rich fluids.

Measurements of the  $\text{Fe}^{3+}/\Sigma\text{Fe}$  in spl, cpx and opx single crystals were performed by in situ synchrotron Mössbauer spectroscopy at ID 18 beamline of the European Synchrotron Radiation Facility (Grenoble, France) with a  $6\text{ }\mu\text{m}^2$  focused beam. The textural and semi-quantitative analysis of the same crystals were carried out with the scanning electron microscope equipped with a AZtec EDS at Sapienza University of Rome. The chemical composition was analyzed by electron microprobe analyses at MEMA laboratory of the University of Florence.

The analyzed olivine crystals show a  $\text{Mg}/(\text{Mg}+\text{Fe})$  ranging between 0.89-0.90; while the  $\text{Cr}/(\text{Cr}+\text{Al})$  of spinels is 0.16-0.18. The  $\text{Fe}^{3+}/\Sigma\text{Fe}$  of spinels varies between 0.10 and 0.14, which is lower than what generally reported for spinel-peridotites (up to about 0.40). Interestingly, in the veined peridotite, the  $\text{Fe}^{3+}/\Sigma\text{Fe}$  of opx varies between the matrix and the metasomatized portion from 0.03 (e.g., in agreement with literature data) to 0.08, respectively. The  $\log f_{\text{O}_2}$  was calculated by using the available oxythermobarometry (Ballhaus et al. 1991) at the P of 0.8 GPa and T of 1000°C and ranges from -1.49 to -1.10 (normalized to the fayalite-magnetite-quartz reference buffer).

Our results of both  $\text{Fe}^{3+}/\Sigma\text{Fe}$  and  $\log f_{\text{O}_2}$ , coupled with the  $\delta^{18}\text{O}$  available for the same minerals of the studies peridotite samples, show a positive correlation in the case of spinel but an opposite trend for olivine, cpx and opx that can be preliminarily explained in terms of preferential  $^{18}\text{O}/^{16}\text{O}$  partitioning.

These data combined with thermodynamic modeling of the C-O-H fluid speciation at the given P, T and  $f_{\text{O}_2}$  can be taken as first evidence of the oxidizing role of  $\text{CO}_2$ -bearing Si-rich fluids released from the subducted continental crust deep into the mantle.

Avanzinelli R., Bianchini G., Tiepolo M., Jasim A., Natali C., Braschi E., Dallai L., Beccaluva L. & Conticelli S. (2020) - Subduction-related hybridization of the lithospheric mantle revealed by trace element and Sr-Nd-Pb isotopic data in composite xenoliths from Tallante (Betic Cordillera, Spain). *Lithos*, 352-353. <https://doi.org/10.1016/j.lithos.2019.105316>.

Ballhaus C., Berry R.F. & Green D.H. (1991) - High pressure experimental calibration of the olivine-orthopyroxene-spinel oxygen geobarometer: implications for the oxidation state of the upper mantle. *Contr. Mineral. and Petrol.*, 107, 27-40. <https://doi.org/10.1007/BF00311183>.

Bianchini G., Beccaluva L., Nowell G.M., Pearson D.G. & Siena F. (2011) - Mantle xenoliths from Tallante (Betic Cordillera): insights into the multi-stage evolution of the south Iberian lithosphere. *Lithos*, 124, 308-318. <https://doi.org/10.1016/j.lithos.2010.12.004>.

Dallai L., Bianchini G., Avanzinelli R., Natali C. & Conticelli S. (2019) - Heavy oxygen recycled into the lithospheric mantle. *Sci. Rep.*, 9, 8793. <https://doi.org/10.1038/s41598-019-45031-3>.



## Chemical and mineralogical modifications during high-pressure melt-harzburgite reaction: constraints from experiments at 1-2 GPa

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*Keywords:* melt-peridotite reaction, mantle heterogeneity, trace elements.

Earth’s upper mantle is mainly composed of peridotites, which can evolve over time due to events of chemical depletion caused by partial melting and/or refertilization, which involves the addition of incompatible elements via reactive melt percolation. In sub-ridge oceanic settings, mantle peridotites undergo melt extraction and concomitant depletion of incompatible elements, which can be followed by refertilization through equilibration with transient melts of varying extents. The interaction between depleted peridotite and MORB-like infiltrating melts is widely recognized to significantly modify the mineralogy and chemistry of residual mantle, and in turn, to affect the isotopic evolution of large portions of the lithospheric mantle. However, the extent and mechanism of chemical equilibration between mantle minerals and percolating melts during melt-peridotite reactions are still poorly understood.

This work aims to provide new experimental constraints by performing piston cylinder experiments of melt-harzburgite interaction at P-T conditions consistent with those of the lithosphere-asthenosphere boundary. The starting material is a mixture of mantle minerals and glass. Harzburgite is modeled as a mix of San Carlos olivine (Fo90) and orthopyroxene separated from a depleted spinel peridotite of the Mt. Maggiore (Corsica, France) ophiolitic massif, residual after MORB-producing partial melting (opx CeN/YbN = 0.0019; Rampone et al., 2008). The initial reacting melt is a tholeiitic basaltic glass sampled at the Romanche Fracture zone, with a relatively low  $X_{Mg}$  (0.60), high alkali (Na<sub>2</sub>O = 3.48 wt%, K<sub>2</sub>O = 0.81 wt%), and an enriched-MORB signature (La<sub>N</sub>/Yb<sub>N</sub> = 5.49). Previous crystallization experiments at 1-2 GPa on the selected starting glass have indicated that clinopyroxene is the liquidus phase.

We performed experiments starting with basalt:orthopyroxene:olivine proportions of 1:1:1 at 1, 1.5, and 2 GPa and 1250-1350°C. Preliminary results indicate that mantle minerals are chemically modified by the interaction with the basaltic melt. Run products consist of orthopyroxene, olivine, and reacted glass, with a few grains of newly crystallized clinopyroxene at 2 GPa. Rims of partially reabsorbed orthopyroxene have acquired high TiO<sub>2</sub> and low Cr<sub>2</sub>O<sub>3</sub> with respect to the initial orthopyroxene composition. Olivine is homogeneous and chemically modified with respect to San Carlos olivine towards higher CaO and lower NiO contents.

Rampone E., Piccardo G.B. & Hofmann A.W. (2008) - Multi-stage melt-rock interaction in the Mt. Maggiore (Corsica, France) ophiolitic peridotites: microstructural and geochemical evidence. *Contrib. Mineral. Petrol.*, 156, 453-475. <https://doi.org/10.1007/s00410-008-0296-y>.

## Reconstructing the P-T structure and composition of the Siberian sub-cratonic lithospheric mantle: clues from spinel, spinel-garnet and garnet peridotite xenoliths from the Udachnaya-East kimberlite

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Keywords: garnet peridotite, sub-cratonic lithosphere, Siberia.

Peridotite xenoliths and diamonds provide direct evidence of the architecture, composition and evolution of the oldest and deepest portions of the Earth's lithosphere. In this study, a detailed chemical-textural characterization of spinel- to garnet-bearing peridotite xenoliths from the Udachnaya-East kimberlite (Siberian craton) was used to reconstruct the T-P-X-t history of the sub-cratonic lithospheric mantle. The samples are mostly harzburgites and dunites, with subordinated lherzolites, orthopyroxene-rich harzburgites (up to 40 vol.% orthopyroxene) and rare wehrlites. Their texture ranges from protogranular (typical of dunites and harzburgites) to highly recrystallized and/or sheared (typical of the more clinopyroxene-rich varieties).

Spinel-bearing rocks have refractory composition, with primary Mg-Ni-rich olivine ( $\text{Fo}_{90-93}$ ; NiO = 0.34-0.46 wt%), Mg-rich and Al-poor primary orthopyroxene (Mg# = 92-94;  $\text{Al}_2\text{O}_3$  = 0.3-3.0 wt%) and clinopyroxene (Mg# = 94-96;  $\text{Al}_2\text{O}_3$  = 1.0-3.5 wt%). In garnet-bearing peridotites, primary olivine ranges from Mg-Ni-rich ( $\text{Fo}_{92}$ ; NiO = 0.45 wt%) to relatively Fe-rich and Ni-poor varieties ( $\text{Fo}_{87}$ ; NiO = 0.25 wt%), mirrored by primary pyroxenes (Mg# from 93 to 87-88;  $\text{Al}_2\text{O}_3$  in orthopyroxene = 0.5-1.1 wt%;  $\text{Al}_2\text{O}_3$  in clinopyroxene = 0.8-2.2 wt%). A combination of the two-pyroxene thermometry and the Al-in-orthopyroxene barometry validated against other methods indicated that the garnet-bearing peridotites equilibrated at P ranging from ~3.2 to ~6.3 GPa, and T comprised between ~800 and ~1350°C. Spinel-bearing peridotites equilibrated at shallower depths, i.e. from ~2.1 to 2.7 GPa or from ~2.8 to 3.8 GPa, depending on the chosen model geotherm (40 mWm<sup>-2</sup> vs. 45 mWm<sup>-2</sup>). Compared to robust P-T estimates for xenoliths from literature (Faccincani et al. 2022; Liu et al. 2022), our results enable to model the thermo-chemical log of the Siberian sub-cratonic mantle and place constraints on the origin of modal, chemical and temperature variations in the thick sub-cratonic lithosphere.

Faccincani L., Cerantola V., Nestola F., Nimis P., Ziberna L., Pasqualetto L., Chumakov A.I., Harris J.W. & Coltorti M. (2022) - Relatively oxidized conditions for diamond formation at Udachnaya (Siberia). *European Journal of Mineralogy*, 34(6), 549-561. <https://doi.org/10.5194/ejm-34-549-2022>.

Liu Z., Ionov D.A., Nimis P., Xu Y., He P. & Golovin A.V. (2022) - Thermal and compositional anomalies in a detailed xenolith-based lithospheric mantle profile of the Siberian craton and the origin of seismic midlithosphere discontinuities. *Geology*, 50(8), 891-896. <https://doi.org/10.1130/G49947.1>.

## Ca-carbonatite mantle metasomatism, and kimberlite-like melt ascent recorded in xenoliths from the Andean Northern Volcanic Zone (Colombia): a window on mantle wedge dynamics

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Keywords: websterite, Andes, metasomatism.

Crustal foundering and relamination in arcs are regarded as mechanisms to explain mass balance at continental roots and geochemical features of the crust, on timescales of  $10^6 - 10^7$  years. Conversely, metasomatism from the subducted slab, partial melting, and magma ascent can occur over very short timescales, sometimes lasting as little as  $10^{-3} - 10^{-4}$  years, i.e. a matter of hours. The lithological evidence of such processes is rare and spatially decoupled. At Mercaderes - Rio Mayo volcanic area, Northern Volcanic Zone (Colombia), an extraordinarily variable suite of high pressure, crustal and mantle xenoliths, from garnet pyroxenites to garnet peridotites, was erupted sampling the entire lithosphere-asthenosphere column below the Andean arc. Here we show that a subset of garnet pyroxenites, equilibrated at  $\approx 1250^\circ\text{C}$  and 3.7 GPa, experienced abundant growth of aragonite, dolomite and calcite, leading to hybrid ultramafic bulk compositions containing up to 30 wt% CaO, at  $X_{\text{Mg}} = 0.91$ .

Microstructural analysis reveals the occurrence of two distinct stages of carbonate precipitation. During the first stage, aragonite is stable alongside garnet and clinopyroxene, while orthopyroxene is replaced by Mg-calcite. The second stage results in heavily zoned dolomites and calcites, similar to those observed in some kimberlitic magmas. The silicate-carbonate phase relationships suggest that the carbonate precipitation resulted from a reaction with a Ca-rich carbonatitic liquid along a decompression path of a rising magmatic column. It is believed that  $\text{CO}_2$  exsolution in the liquid, facilitated by orthopyroxene dissolution, contributed to the engagement of xenoliths, as observed in kimberlites.

The C-O isotopic composition of carbonates reveals that the geochemical signature of mantle wedge metasomatism is governed by subducted organic carbon.

During the ascent process, a suite of intermediate and mafic arclogites that had foundered to pressures exceeding 2 GPa was sampled. However, arclogites and shallower gneisses did not exhibit carbonate metasomatism, implying that the transporting magma was primarily silicate at crustal depths, consistent with the progressive dilution of the carbonatitic component. The diversity of xenolith compositions, the presence of carbonates in websterites, and the microstructural characteristics of calcite-dolomite solid solutions can be best explained by a burst of magma ascending through a sub-arc mantle channel, similar to the earthquake swarms detected in the upper mantle beneath the Mariana and Izu-Bonin arcs. We advocate that arc root foundering and fluid-driven upward propagation of fractures contributing to volcanic activity coexist in the wedge dynamics but operate on different time scales.

## Petrological study of mantle xenoliths from Bou Ibalghatene and Tafraoute maars, Middle Atlas (Morocco)

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**Keywords:** mantle xenoliths, Middle Atlas, metasomatism, upper lithospheric mantle, melt extraction.

Melt extraction and metasomatic processes engraved in mantle-derived xenoliths may provide useful insights into the evolution of Earth's Lithospheric Mantle.

In the Middle Atlas region (Morocco), a major lithospheric attenuation, accompanied by genesis of Miocene to Quaternary basalts, alkali basalts, basanites and nephelinites, caused the rise of the lithosphere-asthenosphere boundary (El Azzouzi et al., 2010; El Messbahi et al., 2015). To shed light on the processes occurring in the Sub-Continental Lithospheric Mantle underneath Middle Atlas, we studied 25 mantle xenoliths from the Bou Ibalghatene and Tafraoute maars.

The studied samples are spinel-bearing lherzolites, harzburgites and wehrlites, with textures ranging from protogranular to mosaic and porphyroclastic. Some rocks contain up to 1 mm sized melt pockets consisting of fine-grained amphibole, olivine, clinopyroxene and spinel as well glass and vesicles. Samples with protogranular texture are made of coarse-grained olivine and orthopyroxene crystals, smaller clinopyroxene and lobate spinel. In the protogranular to mosaic samples, spinel is rounded, while the fine-grained samples have foliated textures. The porphyroclastic rocks are also foliated, with kink-banded elongated olivine and dusty orthopyroxene porphyroclasts, together with smaller orthopyroxene, clinopyroxene and spinel crystals. Transitional textures are also present in some samples.

Preliminary analyses on Tafraoute samples show that primary olivine has Fo contents ranging from 89 to 90, with NiO contents between 0.35 and 0.40 wt%. Olivine in the melt pockets span over a wide compositional range, divided into high Mg and Ni (Fo<sub>91-93</sub>; NiO = 0.30-0.47 wt%), to low Mg-Ni (Fo<sub>86-91</sub>; NiO = 0.15-0.30 wt%). The Mg# of the clinopyroxene ranges between 90.0 and 91.5, with Al<sub>2</sub>O<sub>3</sub> ranging between 4.0 and 8.0 wt%. Clinopyroxene from melt pockets shows a wider range of compositions, varying from Fe-Al-rich (Mg# = 88 to 79; Al<sub>2</sub>O<sub>3</sub> = 8.5 to 14.0 wt%) to Mg-rich and Al-poor (Mg# up to 92; Al<sub>2</sub>O<sub>3</sub> down to 0.7 wt%). The Mg# of orthopyroxene ranges between 88.5 and 91, and the Al<sub>2</sub>O<sub>3</sub> content varies from 1.5 to 5.0 wt%. Spinel has Mg# varying from 70 to 77 and Cr# from 5 to 25. Using the Cr# of spinel as a proxy (Hellebrand et al., 2001) the calculated degree of partial melting is up to 11.5%. However, the presence of melt pockets with basaltic to andesitic glass and olivine, clinopyroxene and spinel with compositions different from those of the rock forming minerals indicate that melt-rock interactions (i.e. metasomatism) took place after the melt extraction, which is consistent with what was proposed in the literature (Natali et al., 2013; El Messbahi et al., 2015).

El Azzouzi M., Maury R. C., Bellon H., Youbi N., Cotten J. & Kharbouch F. (2010) - Petrology and K-Ar chronology of the Neogene-Quaternary Middle Atlas basaltic province, Morocco. *Bull. de la Soc. Géol. Fra.*, 181, 243-257.

El Messbahi H., Bodinier J-L., Vauchez A., Dautria J-M., Ouali H. & Garrido C.J. (2015) - Short wavelength lateral variability of lithospheric mantle beneath the Middle Atlas (Morocco) as recorded by mantle xenoliths. *Tectonophysics*, 650, 34-52.

Hellebrand E., Snow J. E., Dick H.J.B. & Hofmann A.W. (2001) - Coupled major and trace elements as indicators of the extent of melting in mid-ocean-ridge peridotites. *Lett. to Nat.*, 410, 677-681.

Natali C., Beccaluva L., Bianchini G., Ellam R.M., Siena F. & Stuart F.M. (2013) - Carbonated alkali-silicate metasomatism in the North Africa lithosphere: evidence from Middle Atlas spinel-lherzolites, Morocco. *J. S. Amer. E. Scie.*, 41, 113-121.

## Mineral inclusions in eclogitic diamonds from Udachnaya pipe (Siberia) help to track the geochemical and redox evolution of the subducted ancient oceanic crust and the deep volatiles recycle

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Keywords: diamond, eclogite, redox state.

Subduction is the main carrier of oxidized material into the deep mantle and has a key role in changing the mantle redox state and controlling the volatiles cycle (C, O, H, S, N, B). Kimberlite-borne eclogite xenoliths are the product of metamorphic processes that the ancient oceanic crust (protolith) undergoes and are considered fertile diamond source rocks (Aulbach & Stachel, 2022). Due to the inert nature of diamond, the trapped mineral inclusions provide pristine information about chemistry, mineralogy and, in turn, redox state of the eclogite as well as on the early transport of volatiles in depth. In addition, the chemistry of the bulk rock, once reconstructed, allows constraining the nature of the protolith.

In this study, we investigated 19 eclogitic diamonds from the Siberian craton (Russia) with coexisting garnet (grt) and clinopyroxene (cpx) inclusions both exposed (after polishing) and trapped, with sizes ranging from 20 to 100  $\mu\text{m}$ . The grt and cpx hand-picked from the host eclogite of one diamond were also analysed. The crystal-chemistry (major elements and vanadium) was determined by electron microprobe analyses of the exposed inclusions, while the  $\text{H}_2\text{O}$  content of cpx and grt was measured by Fourier Transform infrared spectroscopy supported by X-ray tomography. The  $\text{Fe}^{3+}/\Sigma\text{Fe}$  of both exposed and encapsulated inclusions was measured by Synchrotron Mössbauer spectroscopy. Finally, the Raman spectroscopy was employed to identify additional tiny, trapped inclusions.

Chemical variabilities among the reconstructed bulk rocks are observed in terms of Mg# (0.55-0.75), V concentration (150-450 ppm) and  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratio (0.05-0.10). Pressure and temperature of equilibrium are between 5 and 8 GPa and 1100-1350°C, respectively, and are supported by the finding of coesite as inclusion. The calculated  $\log f_{\text{O}_2}$  ranges between -4 and -0.4 log units ( $\Delta\text{FMQ}$ ). Notably, we observed a similar  $\log f_{\text{O}_2}$  and V bulk rock concentration for the inclusions in one of the investigated diamonds and the corresponding host eclogite, indicating that eclogite mineral assemblages might preserve their redox state even during diamond formation from  $\text{CO}_2$  growth media as proposed by Aulbach & Stachel (2022). Our results provide evidence of heterogeneous redox conditions at local scale, likely indicating both that diamonds grew from diverse fluids from  $\text{CH}_4\text{-H}_2\text{O}$  to  $\text{CO}_2\text{-H}_2\text{O}$  dominated and/or originated from different protoliths.

Aulbach S. & Stachel T. (2022) - Evidence for oxygen-conserving diamond formation in redox-buffered subducted oceanic crust sampled as eclogite. *Nature Communications*, 13(1), 1924.

## **Modelling ancient volcanoes from zoned clinopyroxene populations and cumulitic nodules: dynamics and timescales of Middle-Triassic plumbing systems in the Dolomites (Southern Alps; Italy)**

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*Keywords:* clinopyroxene, mixing, Dolomites.

During the Middle Triassic, the easternmost sector of the Southern Alps experienced short-lived trachybasaltic, trachyandesitic to transitional and strongly alkaline magmatic event. Clinopyroxene populations within the different volcanic products show frequent compositional zoning, allowing us to unravel the architecture and dynamics of the plumbing systems of the main magmatic centres for the first time. Clinopyroxene shows concentric zoning patterns between low Mg# [ $\text{MgO}/(\text{MgO}+\text{FeO}_{\text{tot}})$  mol%], low- $\text{Cr}_2\text{O}_3$  (Mg# 67-78;  $\text{Cr}_2\text{O}_3 < 0.1$  wt%) augitic compositions and high-Mg# and  $\text{Cr}_2\text{O}_3$ -rich diopsidic portions (Mg# 74-91;  $\text{Cr}_2\text{O}_3$  up to 1.2 wt%). The diopsidic domains are less abundant: they occur more frequently as single or multiple bands with variable thickness, in between augitic cores and rims, but are subordinately present also as resorbed or mottled cores. The augitic domains make up the majority of the crystal cores and all the rims. Oscillatory zoning and sector-zoned crystals are also present in minor numbers. Thermobarometric models suggest the presence of shallow to mid-crustal plumbing systems (5-8.5 km) characterised by the presence of a trachyandesitic crystal mush (Mg# 45;  $T = 996\text{-}1148^\circ\text{C}$ ) periodically refilled and remobilized by mafic injections of more primitive trachybasaltic magma (Mg# 56;  $T = 1109\text{-}1204^\circ\text{C}$ ) responsible for the crystallisation of the diopsidic domain around pre-existing augitic cores and the recycling of antecrysts from a deeper diopsidic mush (10-17 km). The latter is present as clinopyroxenitic cumulates outcropping as nodules embedded in dykes manifestation near the Latemar platform (north of Predazzo; Dolomites). Diffusion chronometry computations using the NIDIS model (Petrone et al., 2016) based on Fe-Mg inter-diffusion in clinopyroxene have revealed that the timescale from the mafic injection to the eruption was less than a year to decades with differences between the single centres considered. This study enables us to describe in extreme detail the magma dynamics that fuelled the Middle Triassic occurrence in the Southalpine domain. This ancient magmatism, where the plutonic counterpart of the volcanic sequences crops out and preserve the original geometry, is a proxy for disentangling the behaviour of active volcanic complexes, where the deeper portions of the plumbing system are only indirectly accessible.

Petrone C.M., Bugatti G., Braschi E. & Tommasini S. (2016) - Pre-eruptive magmatic processes re-timed using a non-isothermal approach to magma chamber dynamics. *Nature communications*, 7(1), 12946. <https://doi.org/10.1038/ncomms12946>.



## New insights on the noble gas and CO<sub>2</sub> signature of the lithospheric mantle beneath La Palma (Canary Islands)

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*Keywords:* mantle xenoliths, fluid inclusions, noble gas, carbon.

Fluid inclusions (FI) trapped in mantle xenoliths are a powerful tool to characterize the volatiles circulation in the lithosphere, discriminate the different isotopic reservoirs in the mantle and comprehend the main geodynamic processes. In this opportunity, we present the very first data on noble gas and carbon isotopes in mantle xenoliths hosted in basanitic lavas erupted in 1677 A.D. by the historical volcano of San Antonio at La Palma (Canary Islands). The analyses were performed at the Istituto Nazionale di Geofisica e Vulcanologia (INGV) of Palermo. We analyzed FI hosted in olivine and orthopyroxene in 14 xenoliths with harzburgitic to dunitic composition (Sandoval-Velasquez et al., 2023). The estimated Rc/Ra (3He/4He corrected for atmospheric contamination) average for La Palma xenoliths is  $6.93 \pm 0.16$  (1s). Although the average is in the lower limit of the MORB range ( $8 \pm 1$  Ra; Graham, 2002), values as low as 6.5 have been observed in both olivine and orthopyroxene, suggesting the presence of a radiogenic component in the local mantle. This contrasts with the information obtained from the lavas previously erupted along the Cumbre Vieja ridge (southern La Palma) and the mantle rocks in the neighboring island of El Hierro, where FI show MORB-like 3He/4He signature (Day & Hilton, 2011; Sandoval-Velasquez et al., 2021b). We propose that the relatively low radiogenic signature of the San Antonio xenoliths reflects a recycled oceanic (crustal/lithospheric) component in the local mantle. On the other hand,  $\delta^{13}\text{C}$  measured in FI vary between -4.4 and -2.2, showing a similar variability to the values reported in the Dos Aguas Spring (northern La Palma) and partially agreeing with the positive values reported in El Hierro ( $\delta^{13}\text{C} > -2.5$ ; Sandoval-Velasquez et al., 2021b). This fosters question upon the origin of the  $\delta^{13}\text{C}$  variability, and its potential relationships with recycling of crustal components into the lithospheric mantle or fractionation processes between fluid, melt or solid phases.

Day J.M.D. & Hilton D.R. (2011) - Origin of 3He/4He ratios in HIMU-type basalts constrained from Canary Island lavas. *Earth Planet. Sci. Lett.*, 305, 226-234. <https://doi.org/10.1016/j.epsl.2011.03.006>.

Sandoval-Velasquez A., Rizzo A.L., Aiuppa A., Remigi S., Padrón E., Pérez N.M. & Frezzotti M.L. (2021b) - Recycled crustal carbon in the depleted mantle source of El Hierro volcano, Canary Islands. *Lithos*, 400-401, 106414. <https://doi.org/10.1016/j.lithos.2021.106414>.

Sandoval-Velasquez A., Rizzo A.L., Casetta F., Ntaflos T., Aiuppa A., Alonso M., Padron E., Pankhurst M., Mundl-Petermeier A. & Perez N.M. (2023) - The 2021 Cumbre Vieja eruption (La Palma, Canary Islands): new perspectives on the geochemistry of lavas and noble gases isotopes trapped in fluid inclusions. <https://doi.org/10.5194/egusphere-egu23-14572>.

Sano Y. & Marty B. (1995) - Origin of carbon in Fumarolic gas from island arcs. *Chem. Geol.*, 119, 265-274. [https://doi.org/10.1016/0009-2541\(94\)00097-R](https://doi.org/10.1016/0009-2541(94)00097-R).

## Heterogeneous mantle domains in a modern OCT: new insights from the West Iberian margin (ODP Legs 149 and 173)

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*Keywords:* ocean-continent transitions, mantle, West Iberian margin.

Magma-poor ocean-continent transition zones (OCTs) represent wide areas of tectonically uplifted mantle. While an important body of literature has dealt with the investigation of fossil analogues (e.g. Picazo et al., 2016, and references therein), studies on mantle sequences exhumed in modern OCTs remain a few (e.g. McCarthy et al., 2020), leaving our knowledge somehow fragmentary. In particular, how, where and when lithospheric breakup occurs, the timing of melt production, and the nature of the mantle source involved remain hotly debated issues.

Among the best-documented continental margins worldwide, the West Iberian margin represents a unique site where mantle has been accessed through scientific drilling more than three decades ago (e.g. Boillot et al., 1989). However, these peridotites have remained poorly characterized, partly because of their pervasive serpentinization.

In this contribution, we present the results of an in situ petrological and geochemical study performed on a set of mantle peridotites from ODP Holes 899B, 1068A, and 1070A. In Hole 899B, relatively fresh spinel- and plagioclase-bearing harzburgites (cpx  $\approx$  2-8 vol.%) occur. In contrast, highly serpentinized plagioclase lherzolites and spinel harzburgites were sampled in Holes 1068A and 1070A.

Hole 899B spinel harzburgites bear refractory compositions, as attested by the low clinopyroxene contents ( $\approx$  2-3 vol.%), coupled to moderate spinel Cr# (0.230-0.343) and low pyroxene  $Yb_N$  ( $\approx$  1-2). Geochemical modeling based on pyroxene trace element compositions points to significant degrees of melt extraction (up to  $\approx$  15%), starting in the garnet stability field, followed by post-melting metasomatism.

Holes 899B and 1068A plagioclase-bearing samples share remarkable similarities, i.e. frequent occurrence of (altered) plagioclase rims mantling elongated dark spinel, Na<sub>2</sub>O- and Al<sub>2</sub>O<sub>3</sub>-rich clinopyroxene associated with high TiO<sub>2</sub> spinel (up to 0.66 wt%). Clinopyroxene shows convex-upward REE patterns, yielding negative Eu anomalies and higher HREE contents compared to abyssal peridotites. Hence, these peridotites are not simple partial melting residues but experienced melt-rock interaction processes and re-equilibration in the plagioclase stability field.

Hole 1070A peridotites exhibit contrasting signatures, as highlighted by the presence of Na<sub>2</sub>O-rich, Al<sub>2</sub>O<sub>3</sub>-poor clinopyroxene coupled to spinel with high Cr# (0.246-0.428) and TiO<sub>2</sub> below the detection limit. Orthopyroxene trace element investigation of these samples revealed hump-shaped patterns with variable LREE-MREE fractionation ( $La_N/Sm_N = 0.003-0.16$ ) and low  $Yb_N$  ( $\approx$  1-2).

Our new data attest a wide spectrum of petrological and geochemical characters shown by mantle rocks exhumed in a modern OCT. This heterogeneous nature possibly reflects a complex interplay between rifting-related processes and previous depletion history inherited from the last Wilson cycle.

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## Geochemical laboratory at DST UNIMI: toolbox for investigating the Earth

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*Keywords:* geochemistry, geochronology, isotope geology.

A new advanced geochemical laboratory for in situ characterisation of geological materials has been recently developed at the Dipartimento di Scienze della Terra “Ardito Desio” (DST) of the University of Milano (UNIMI) thanks to funding received in the frame of the “Progetto Dipartimenti di Eccellenza” 2018-2022 and 2023-2027.

Solid sampling is carried out with a 193nm excimer laser ablation microprobe (Analyte Excite Teledyne Photon Machines) equipped with a two volume ablation cell and the rapid sample introduction system (ARIS). The ablated material can be analysed either with a single quadrupole ICP-MS (iCAP RQ - Thermo Scientific) or with a multi collector (MC)-ICP-MS (Neptune XT - Thermo Scientific).

When coupled with the single collector ICP-MS, the laser ablation system allows very high signal/background ratios and thus trace elements quantification down to the ppb levels in many geological materials even with very small spot sizes (<10 mm). The stability and sensitivity of the instrument also guarantee accurate and precise geochronological results in the U-Th-Pb system for U-rich phases. The availability in the laboratory of multiple matrix-matched standards allow geochronological characterisation of zircon, titanite, apatite and monazite and, subordinated to their U concentrations, of carbonates. Excellent results have been obtained also with characterisation of the whole rock composition of samples in the form of powder pressed pellets for major, minor, and trace elements.

When combined with the multi collector-ICP-MS, the laser microprobe returns the high-precision and high-resolution isotopic characterisation of geological materials and in particular allows to constrain micro-scale isotopic disequilibria that are the key for understanding the evolution of the lithosphere. Among the newly developed methods and applications we provide examples from the study of fluid-rock interaction mechanisms in subduction setting as well as the evolution of mantle-derived melts using the  $d^{11}\text{B}$  and  $d^7\text{Li}$  signature of phases enriched in these elements (e.g. tourmalines, micas, serpentines). Additionally, first results are presented for the  $d^{49}\text{Ti}$  in Ti-rich minerals that represents a new frontier to track processes that affect the composition and evolution of primitive mantle-derived melts through Earth's history. The instrument routinely analyses Hf isotopic ratio in zircon providing information on the parental magma petrogenesis and heterogeneities derived from mixing of melts with different origin. A method for the determination of  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in plagioclase, amphibole, clinopyroxene and carbonates has been developed and successfully applied to identify different melt sources in the frame of a single mineral or rock system.

Laser ablation trace element mapping is under development using the available analytical facilities and in the next future compositional maps will be produced using a time-of-flight ICPMS system that will be installed in 2024.

## Mantle eclogites and eclogitic diamonds: witnesses of Archaean deep mantle heterogeneities and robust redox buffers

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To date, cratonic eclogites distributed worldwide show redox conditions expressed in oxygen fugacity ( $f_{O_2}$ ) varying from -6 to -0.1 log units normalized to FMQ buffer (Mikhailenko et al., 2020; Aulbach et al., 2022). On the other hand, reconstructions of magmatic  $f_{O_2}$  from geochemical analyses of ancient unaltered eclogites suggest that Archaean mantle source conditions are reducing (Aulbach and Stagno 2016). Few available data on eclogitic inclusions trapped in lithospheric diamonds also record wide range of  $f_{O_2}$  compatible with the presence of either  $CO_2$ -rich melts or methane-bearing fluids.

In this study, we focused on a suite of diamond-free eclogitic nodules from V. Grib kimberlite pipe belonging to the Arkhangelsk Diamondiferous Province (NW Russia), one of the main diamond extraction sites in Russia. We determined  $Fe^{3+}/\Sigma Fe$  by milliprobe Mössbauer spectroscopy of coexisting (and unaltered) garnet and clinopyroxene extracted from 17 eclogites (5 high-Mg eclogites and 12 low-Mg eclogites), while the chemical composition of the same samples was determined by electron microprobe. The  $Fe^{3+}/\Sigma Fe$  ranges between 0.03 and 0.20 for garnet and from 0.18 to 0.38 for clinopyroxene, the former reaching higher values than what was measured previously in garnets equilibrated at mantle conditions. Thermobarometric calculations resulted in equilibration pressures of about 4 to 8 GPa and temperatures of 950-1300 °C both for high-MgO and low-MgO eclogites. The  $\log f_{O_2}$  calculated using the available oxythermobarometry varies between -2.4 to -0.9 log units ( $\Delta FMQ$ ) for the high-MgO eclogites and from -3.10 to 0.6 log units ( $\Delta FMQ$ ) for the low-MgO eclogites. The average values of -1.85 ( $\pm 0.57$ ) log units for the former and -0.76 ( $\pm 1.09$ ) log units for the latter indicates the different redox path of the protolith during subduction.

Our data are compared with the P-T- $f_{O_2}$  determined from few eclogitic garnets and cpx pairs trapped in lithospheric diamonds.

The majority of eclogitic garnets display lower  $Fe^{3+}$  content (between 0 and 10%  $Fe^{3+}/\Sigma Fe$ ) than peridotitic ones at similar  $\log f_{O_2}$  (up to about 20%; Stagno, 2019). Such low ferric iron content of garnet can be explained to a first approximation as a consequence of the high modal proportion of garnet in eclogites compared to peridotites (up to 15%) within which  $Fe^{3+}$  of the mafic protolith is partitioned into.

These results provide evidence of the redox variability of eclogites of Archaean age and suggest the oxidizing nature of the subducted mafic rocks to be a likely consequence of either the mantle source where the magma formed or exposure to the first *whiffs* of oxygen into the Early Archean atmosphere.

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## **Project DIVE: Probing the continental lower crust and its transition to the mantle through scientific drilling**

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*Keywords:* ICDP drilling, Moho transition, continental crust.

DIVE (Drilling the Ivrea-Verbano zone) is an international scientific project that aims to explore the nature and evolution of the Earth's deep continental crust and crust-mantle transition zone through scientific drilling. The DIVE project is sponsored by the International Continental Scientific Drilling Program and by other national and international funding agencies. Drilling activities, including continuous wireline coring, focus on deep crustal and mantle units of the Ivrea-Verbano Zone (Western Alps, Italy), one of the most complete and best studied archetypes of a continental crust–upper mantle sections on Earth. Phase 1 of the project involves two deep scientific boreholes in Val d'Ossola, to obtain continuous sampling and logging through the pre-Permian metabasic and metasedimentary lower crust of the Ivrea-Verbano Zone. One borehole has already been drilled in Ornavasso, reaching 578 m depth. The cores (100% recovery) mostly consist of amphibolites and garnet-bearing metapelites with variable presence of migmatitic structures, and with local high and low temperature shear zones, pegmatitic dikes, and open fractures. Continuous monitoring of borehole fluids and two main sets of logging measurements were performed. The second borehole is planned to take place in Fall 2023 in Megolo (Pieve-Vergonte municipality), very close to the Insubric Line, with the goal to reach ca. 1 km depth into felsic and mafic granulites and ultramafic mantle rocks, depicting a fossil Paleozoic transition from the lowermost continental crust and the upper mantle. Scientific investigations are highly multidisciplinary, including geophysics, petrology, structural geology, rock-fluid geochemistry, and microbiology. In this contribution, we will present the scientific background, the major interdisciplinary steps of the project, from planning to operations, and the first results obtained in the first borehole in Ornavasso in Val d'Ossola.

**S29.**

**Extraterrestrial materials: from meteorites to planetary bodies**

*CONVENERS AND CHAIRPERSONS*

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## More quasicrystals in the cosmos? Preliminary observations of new khatyrka-like fragments

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Keywords: micrometeorites, quasicrystals, CuAl alloy.

Each year thousands of tons of microscopic particles of extraterrestrial material, named micrometeorites (MMs), fall on Earth, suffering variable processes of melting and vaporization. Recently, two remarkable fragments have been found at Monte Gariglione (Catanzaro, Italy) and are under investigation. The particles consist of a micro-spherule of about 400  $\mu\text{m}$  in diameter and an irregular fragment of about the same size. Both grains are dark gray with visible portions that exhibit metallic luster. The micro-spherule shows a singular scoriaceous structure, vesicles, and little protruding spherical metal particles. To optimize the investigation, preserving at first the integrity of the fragments so as not to lose valuable information, the analyses have been carried out in a nondestructive way using micro-Computed X-ray Tomography ( $\mu\text{-CT}$ ) and Scanning Electron Microscopy (SEM).

Preliminary results obtained by SEM-EDS reveal that both particles exhibit extraterrestrial features, including forsteritic olivine crystals in a porous matrix of silicates, Fe-Ni metals, Fe-Ni sulfides, and oxides. Most of the metallic portions result to be Al-Cu alloys with very low content of Fe. The alloys consist of worm-like intergrowths of nearly pure Al in khatyrkite ( $\text{CuAl}_2$ ) and stolperite ( $\text{CuAl}$ ). The 3D reconstruction obtained by  $\mu\text{-CT}$ , which represents a useful approach to obtain information about the spatial distribution and the relationships of mineralogical phases (Manzari et al., 2023), evidenced that the interior of the spherule is enriched of metallic alloys intermixed with silicates and voids.

This finding represents the third independent discovery of naturally occurring intermetallic Al-Cu-Fe alloys. It is thus similar to the previously reported Khatyrka meteorite - a CV3 chondrite containing near-identical alloys and the only known natural quasicrystals (MacPherson et al., 2013). However, the scoriaceous structure and the low amounts of Fe in the alloy suggest a greater similarity with KT01, the second CO-like micrometeorite characterized by the presence of Al-Cu intermetallic alloys found in 2013 in the Nubian desert, Sudan (Suttle et al., 2019).

Does the third independent occurrence of these exotic extraterrestrial objects mean that Al-Cu alloys must be common in space? The answer is likely no, but these materials may prove to be more frequent than previously thought.

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## Petro-mineralogical and geochemical study of lunar meteorite NWA 13859

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Keywords: Lunar meteorite, feldspathic breccia, trace elements.

The composition of the lunar crust provides key information on the petrological evolution of the Moon. Studies mostly based on analyses of Apollo samples revealed the presence of two well distinct groups of rocks within the Highlands, Ferroan Anorthosites (FAN) and Mg-suite. The presence of these two well defined groups represents a key evidence for the Lunar Magma Ocean model (Warren & Taylor, 2014). Data from lunar meteorites, which may sample a larger portion of the lunar surface, have shown the presence of a more widespread compositional range leading to a re-evaluation of the Lunar Magma Ocean model (Gross et al., 2014). However, the “pristine” character of lunar meteorites has been questioned as they may represent impact-mixtures.

In the framework of the MELODY project, we investigated the lunar meteorite NWA 13859, a polymict feldspathic breccia made up by several lithic clasts of variable lithologies (anorthosites, gabbroic anorthosites, troctolites, anorthositic norites, gabbroic norites) surrounded by a fine grained and sometimes glassy matrix.

Major and trace elements of the mineral phases within the clasts and the matrix glass were analysed by Electron Microprobe (EMPA) and Laser-Ablation ICP-MS (LA-ICP-MS). Few clasts (mainly gabbroic anorthosites and anorthositic norites) fall within the field of FAN, whilst gabbroic norites have mafic minerals with high Mg#, sometimes reaching the composition typical of Mg-rich suites. However, most of the data fall at intermediate Mg# values. Matrix glasses have major elements compositions broadly resembling the average of the mineral phases of the clasts.

Rare earth elements (REE) contents in plagioclase and pyroxene show large variations, with values in the range of previous data on feldspathic lunar meteorites, arguing against simple fractional crystallization from a single Lunar magma Ocean (Russell et al., 2014). Every plagioclase exhibits a positive Eu-anomaly whilst pyroxene have ubiquitous Eu negative anomalies. Matrix glasses have REE abundances and Eu positive anomalies similar to those of plagioclase with LREE higher, on average, than those of all the other mineral phases hosted in the lithic clasts. Similarly, Ni contents of matrix glasses are high, similar to those of olivine. The trace element composition of matrix glasses is compatible with an origin as impact melts derived from the sum of the various mineral phases making up the clasts. However, their high Ni and REE contents indicate a contribution from extra-lunar material related to the impactor that blasted the meteorite off the Moon, or to micrometeorites associated with regolith gardening and maturation.

Overall, our data suggest that the contribution of exogenous material in the meteorite NWA 13859 is mainly concentrated in the matrix glass, whilst the single clasts (and the minerals within them) may preserve the composition of the original lunar crust.

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## Shock evidences on Frontier Mountain ureilites fragments

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*Keywords:* ureilites, carbon phases, degree of shock.

Ureilites meteorite fragments present different levels of shock classified on the basis of optical observations of shock features in silicates. In this study, we have investigated by scanning electron microscopy (SEM), micro X-Ray Diffraction (XRD) and Micro-Raman Spectroscopy (MRS) five ureilitic fragments with increasing degrees of shock (from S2 to S6) with the purpose to observe if there is any correlation between the level of shock recorded by silicates and the presence of the different carbon polymorphs formed by shock. The selected fragments are FRO 95028 (S2), FRO 01089 (S3), FRO 97013 (S3/4), FRO 01088 (S5) and FRO 01012 (S6).

The XRD results showed that all investigated samples contain nano-graphite. In addition, the results revealed that sample FRO 95028, with S2 degree of shock, contains diamond only at nanometric size, while samples from level of shock S3 to S6 contain both nano-and micro-diamond. XRD results support the shock formation of micrometer-diamonds found in FRO 01089, FRO 97013, FRO 01088 and FRO 01012 with the assistance of (Fe, Ni)-alloys as catalysts at pressure >10 GPa (S3 shock level recorded by silicates). The formation of polycrystalline diamond is already allowed at a pressure between 5-10 GPa. Temperature estimated by a graphite-thermometer based on MRS data, provided values in the range of 1291 to 1398°C ±120°C, revealing that there is not a considerable variation of the graphite temperature with the increasing degree of shock.

This work was supported by the Italian PNRA 2018 00247-A project to F. Nestola "COMMANDER".

## Thermal expansion of oldhamite(CaS) on the surface of Mercury

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*Keywords:* Mercury, oldhamite, calcium sulfide, thermal expansion coefficient.

The temperature excursion variation of the surface of Mercury significantly changes the crystal structure of surface-comprising minerals. With the main aim to validate the presence of CaS on Mercury's surface its thermal stability was investigated. X-Ray Powder Diffraction (XRPD) and Thermogravimetric Analyses (TGA) on synthetic powder calcium sulfide (Alfa Aesar) were performed with the aim of confirming its stability up to 723.15 K, the highest temperature that is recorded for the surface of Mercury.

Our results by XRPD and TGA results confirmed that CaS phase is stable within the daily temperature excursion on Mercury surface. Thermal expansion analyses determined the thermal expansion volume coefficient of  $\alpha_v = 4.03 \cdot 10^{-5} \text{K}^{-1}$ . The results of this work support the presence of Ca-sulfide phases on Mercury's surface and provide valid tools for interpreting the data that will be collected by the BepiColombo space mission (European Space Agency and Japanese Aerospace Exploration Agency) to Mercury.

This work was supported by the Italian PNRA 2018 00247-A project to F. Nestola "COMMANDER".

## TiO<sub>2</sub>II: the high-pressure Zr-free srilankite in impact rocks

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Keywords: TiO<sub>2</sub>II, Australasian tektite strewn field, high pressure polymorphism.

TiO<sub>2</sub> II is a high-pressure polymorph of TiO<sub>2</sub> with orthorhombic  $\alpha$ -PbO<sub>2</sub> structure (space group Pbcn; columbite-type structure), synthesized by static HP and shock wave experiments. In nature, TiO<sub>2</sub>II occurs in ultra-HP metamorphic and impact rocks. TiO<sub>2</sub>II structure seems to have the same topology of srilankite (Ti,Zr)O<sub>2</sub>, a low-T hydrothermal phase in metamorphic and igneous rocks. However, srilankite has a Ti content always  $\leq 0.7$  (Willgallis & Hartl 1983), resulting in a compositional gap between srilankite and TiO<sub>2</sub>II.

Natural TiO<sub>2</sub>II has always been recognized by comparing the Raman spectrum or cell parameters (via XRPD) with synthetic analogues (El Goresy et al., 2001). No *ab initio* structure of natural TiO<sub>2</sub>II has been performed so far, due to its typical micro-to-nanometre scale.

Here, we study TiO<sub>2</sub>II by three-dimensional electron diffraction (3DED, Gemmi et al., 2019) in two impact ejecta in the Australasian tektite strewn field. TiO<sub>2</sub>II occurs either in fibrous or in peculiar cage-like aggregates. ED and HRTEM reveal that the fibrous aggregate is composed entirely of TiO<sub>2</sub>II with different crystals reciprocally misoriented and with pervasive planar defects and districts with mottled contrast. The cage-like TiO<sub>2</sub> aggregate results to be made of finely intermixed rutile and TiO<sub>2</sub>II nanocrystals. The two Ti-polymorphs alternates with Si-rich areas, in which 3DED reveals the presence of coesite. The PACOM map (EBSD-like) reveals the Ti-area being composed of TiO<sub>2</sub>II in the middle and surrounded by rutile, suggesting a direct transition from rutile to TiO<sub>2</sub>II.

3DED data within the fibre aggregate delivered a cell consistent with TiO<sub>2</sub>II, with a significant diffuse scattering along the *c*\*direction. The cell parameters refined by PETS: *a* = 4.547(3) Å, *b* = 5.481(4) Å, *c* = 4.891(4). The *ab initio* model obtained by direct methods based on 3DED data resulted in the structure-type of srilankite (Ti,Zr)O<sub>2</sub>. Ti atoms are coordinated by 6 O in octahedra (connected by vertexes) with very pronounced Jahn-Teller distortion. The model was later refined considering the dynamical scattering (Palatinus et al., 2013) by JANA2020. Our cell parameters plotted well in agreement with all data of both TiO<sub>2</sub>II and srilankite in the literature, following a clear trend connected with Ti/(Ti+Zr). In particular, *a* and *c* decrease linearly with the Ti content, while *b* shows a slight increment. The average Ti-O distance and the Jahn-Teller distortion of the octahedra fit with previous data of synthetic TiO<sub>2</sub>II and follow a trend connected with the overall Ti content.

This work reports the first ED study of TiO<sub>2</sub>II, enabling an extremely precise petrographic and crystallographic investigation at the nanometre scale, and allowing to address outstanding open questions in shock metamorphism field, such as the HP polymorph transformation mechanisms induced by the passage of shock waves.

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## Detailed study on ungrouped achondrites combining trace elements and Cr isotopes as geochemical tools

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*Keywords:* cosmochemistry, ungrouped achondrites, mineral chemistry, Cr isotopes.

The direct investigation of Solar System bodies has always represented one of the most challenging topics for many scientific disciplines due to the relative difficulty to have access to materials directly fallen on the Earth's surface and even more to the sample return missions.

Among meteorites, ungrouped achondrites represent fundamental natural sampling of different parent bodies and provide fundamental information about their genesis, as well as the processes associated with the origin and the evolution of the Solar System.

Indirect methods of analysis (e.g., using radar or spectroscopy), although allowing the characterisation of a large number of samples, usually are not able to achieve the high-precision level provided by direct analytical methods, fundamental for classification purposes.

We present preliminary results of geochemical and isotopic composition on a significant set of samples of ungrouped achondrites, which have been investigated through a combined approach of direct (i.e., mineral chemistry) and indirect (i.e., reflectance spectroscopy) methods, yielding a partial attribution to specific meteorite groups and potential parental bodies. In order to further corroborate the evidence derived from these analyses, we performed high-precision analyses of bulk major and trace element abundances (by ICP-MS) and we set up the method for Cr isotope ( $^{53}\text{Cr}/^{52}\text{Cr}$ ,  $^{54}\text{Cr}/^{52}\text{Cr}$ ) determination. Chromium isotopes systematic represents an important tool to discriminate different meteorite types by the presence of the heterogeneously distributed  $^{54}\text{Cr}$  nucleosynthetic anomalies and similar  $^{53}\text{Cr}$  excess.

Few of the investigated samples, whose geochemical and isotopic composition were already available from previous studies, were used as reference to test the reproducibility of the methods. The same was done on other types of meteorites (such as Allende and some ordinary chondrites), for which we obtained promising correspondence that assessed the validity of the analytical methods. Along with meteorite samples we also test the reproducibility of the isotopic measurements in particular on the isotopic standard NIST979 and NIST3112a yielding good results.

Therefore, the obtained results on ungrouped achondrites were compared to literature values to recognise the respective classification groups and thus further constrain the association of the studied samples with potential parent body families. Major and trace element compositions substantially confirmed the attribution provided by the preliminary analyses with few exceptions that are likely due to sample alteration. The Cr isotope analysis, which is still in progress, will provide the final attribution to the preliminary classification.



## Water content of an andesitic planetesimal at the dawn of the solar system: a study of achondrite Northwest Africa 11119

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Franchi I.A.<sup>3</sup>, Füri E.<sup>8</sup>, Nottingham M.<sup>9</sup>, Stephant A.<sup>10</sup>, Perea D.<sup>11</sup>, Darling J.<sup>12</sup> & Ziberna L.<sup>4</sup>

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*Keywords:* NWA11119, NAMs, water.

Achondrites are meteorites that originate from differentiated planetesimals that accreted during the earliest stages of the solar system formation. Most of the early-formed planetesimals were destroyed due to collisional processes, but some survived until present (e.g., 4 Vesta). Protoplanets covered by andesitic crusts, parent bodies of meteorites such as NWA11119 or Erg Chech 002, were probably frequent. However, no asteroid shares their spectral features, indicating that almost all of these bodies have disappeared (Barrat et al., 2022).

Chronology and composition of achondrites provide evidence that melting, differentiation and crustal formation on their parent bodies took place as early as ~3–5 million years (Ma) after the birth of the solar system; however, they remain poorly understood due to the scarcity of available samples. Importantly, understanding water budget and its isotopic composition of ancient achondrites can lend important insights into the outstanding question of the crustal formation as well as the source(s) of water in the earliest stages of inner solar system.

Northwest Africa (NWA) 11119 is one of the oldest achondrites and igneous meteorites yet dated at  $4563.3 \pm 2.9$  Ma (Srinivasan et al., 2018), or 1.24 Ma younger than the oldest dated Erg Chech 002. It is a chemically evolved extrusive volcanic rock that has a silica-rich (andesite-dacite) bulk composition, lower alkali content, and the highest modal abundance (~30 vol. %) of free silica of any known achondrite. Intrigued by the fact that silicic volcanism on differentiated planets such as the Earth or Mars is promoted by abundant water dissolved in parental magmas, we investigated the water abundance and its isotopic composition as recorded by the phenocrysts in NWA 11119. We re-measured water abundance and H-isotopic composition within tridymite, low-Ca and high-Ca pyroxene using NanoSIMS instrument at The Open University. These values were corrected for cosmic exposure ages obtained in this study (up to ca. 100 Ma) using abundances and isotope ratios of He, Ne, and Ar measured at CRPG Nancy. We find that tridymite has up to 5 ppm H<sub>2</sub>O, while pyroxene has up to 2 ppm H<sub>2</sub>O (background 1 ppm H<sub>2</sub>O and in contrast to the values we reported before Černok et al. 2020). Using partition coefficients of H<sub>2</sub>O ( $D_{\text{H}_2\text{O}}^{\text{Cpx/Melt}}$ ) between phenocrystals of clinopyroxene and the surrounding melt that the crystals grew in equilibrium with, we estimated that the parental magma of NWA 11119 contained 100–200 ppm H<sub>2</sub>O, similar to those estimated for other primitive achondrites (e.g., urelites; Peterson et al., 2023) or angrites (Deligny et al., 2021), implying that the crystallization took place in highly reduced, water- and alkali-poor but silica-saturated conditions. In addition, we inspected the nanostructure of tridymite using atom probe tomography at Pacific Northwest National Laboratory, to understand possible H<sub>2</sub>O retention mechanism.

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## Iron oxidation state in impact glass from the K/Pg boundary at Arroyo El Mimbral (Mexico) by Fe K-edge XANES spectroscopy

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Keywords: impact glass.

We examined the iron oxidation state and coordination number in five green and red impact glasses from the Cretaceous-Paleogene (K/Pg) boundary section at Arroyo El Mimbral, NE Mexico, which formed as the result of impact melting during the Chicxulub impact event. The samples have been analyzed by Fe K-edge X-ray Absorption Near Edge Structure (XANES) spectroscopy, and the resulting data on Fe oxidation state and coordination number have been compared with literature data on 9 black impact glasses and 1 High Si-K impact spherule (Giuli et al., 2005) and other five yellow spherules from another K/Pg impact layer at Beloc (Haiti) (Giuli et al., 2008).

Although there are several studies on the chemical and isotopic composition of these impact glasses, very few studies on the Fe coordination number and oxidation state have been reported. Such studies, however, can be important to reconstruct the oxygen fugacity and temperature conditions prevailing during impact melt formation.

The Fe K-edge high-resolution X-ray Absorption Near Edge Structure (XANES) spectra have been recorded at the BM08 beamline of the ESRF storage ring (Grenoble, F). The pre-edge peaks of our XANES spectra display noticeable variations in intensity and energy, which are indicative of significant changes in the Fe oxidation state, spanning a wide range from about 35 to 100 mole% trivalent Fe. All data plot along a trend, which is compatible with the presence of <sup>6</sup>Fe<sup>3+</sup> and <sup>6</sup>Fe<sup>2+</sup>. The intensity of the pre-edge peak is rather low compared to that of other silicate glasses and, more in particular tektites (e.g., Koeberl et al., 2022; Rochette et al., 2019).

Mimbral green and red impact spherules display higher Fe<sup>3+</sup>/(Fe<sup>2+</sup> + Fe<sup>3+</sup>) ratios when compared to black impact glasses from Haiti (from 20 to 75 mole % trivalent Fe) and high Si-K glass (20 mole % trivalent Fe); and display also a wider range compared to Haiti yellow glasses (from 75 to 100 mole % trivalent Fe). Our observations can be explained by a very large variety of oxygen fugacity conditions prevailing during impact melt formation. Furthermore, there is a positive relationship between the Fe<sup>3+</sup>/(Fe<sup>2+</sup> + Fe<sup>3+</sup>) ratio and the Ca content of the studied glasses, suggesting that the Fe oxidation state was affected by a variable contribution of the Ca-sulphate bearing sedimentary rocks overlying the target rock at the impact site.

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## Glass of possible impact origin from Pica (Chile)

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Keywords: impact glass.

Impact glasses are features associated with many terrestrial impact craters or impact structures that can provide important clues for dating impact events or even discovering new impact structures (French & Koeberl, 2010). Also large airbursts have been proposed to be able of melting the soil surface by radiation. As pointed out in French & Koeberl (2010), it is often difficult to ascribe an impact origin to such glasses, which closely resemble non-impact glasses such as fulgurites, volcanic glasses or metallurgical slags. The origin and mechanism of formation of these glasses is thus strongly debated. Hence, proving or disproving the impact origin of these glasses has implications for estimating the flux of airburst producing bolides to the Earth surface. Massive glassy formations (called Pica Glass) were recently discovered in Chile near the town of Pica (Ropert et al., 2017). These glasses have been found in several outcrops forming a line as long as 70 km, lying on the surface along the eastern margin of the Tamarugal–Llamara basin in the Atacama Desert. They have been variously interpreted by several authors as fulgurites, impact glasses, or glasses resulting from large fires melting the surface sediments (See Ropert et al., 2017 and references therein). Also, they have been interpreted as the consequence of a major airburst (Schultz et al., 2021). Preliminary results found by our group strongly suggest the presence of a meteoritic component in the glass, thus indicating that the melt originated from an impact or an airburst. We accurately analysed by FESEM, 15 thin sections made from samples coming from the 4 studied glass outcrops. The samples consist of a vesicular silicate glass (ca 54 wt% SiO<sub>2</sub>) embedding many clasts of the sand from which the melt probably originated. We found the ubiquitous presence of sulphide blebs of troilite composition. A small fraction of these troilite blebs contains also appreciable amounts of Ni. Other phases of possible meteoritic provenance include:

- spherules with a fine intergrowth of Fe phosphide and native iron usually mantled by troilite.
- metallic spherules with sizes from 4 up to 20 micrometer and Ni/(Ni+Fe) ratios ranging from 0 to 0.6 (average 0.28 ± 0.09).
- merrillite and apatite-(Cl). Remarkably, in one sample also two chondrules have been found embedded in the glass which consisted of euhedral diopside crystals, troilite, merrillite, and recrystallised mesostasis.

Despite other mechanisms may be invoked for the formation of reduced phases, we suggest that the phases we detected are of meteoritic provenance. In particular, despite extensive fires in presence of a reducing agent may be invoked for the formation of metallic Fe spherules, the ancient fire hypothesis (Ropert et al., 2017) would not explain the presence of Fe-Ni alloys.

Several issues should be further addressed to better interpret these finds. In our opinion, the mineralogy of the clasts interpreted here as relicts of the projectile, the presence of chondrules, and the presence of numerous Fe-Ni spherules (including two non spherical fragments of kamacite with troilite inclusions) may point to a projectile of ordinary chondritic composition, in contrast to the hypothesis of Schultz et al (Schultz et al., 2021) that instead invokes a cometary projectile.

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## Partial melting experiments on a CM2 chondrite: implications for differentiation of oxidized planetesimals and angrite parent body formation

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*Keywords:* Carbonaceous chondrite, partial melting, angrite.

Chondrites are meteorites that did not experience igneous differentiation and are thus considered the building blocks of planetary bodies. Modelling the petrological evolution of these bodies is challenging because of the broad compositional variability of the chondritic precursors and the complexity of the processes involved in the formation of differentiated (achondritic) parent bodies. In this context, we investigated experimentally ( $P = 1$  GPa,  $T = 1050$ - $1400^\circ\text{C}$ ) the effect of partial melting of a CM2 chondrite (MCY12002) to gain a better understanding of the differentiation of hydrated, oxidized planetesimals (i.e. angrites parent body).

The starting material MCY 12002 has 20 area% chondrules, 15 area% tochilinite-cronstedtite intergrowths, and <1 area% Ca–Al-rich inclusions in a 65 area% fine-grained matrix. It also contains 1.5 area% carbonates, 0.8 area% Fe-sulfides, and 0.14 area% FeNi metal. The increase in temperature led to substantial textural modifications, with the complete obliteration of the chondritic texture at  $T > 1100^\circ\text{C}$ , and the transformation of the matrix into a mixture of silicate minerals of new formation (olivine, pyroxene, spinel, kirschsteinite ( $\text{CaFeSiO}_4$ ), and Ca-phosphate) and silicate glass with the composition varying from picrobasaltic to basaltic-andesite ( $\text{SiO}_2$  41-57 and  $\text{K}_2\text{O} + \text{Na}_2\text{O}$  0.5-4) and increasing in volume from 5 area% at  $1050^\circ\text{C}$  to 13 area% at  $1400^\circ\text{C}$ . Relict olivine crystals characterized by Fo-rich cores (Fo98-100) and Fo-poor rims (Fo20) occur in all experiments. Additionally, an interstitial S-rich melt (8 area%) occurs as rounded blebs embedded in the silicate melt.

Partial melting experiments of carbonaceous chondritic materials demonstrate that significant textural and chemical modifications can occur at relatively low temperatures (even lower than  $1050^\circ\text{C}$ ) in oxidized planetesimals. This may have implications for interpreting the formation of the angrite parent body, as suggested by the similarity between the compositions of the experimentally produced phases (silicate melts and minerals) and those (bulk and mineral) observed in natural angrites. Furthermore, volcanic angrites are characterized by olivine crystals with compositional zoning very similar to that observed in our experiments. Overall, these data support the hypothesis that the angrite parent body formed from a carbonaceous chondrite-like precursor.

## Multispectral analyses techniques on X-Ray data in meteorite research

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Keywords: chondrite, meteorite, mineralogy, multispectral, X-ray maps.

The investigations for meteorite characterization and classification often involve the use of SEM-X-Ray Maps to obtain the modal composition. To extract the major amount of information from the different elemental maps related to the whole thin section area, usually one approach is the multispectral X-Ray map data analyses. In this approach, the X-Ray maps of 18 elements are stacked in a single file resulting in a multispectral cube in which each pixel is associated to a “spectrum” of the elements occurring in the X-ray maps. Then, there are several algorithms to classify and calculate the modal mineralogy: these can be grouped in supervised and unsupervised. If properly used, keeping into account the edge pixel effects at grain boundaries and the dependence on the counting scale used for each elemental map, during X-ray map acquisition, multispectral data methods can be very promising to gather information on meteorites. For this research, we are using multispectral analyses to explore the chance to better localize and identify minerals or textures not yet described during the routine analyses for the meteorite classification, in other words, further accessory minerals or unexpected minerals or mineral-chemistry.

We are currently investigating a thin section of Northwest Africa 14897, ordinary chondrite recently classified in 2022 as LL7 (Moggi Cecchi et al., 2022). This interesting meteorite has a markedly equilibrated texture and belongs to a group of chondrites that is considered by some authors one of the joining links between chondrites and primitive achondrites (Li et al., 2020; Friedrich et al., 2014; Grady et al., 2014). It has a cata-clastic breccia texture consisting of equilibrated olivine and orthopyroxene clasts in a fine matrix mainly consisting of the same minerals, together with diffuse recrystallized plagioclase, and no chondrules. Due to extensive weathering (W4) iron oxides are the most common opaques with no tracks of relict kamacite or taenite. Accessory phases include troilite, Ti-chromite, chlorapatite and merrillite, plus minor tetrataenite and secondary calcite. A modal estimate obtained from the SEM X-ray spectral maps provided the following results: 48% olivine, 25% low-ca pyroxene, 9% ca-pyroxene, 11% sodic plagioclase, 3% Fe-oxides, 0.6% chromite, 0.4 Cl-apatite, 3% calcite.

For this investigation we used ENVI+IDL. We customized a routine in IDL for stacking the BSE image and elemental maps of the whole thin section in a unique multispectral file. By this method, besides comparing the modal composition obtained from SEM data with those resulting from the multispectral analyses on the whole section, we will search for further eventually occurring mineralogical phases in this meteorite.

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## Cosmic impact laboratory simulations on rubrene nanoparticles: new insights on the generation of prebiotic molecules

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*Keywords:* laboratory analogue, cosmic impact, space weathering.

The polycyclic aromatic hydrocarbons (PAH) are among the major responsible of the infrared spectral features characterising the cosmic background radiation (e.g., Tielens, 2008). These carbon rich materials, as for silicate dust, with micro- and nano-metric sizes are subjected to several weathering processes, such as impact shock events, in various astrophysical environments that modify their chemistry and structure, thus contributing to the chemical richness of the cosmic environment (e.g., Murri et al., 2022). In particular, the study of the chemical and structural changes of PAH aggregates in the presence of water is relevant to understand the mechanism of formation of prebiotic molecules.

Nanosecond pulsed laser ablation of a water-dispersed nano-phase of rubrene (5,6,11,12-tetraphenyltetracene) was performed to reproduce the high energy-density conditions occurring in shock events in the interstellar medium, while ensuring the presence of a water environment (e.g., Patil et al., 1987). We studied the structural and chemical evolution of the dispersed rubrene nanocrystals upon laser treatment by means of high-performance liquid chromatography-mass spectroscopy and nuclear magnetic resonance. Our results show that rubrene undergoes a fragmentation process producing water soluble species. Furthermore, the obtained data demonstrate that the extreme conditions occurring in cosmic environments coupled with the presence of water are sufficient conditions for the formation of the prebiotic building blocks of life starting from PAH aggregates.

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## Volcanic glasses and geochemical signatures: a new resource to decipher volcanic products on planetary surfaces

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*Keywords:* igneous, spectroscopy, database.

Interpretation of spectral data acquired remotely and/or in situ from other planets requires an exhaustive database taking into account well-characterized spectra. While crystalline phases are deeply investigated through vibrational spectroscopy, amorphous phases are often ignored because of their blurred spectral response and the supposed lack of information they can provide. Tough, silicate glasses represent an important component in volcanic products, and since volcanism occurred on all terrestrial planets in the solar system, they might influence the spectral response of portions of planetary surfaces.

In the past years, we used experimental petrology to produce glassy samples having a wide variety of chemical compositions, and we characterized them by means of reflectance and emissivity in different spectral ranges, to observe the variation of their spectral characteristics with changing chemical composition and with varying granulometric characteristics.

Through different studies, we have observed how: i) reflectance spectra in the Mid-Infrared range show a systematic shift of spectral features can be modelled with  $\text{SiO}_2$  and  $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2$  content, whereas the shape of the spectra is determined by a complex interaction of chemical and granulometric characteristics (Pisello et al., 2022a) ii) emissivity spectra of such glasses, acquired at different temperatures, show a weak but non-negligible temperature dependency of the shift that must be taken into account when characterizing planets having large thermal excursion like Mercury (Pisello et al., 2019) iii) shape of reflectance spectra change deeply even for silicate glasses having identical chemical composition but different granulometric characteristics (Pisello et al., 2023) and, finally, iv) reflectance spectra in the Visible and Near Infrared, show a correlation between spectral slope and the iron content and speciation (Pisello et al., 2022b).

Our observations suggest that, accounting for the spectral properties of silicate glasses when interpreting spectral data obtained from the surface of terrestrial planets, will help in the characterization of magmatic bodies and volcanoclastic materials. Thus, we offer an publicly accessible interactive catalog of collected spectra within the Space Science Data Center (SSDC), a facility of the Italian Space Agency (ASI) which includes data processing and data archiving center (<https://www.ssdsc.asi.it/rockspectra/>).

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## Assessing the role of impacts in volatile addition to the inner solar system

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Keywords: hydrogen, angrite impact.

The timescales, mechanisms, and source(s) of water delivery to the inner Solar System remain debated. Two prevailing models for the origin of inner Solar System water exist: 1) Early presence of isotopically CM-like H in the inner Solar System prior to the separation of the NC and CC reservoirs and 2) the influx of volatile-rich materials from the outer Solar System due to the growth and/or migration of Jupiter (Deligny et al., 2021). An oxygen isotopic disequilibrium has been revealed in the quenched angrites, implying an impact melt origin with olivine ‘xenocrysts’ representing relict grains that survived impact melting. Furthermore, it is considered that the mixing event was caused by the gravitational excitement resulting from the growth and/or migration of Jupiter (Rider-Stokes et al., 2023). Angrites are thus ideally suited for investigating whether volatiles were added through impacts as a result of Jupiter’s formation and/or migration. In this study, we present  $\delta D$  values and H<sub>2</sub>O abundances of nominally anhydrous minerals in the quenched angrites to determine if any variation exists between the relict olivine grains and the groundmass of the quenched angrites. Additionally, plutonic, intermediate and dunitic angrites are investigated to provide insights into the history and evolution of H in the angrite parent body (APB).

$\delta D$  values and H<sub>2</sub>O abundances for all samples were obtained using a Cameca NanoSIMS 50L at Open University following established procedures (Stephant et al., 2021). We used the CAMECA IMS 1280 ion probe located at the NordSIMS facility in the Swedish Museum of Natural History for Pb-Pb analysis on phosphates within NWA 8535 following established procedures (Snape et al., 2016).

Unlike oxygen isotopic compositions, the  $\delta D$  values and H<sub>2</sub>O abundances of relict olivine grains ( $-362 \pm 439$  to  $322 \pm 208$  ‰ and  $3.3 \pm 0.1$  to  $6.8 \pm 0.3$  µg/g) and olivine present in the groundmass ( $-495 \pm 254$  to  $345 \pm 183$  ‰ and  $3.8 \pm 0.1$  to  $8.1 \pm 0.3$  µg/g) within A 12209, are indistinguishable from one another. The ancient age of A 12209 ( $4562.2 \pm 0.7$ ; Zhu et al., 2019) and the lack of variation in  $\delta D/H_2O$  abundance implies that the APB had acquired a CC-like H composition prior to impact mixing and that the impactor was either dry or had similar H isotopic compositions. To constrain the evolution of H in the early inner Solar System, we determine a chronological constraint on the dunitic angrite, NWA 8535 ( $4515 \pm 30$  Ma). NWA 8535 exhibits positive  $\delta D$  values ( $900 \pm 110$  ‰) and slightly elevated H<sub>2</sub>O contents ( $7.0 \pm 0.3$  to  $9.1 \pm 0.3$  µg/g) compared to the quenched angrites. The higher  $\delta D$  values suggest degassing and H loss. If this is the case, then NWA 8535 may have elevated water contents compared to the earlier formed quenched angrites. As the plutonic angrite (NWA 4590) shows similar  $\delta D/H_2O$  abundances to the quenched angrites, the addition of water to the APB must have post-dated its crystallization.

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## Petrography, mineralogy and geochemistry of the K/Pg layer at the Bottaccione Gorge of Gubbio, Italy

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*Keywords:* iridium, K/Pg, mass extinction.

In 1980, Walter Alvarez discovered an iridium (Ir) anomaly (5.5 ng/g) within a pelagic clay greenish layer in the Umbrian-Marche Apennines of the Bottaccione Gorge in Gubbio, central Italy. This clay layer (about 1 cm thick) dated 66 million years ago corresponds to the Cretaceous/Paleogene (K/Pg) boundary and marks the mass extinction occurred on our planet that caused the disappearance of 75% of living species. Such discovery led to the asteroid impact theory (Alvarez et al., 1980) as main mechanism for the K/Pg extinction that followed the formation of a 180km-diameter Chicxulub impact crater, buried under the Yucatán Peninsula, Mexico. Following the discovery by Alvarez, Ir anomalies have been found at over 80 K/Pg sections distributed worldwide, making this a globally recognizable feature. Noteworthy, Ir enrichments up to 7.5 ng/g have been reported also in ash particulates from an eruption of the hot-spot volcano Kilauea in the Hawaiian belt (Finnegan et al., 1990), and in volcanic-origin debris belts in Antarctica stranding zones (Koeberl, 1989). Across the Cretaceous-Paleogene boundary, Deccan Traps were active and erupted over >10<sup>6</sup> km<sup>3</sup> of flood basalts that might have contributed to the anomalies of Ir, but also Hg as often reported in literature. Mercury (Hg) anomalies in sedimentary rocks are extensively used as a geochemical marker of large magmatic events (e.g., Gu et al. 2022).

In this study we sampled the K/Pg layer at the Bottaccione Gorge in Gubbio (Italy) and some samples from the Scaglia Rossa formation at the top and bottom of the Ir-rich layer. The samples were analysed by scanning electron microscope (SEM), X-ray powder diffraction (XRPD), and optical microscopy with polarized transmitted light. Additional measurements consisted of Hg and total organic carbon (TOC) analyses.

The results will allow us to verify whether an asteroid impact or large magmatic events produced geochemical correlations between the anomalous elements especially Hg and Ir, and the results of a comparative study will show the Ir bulk content of Earth and partitioning between primitive melts and rock-forming minerals.

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**S30.**

**Geology, mineralogy and petrology in space:  
exploring planetary bodies in the Solar System and beyond**

*CONVENERS AND CHAIRPERSONS*

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## Clustering analysis to unravel polyphase tectonics settings on planetary surfaces: the case of the Claritas Fossae, Mars

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Keywords: Mars, tectonics, clustering.

The Claritas Fossae (CF) is an elongated system of scarps and depressions 900 km long. It is located to the S of Tharsis and represents the western limit of the trapezoidal-shaped region that includes Syria, Solis and Sinai *plani* and that is bounded by the Valles Marineris to the N-NE and by the Thaumasia Highlands to the S-SE. In the past decades, several authors highlighted the tectonic nature of the CF (Hauber & Kronberg, 2005; Montgomery et al., 2009). Nevertheless, the mechanisms that led to its formation are still debated. In this work we aim at better understanding the tectonic evolution of the CF by analysing the structural and morphological forms derived from satellite data (THEMIS and MOLA DEM mosaic datasets) and by applying original clustering analysis on the tectonic lineaments that we visually identified (Balbi et al., 2022).

The clustering analysis allows objectively defining groups of tectonic elements on the basis of the attributes associated to each element. Here we apply the Hierarchical-Agglomerative Clustering (HAC - Kaufman & Rousseeuw, 1990) that initially defines a single cluster for each element, then moves up the hierarchy by coupling pairs of clusters until a single cluster containing all the elements is obtained. The clustering algorithm is based on two main steps:

Calculation of the distance between each element resulting in a dissimilarity structure;

Hierarchical cluster analysis on the dissimilarity structure.

It is necessary to determine *a priori* the number of clusters in order to stop the iterations when the expected number of clusters is achieved. The Silhouette index (S) allows evaluating the reliability of the analysis and thus defining *a priori* the best number of clusters. Satisfactory results are achieved with  $S > 0.5$ .

In our case, the analysed elements consist of the tectonic lineaments we identified through the structural mapping within the CF. We described each feature with i) coordinates of the tips; ii) coordinates of the centroid; iii) length, iv) azimuth; and v) sinuosity. Through azimuthal analyses by polymodal Gaussian fit, we identified four sets of lineaments: Set 1 includes 31 faults with main azimuthal trend of 352°; Set 2 includes 168 faults with main azimuthal trend of 20°; Set 3 includes 39 faults with main azimuthal trend of 272°; and Set 4 includes 13 faults with main azimuthal trend of 320°. The relations between sets suggest polyphasic deformation of the CF with strike-slip and dip-slip regimes (Balbi et al., 2022). Results of the clustering analysis confirm the existence of the four azimuthal sets. The analysis considered i) azimuth; ii) azimuth and length; and iii) azimuth, length and position of the centroids, defined as the distance of the centroid from the origin (i.e., 0° of latitude and 0° of longitude). These results are further confirmed by the spatial distribution of intensity of brittle deformation quantified for each set by the L/S parameter (L = lineament length, S = spacing).

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## Exploring the potential of machine learning techniques to analyze remotely sensed hyperspectral data on Mars

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Keywords: hyperspectral data, remote sensing, machine learning.

Remotely sensed spectral and hyperspectral data provide essential information about the composition of planetary surfaces. On Mars, high resolution hyperspectral reflectance data are provided by the CRISM instrument, a spectral imager onboard NASA's Mars Reconnaissance Orbiter. CRISM datasets are traditionally explored through RGB mineral maps, or browse products, which are an effective way to quickly assess the surface mineralogy of a scene. These RGB products combine spectral parameters such as band depths or spectral slopes, in order to highlight specific mineralogical phases (e.g. aqueous and mafic minerals, carbonates). To guide the user in the mineralogical exploration, the CRISM team provides a set of standard browse products, specifically designed on the main known surface composition and mineralogical variability of Mars (Viviano-Beck et al., 2014). Usually, at least four/five different RGB images are needed to derive the mineralogy of a certain area. However, this approach does not fully exploit the potentials of a hyperspectral dataset like that of CRISM, as it focuses on a few wavelengths at once. Machine learning techniques such as unsupervised clustering can instead help us to explore these datasets by exploiting the whole spectral range of the instrument.

One of our initial steps involves applying some algorithms available in the Python library scikit-learn, such as k-means clustering (Tou & Gonzalez, 1974), to study the mineralogy of some CRISM scenes in the area of Meridiani Planum, a region near Mars' equator. Here, sedimentary sequences with a great variety of spectral characteristics are observed (Flahaut et al., 2015) and provide both a relevant scientific target and a good training ground for the application of the algorithms.

The clustering technique is applied to the corrected I/F CRISM Map Projected Targeted Reduced Data Records (MTRDR) dataset in the 1.0-2.6  $\mu\text{m}$  range. The spectral characteristics of the scene can be summarized by the mean or the median spectrum of each cluster. Inter-cluster standard deviation indicates how much the group varies at each wavelength, which can guide further investigations. With the correct tuning, the k-means algorithm, albeit being a basic widespread tool, successfully distinguishes different mafic and several hydrated phases, and provides a clean selection of single layers in sedimentary rocks observed in some of our datasets, whose mineralogical investigation is particularly relevant for understanding the characteristics and evolution of water rich paleoenvironments on Mars (Baschetti et al., 2022). Clustered images can be georeferenced and loaded on a GIS program to combine their information with other data such as high resolution images or DTMs. Other algorithms will be tested and compared with k-means. One of the goals is to help discover, in a semi-automated way, interesting compositional/geomorphological features, allowing researchers to focus more on scientific interpretation.

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## **Analysis of Spectral Variations in the Craters of the Moon Basaltic Flow Using Terra Advanced Spaceborne Thermal Emission and Reflection Radiometer**

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*Keywords:* ASTER, MERTIS, NVP.

This study focuses on the analysis of ASTER (Terra Advanced Spaceborne Thermal Emission and Reflection Radiometer) emissivity data and surface reflectance data for the Craters of the Moon basaltic flow (CMBF), aiming to identify spectral variations within the flow that may not be evident in the visible bands. The Craters of the Moon National Monument and Preserve, located in the state of Idaho, United States, is an area characterized by a vast expanse of basaltic lava flows that covers over 15,000 years of volcanic activity, with the last eruption occurring some 2,000 years ago. Despite the area is not appropriate for life, different vegetation present in different areas of the flows could contribute to differences in alteration and chemical composition of the various eruptive events constituting the CMBF as well as having an important component in the spectral response that varies according to the quantity of the different plant species, having however a noise due to the vegetation also considering AG100 v004 dataset. To eliminate this variable, the idea of studying basaltic flows through TIR and NIR observations on other planets such as Mars and Mercury, where the presence of vegetation is not a factor, has been proposed to verify if similar results are obtained. This comparison could provide further insights into the relationship between flow composition and alteration, making possible to identify different eruption phases and to better understand the geochemical evolution of lava flows over time and understand the mechanisms that drive subsurface heat transfer. TIR investigation will be useful in order to better understand new data from MERTIS (Hiesinger et al., 2020) part of the payload on the joint ESA and JAXA BepiColombo Mission for the exploration of Mercury, being able to contribute significantly in the study of plateaus of volcanic products such as the smooth plains and the Mercury Northern Volcanic Province (NVP; Denevi et al., 2013) in particular.

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## Spectroscopic characterization of Martian analog mineral mixtures

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*Keywords:* reflectance spectroscopy, Mars mineralogy, analog mineral mixtures.

Given the strong astrobiological implications, the exploration of Mars is a compelling ongoing scientific activity since many decades. Several space missions investigated the planet and are still scouting its surface through orbiters (hyperspectral imaging) and robotic rovers (mineralogy and spectroscopy). In particular, the in-situ exploration is revealing a complex mineralogical diversity exemplified by a wide range of magmatic and sedimentary rocks. Very often, remotely and in-situ acquired data are characterized by a non-optimal signal-to-noise ratio making the interpretation of the results challenging and ambiguous. In order to correctly understand and interpret data from robotic rovers and orbiting spacecrafts it is of paramount importance to know exactly how the mineralogical complexity of the Martian surface affects its spectral properties. For this reason, we investigated in the laboratory the spectroscopic properties of synthetic Martian analog mixtures characterized by a high mineralogical complexity. We focused our efforts on two regions of Mars, namely the Jezero crater (JC) and the Gale crater (GC). In both sites the remote spectroscopic characterization from spacecrafts is coupled with a partial in-situ spectroscopic and mineralogical characterization carried out by robotic rovers (Perseverance and Curiosity respectively). To produce our mixtures, we used a set of selected natural minerals and synthetic materials (glass) whose relative abundances were varied in such a way to represent different geologic scenarios (i.e. degree of aqueous alteration under a variety of conditions). The produced mixtures were investigated by visible-near infrared (VNIR) reflectance spectroscopy while we used Raman spectroscopy (RS) to characterize the constituent materials. Laboratory data on mixtures were then compared with the available spectroscopic data collected from the rovers. Our study emphasizes the importance of the alteration products (clays, oxides and sulfates) in determining the VNIR spectroscopic features of the Martian surface and allow to put quantitative constraints on mineral type and abundance on Mars.

## Comparing Hyperspectral Data from PRISMA and CRISM: Analyzing geological and mineralogical differences in terrestrial and Martian deltas

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Keywords: PRISMA, CRISM, Delta.

The comparative analysis of hyperspectral data from different instruments can provide detailed information on the composition and geology of similar environments on different planets. This study aims to compare data acquired from the PRISMA satellite (Caporusso et al., 2020), used for Earth observation, with data collected by the CRISM spectrometer onboard the Mars Reconnaissance Orbiter, orbiting Mars, in order to analyze the geological and mineralogical differences between the morphologies present on the two planets of interest (Zinzi et al., 2023). The comparison of these data will allow us to examine the mineralogical composition, highlighting the similarities and differences between the Terrestrial and Martian environments.

In this study, based on the work of Sekine et al. (Sekine et al., 2020), we have identified areas of interest on Earth, located in the Gobi Desert. The Gobi is characterized by an arid climate and extreme temperature fluctuations, and there are some deltas and rivers systems that can offer a unique point of comparison for Martian environments. The areas examined were analyzed using X-ray diffraction technique and revealed the presence of sediments containing phyllosilicates, quartz, albite, and sporadic calcite (Sekine et al., 2020). Although quartz and albite do not show strong, unequivocal diagnostic absorption features in the PRISMA spectral range, we deduced them by observing the reflectance values and more uniform spectra. We confirmed the presence of phyllosilicates, in particular, with the absorption associated with the Al-OH bond, around 2.19  $\mu\text{m}$ , in the structure of illite, smectite, and kaolinite. We did not observe carbonate-related absorptions in the studied ROIs. This may be due to the negligible abundance of carbonates at the PRISMA scale. Furthermore, we are examining another delta in the Gobi Desert, chosen based on a probable basaltic composition, as suggested by Mason et al. (2021). This basaltic composition makes the delta in question more similar to the rocks present on the Martian surface. These data will subsequently be compared with those acquired by CRISM in the fluvial delta present in the Jezero crater.

The results of this study could contribute to the understanding of geological and hydrological processes on Mars and Earth, improve the calibration and interpretation of hyperspectral data, and guide future Space missions in the search for extraterrestrial life.

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### 3D reconstruction and kinematic analysis of wrinkle ridges on Mars: symmetric, asymmetric, and double-ridges examples

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*Keywords:* Mars tectonics, wrinkle ridges, geometric and kinematic modelling.

Wrinkle ridges represent the most prevalent tectonic landforms observed on terrestrial planets, including Mercury, Venus, Mars and Moon. These highly variable, positive relief structures exhibit linear, sinuous, and discontinuous morphologies, sometimes bifurcating or forming en-echelon arrays. They can reach heights of hundreds of meters and widths of several tens of kilometers and are commonly interpreted as folds overlying blind or non-surface breaking thrust faults.

On Mars, wrinkle ridges typically appear on flood basalt-like units on volcanic plains and within large impact basins. Investigating these features can yield valuable insights into the geological history of Mars. The orientation of wrinkle ridges can be used to infer lithospheric stresses and strain, while their structural style may give clues to the mechanical properties and stratification of the involved crustal rocks.

Despite their ubiquity, wrinkle ridge formation remains a topic of debate with several unresolved questions, including: i) their thin- or thick-skinned nature, ii) the geometry and likely structural style of associated blind faults, iii) fault dip angles and depth, iv) the number and role of faults, and (v) the amount of shortening accommodated by both faulting and folding. Various methodologies have been employed to address these questions, such as elastic dislocation modeling, boundary element modeling, and balancing techniques (Watters, 2004; Okubo and Schultz, 2004; Karagoz et al., 2022). However, these approaches are predominantly executed in 2D, lacking information on short-distance lateral variations and the ability to model complex fault geometries.

In this work, we use the Move software package (Petex) to conduct a 3D geometrical reconstruction of a set of wrinkle ridges situated around Tharsis, by analyzing and reproducing their morphometric characteristics. We selected our case studies based on the availability of high-resolution data and morphometric properties. Adhering to the most recent wrinkle ridge classification proposed by Andrews-Hanna (2020), we chose a few representative examples of each wrinkle ridge structures, including symmetric, asymmetric, and double ridges. We prioritized structures with comprehensive high-resolution data coverage, primarily derived from the Mars Orbiter Laser Altimeter (MOLA) and the Context Camera (CTX), which were processed to obtain high-resolution Digital Elevation Models (DEMs).

In Move, we applied the Fault Parallel Flow algorithm, which can model complex fault geometry by assuming area conservation and plane-strain deformation, to determine the fault geometry that best fits the observed topography and the measured outcropping fault dip angles. This analysis allowed us to extract information regarding the 3D geometry (dip, depth) of the fault as well as the amount and distribution of accommodated shortening, which we used to discuss possible mechanical stratigraphy and tectonic evolution of Mars.

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## A multi-approach hyperspectral analysis for the mineralogical characterization of Zn-Cu-Pb vanadate ores in the Otavi Mountainland (Namibia)

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*Keywords:* remote sensing, hyperspectral analysis, geological mapping.

The Otavi Mountainland (OML) is located in northern Namibia belonging to the northernmost part of the Damara fold-thrust belt. The area is characterized by base metals sulfide and nonsulfide deposits hosted by Neoproterozoic platform carbonates of the Otavi Group (Laukamp, 2007). The Zn-Cu-Pb vanadate ores (i.e., descloizite, vanadinite and mottramite; now mostly exhausted) of supergene origin occur in different styles, like veins or cements in karst breccias and cavities (Boni et al., 2007). Country rocks (limestones and dolomites), Fe-oxy-hydroxides and V-ore minerals have diagnostic spectral absorptions in the Visible-Near to the Shortwave Infrared regions (VNIR-SWIR), allowing their identification and mapping through hyperspectral methods (Laukamp et al., 2021; Chirico et al., 2022). However, the spectral response of V-bearing minerals is poorly described in literature so far.

The aim of this study is to characterize the OML vanadium ores, in order to better define the mineralization styles, textures and minerals mutual relationships, as well as expand the knowledge regarding the spectral behavior of V-bearing minerals by adopting a multi-technique approach based on the integration of laboratory-based hyperspectral bulk spectroscopy (through FieldSpec Pro3) and imaging (using Headwall Photonics Nano- and Micro-Hyperspectral cameras), both covering the 400-2500 nm spectral range. The data processing was performed by applying feature-extraction band ratios and indexes and the XRPD mineralogy was used for validating the results. The analyses allowed to detect Fe-oxy-hydroxides based on the Fe absorption feature at 900 nm, to recognize vanadate minerals through the peak at 620 nm and double features at 1990 and ~2400 nm, as well as to map and distinguish dolomite from calcite depending on the wavelength position of the CO absorption band at 2317-2321 to 2340 nm, respectively.

The use of multi-source high-resolution hyperspectral data represents a powerful tool for mineral exploration and can be also used for supporting satellite-scale hyperspectral remote sensing for mapping the outcropping host rocks and supergene alteration associated with orebodies at regional scale.

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## Compositional studies and laboratory comparison of the North Polar Layered Deposits exposed on a steep scarp (Mars)

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Keywords: compositional, stratigraphy, map.

The residual polar cap at the North Pole of Mars is made up of two macro-units: Basal Unit (BU) and North Polar Layered Deposits (NPLD). The North Polar Layered Deposits are a 2 km thick continuous sequence of bright and dark strata. The alternation of layers is composed of water ice and variable content of lithic inclusions and/or CO<sub>2</sub> ice. This alternation is probably due to climatic and orbital variations (Byrne, 2009). The upper part of the North Polar Layered Deposits is exposed along scarp of polar troughs that are eroded by the action of katabatic winds. The exposure of the NPLD allows the stratigraphic analysis and definition of units like the previous work of Tanaka et al. (2008). We try to perform a similar analysis but with higher detail and much more focus on the spectral aspect of the stratigraphy. We select a data-set composed of Context Camera (CTX) and High Resolution Imaging Science Experiment (HiRISE) images for stratigraphic interpretations and Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) hyperspectral cube for spectral studies. We also consider the possible join of surficial compositional variability with the SHallow RADar (SHARAD) radargrams, the record of the variations of the layer reflectance and thus the compositional variation within each unit (Putzig et al., 2009). Our preferred working areas are the equator-facing polar scarps where winds exposed fresh layered material. Here, after the definition of the Regions of Interest (ROIs) in CRISM cube, we extract the average spectra. Spectral features confirm the high amount of water and reveal the evident variability in H<sub>2</sub>O and CO<sub>2</sub> ices and basaltic dust amount. The comparison of CRISM-extracted spectra with laboratory ones can help the characterization of the spectral absorption bands and thus infer the composition of the layers. This step allows us to select the suitable indexes from Viviano-Beck et al. (2014) to produce false-color images used for geological mapping purposes. The RGB images indicate the presence/absence and the varying distribution of specific minerals on the study areas. At this point, we map over the CTX and HiRISE images considering the spectral and stratigraphic characterization performed with CRISM data. The result is a high-detail stratigraphic map with units, on average thick less than 10 m, and compositionally constrained. Another compositional constraint can also be the reflectance variations in radargrams due to dielectric properties that change with the depth (Putzig et al., 2009). We see a good matching between geological units and radar reflectors.

In conclusion, the aim of this work is to understand deeply the composition and its variation in the stratigraphic column of the exposed upper part of the North Polar Layered Deposits not only using the spectral and imaging data from remote sensing but also laboratory analysis and subsurface information achieved by radar instruments.

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## Reflectance spectra of mascagnite and salammoniac minerals: effect of viewing geometry variation

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Keywords: reflectance, ammonium-bearing minerals, icy bodies.

Ammonium-bearing minerals have been hypothesized on icy planetary bodies such as Pluto and Ceres (e.g., De Sanctis et al., 2016; Cruikshank et al., 2019). The presence of  $\text{NH}_4^+$ -minerals could be associated with upwelling of ice from possible subsurface oceans (e.g., Cruikshank et al., 2019). Given the presence of surface roughness and morphology variation, the surface reflectance spectra of all Solar System bodies are affected by observation geometries (e.g., Cruikshank, 2015). In this work we analyse the effects of viewing geometry variations on the near-infrared reflectance spectra of mascagnite- $(\text{NH}_4)_2\text{SO}_4$  and salammoniac- $\text{NH}_4\text{Cl}$  samples. The two samples selected in this work could represent the two most promising candidates as ammonium-bearing minerals on icy bodies. Bi-directional reflectance spectra are collected in the 1 - 4.2  $\mu\text{m}$  range considering a set of 3 incidence ( $i$ ) angles ( $i = 0^\circ; 30^\circ; 60^\circ$ ) and 9 emergence ( $e$ ) angles between  $-70^\circ$  and  $70^\circ$  at room temperature. The reflectance spectra analysed in this study were collected using the custom-made bidirectional reflectance spectro-goniometers SHINE (SpectroPHotometer with variable INcidence and EMergence) at the Cold Surface Spectroscopy facility (CSS) of the IPAG laboratory (<https://cold-spectro.sshade.eu>) in the frame of the Trans-National Access program, project number 20-EPN2-081, of Europlanet 2024. The  $\text{NH}_4^+$  bands located at  $\sim 1.09, 1.32, 1.62, 2.04, 2.2$  and  $3.05 \mu\text{m}$  are experimentally investigated. Changing observation geometry, the absorption bands parameters (area, depth and FWHM), reflectance values and spectral slope show important variations in the BRDF spectra. On the other hand, the bands position remains unchanged. Bands' area and depth parameters show the highest variability for  $i \geq 30^\circ$  and  $e$  greater than  $\pm 40^\circ$ . The area and depth parameters of these bands show a dual behaviour: (1) for the weak-medium spectral features below  $2 \mu\text{m}$  the area and depth decrease as the phase angle increases. (2) The strong spectral features above  $2 \mu\text{m}$  increase their values only at phase angles above  $90^\circ$ , but also at low phase angles for high incidences,  $i \geq 30^\circ$ . We observe important dependence of band depth and area on the incidence angle, up to  $60^\circ$ , compared to moderate variation with emergence angles. Furthermore, the  $\sim 3 \mu\text{m}$  features becomes less saturated at  $\pm 70^\circ$  emergence angles. A general trend of spectral bluing with change in observation geometry is observed. This data set represents a contribution in the framework of present and future space missions focused on the nature and quantification of  $\text{NH}_4^+$ -bearing minerals on icy bodies. The  $\text{NH}_4^+$ -minerals identification has a strong impact on understanding their thermal evolution and the construction of geophysical internal models providing information on ocean/brine compositions, possible explanations of geological phenomena, like cryovolcanism, and implications for biological activity. Spectra will be available in the SSHADE database ([www.shade.eu](http://www.shade.eu)).

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## Segmentation and length-distribution analysis of lobate scarps on Mercury

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Keywords: Mercury, segmentation, linkage.

We studied the pattern of fault displacement and length distribution analysis in the Victoria (H-02) and Discovery (H-11) quadrangles that allow to test hypothesis of fault segmentation and linkage. The NNW-SSE striking Victoria Rupes-Endeavour Rupes-Antoniadi Dorsum (VEA) fault system in the H-02 quadrangle is one of the longest (~4500 km) lobate scarp alignments on the planet. Kinematic analysis indicates the fault system is composed by predominant thrust faults and accompanying oblique ramps.

A detailed mapping of the VEA showed that it is segmented into three arrays, namely the Victoria Rupes (VEA-VR), Endeavour Rupes (VEA-ER) and Antoniadi Dorsum (VEA-AD). These individual arrays are distinguished based on systematic changes in fault trends and in width of the fault zone, and on the local occurrence of volcanic vents that help define segment boundaries. Based on the previous mapping results, we analyzed the length-frequency distribution of individual fault segments within the three arrays. Using different length bins for sampling the fault frequency, we found the most satisfactory results for bins between 15-30 km, which documents that the number of segments is inversely proportional to their length, in agreement with studies conducted on terrestrial faults.

We tested the distribution of fault segments defined by structural mapping through the analysis of displacement profiles along the three VEA fault arrays. We estimated vertical displacements along the three arrays by measuring the height of the lobate scarp (assuming no erosion of the scarp) along 22 profiles.

Each of the fault arrays has a maximum displacement in the central part of the fault trace, gradually decreasing toward the tips. Whereas the VEA-VR array has a broader, elliptical shape, the VEA-ER and VEA-AD arrays resembles the more traditional bell-shape profile. The findings of three distinct elliptic or bell-shaped curves documents that the three lobate scarps grow as individual faults before linking into a longer fault system. We also show that the VEA-VR, VEA-ER and VEA-AD are in turn made up of individual fault segments that were linked at an early stage of growth of the fault system. In the Discovery (H-11) quadrangle, fault segmentation and linkage have been studied along the NE-SW trending, right-transpressive Discovery, Adventure and Resolution Rupes (DAR) lobate scarps. Analysis of scarp height on 38 profiles across these faults shows that the ~550 km long Discovery Rupes grow linking two different faults, each composed of several segments and sub-segments. The Adventure and Resolution Rupes in turn forms a ~500 km long linked system that trends en-echelon with the Discovery Rupes. Given the large separation, the Adventure-Resolution and the Discovery Rupes are not physically linked. However, the cumulative displacement of the two lobate scarps shows a central maximum consistent with a soft-linked kinematics connection between the two fault systems.

## VIS-NIR measurement and sampling campaign in the Río Tinto area in support of the Ma\_MISS scientific activity

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Keywords: spectroscopy, planetary field analog, Mars.

A field campaign in the Río Tinto area and laboratory measurements on the collected samples were performed in support of the Ma\_MISS (Mars Multispectral Imager for Subsurface Studies) experiment (De Sanctis et al., 2017) in the context of the Rosalind Franklin rover mission. Río Tinto is an acidic river (pH 2.3), 92 km long with a high concentration of soluble metals that flows in the south of Spain (Huelva province, Andalucía) draining an area characterized by numerous massive sulfide deposits that are hosted by a volcano-sedimentary sequence. The microbial and physical characteristics of the river have been suggested as evidence for a subterranean ecosystem sustained by chemolithotrophic anaerobic metabolism of iron and sulfur minerals (Amilis et al., 2007). These characteristics make the Río Tinto site an analog planetary field of astrobiological interest where the preservation of organic matter in conditions of extreme acidity is of great interest to researchers studying the nature and diversity of life in extreme conditions.

Oxia Planum, the selected landing site of the mission shows mineralogical and morphological evidence that it was characterized by a long duration of aqueous superficial activity (Ferrari et al., 2023). This is consistent with conditions favorable to life development. In this framework, we made this field campaign where we performed a wide set of VIS-NIR measurements using the ASD Fieldspec4 portable spectrometer both on biosignature-bearing rocks and alteration hydrated products. In addition, for each analyzed mineral/rock on-field, we collected representative samples that we are measuring in the laboratory with different setups/techniques. This activity with analogs sites and samples can be useful for defining the priorities in the identification and the down-selection of samples on Mars.

During the field trip to the Río Tinto area, we visited five different locations and we performed several spectral measurements on different types of rocks/sediments like acidic altered outcrops, mining waste sediments, and various types of salts and sulphatic encrustations. The spectral data obtained during the measurement campaign carried out in the Río Tinto area will be compared with measurements made in the laboratory on the respective collected samples. This further phase of the investigation will improve our understanding of the mineralogy and alteration processes that have occurred on the rocks and soils of the studied area.

The collected samples were measured at the INAF-IAPS laboratories in Rome using different setups. In particular, micro-Raman spectroscopy was performed on samples of astrobiological interest. These laboratory measurements provide the chance to better characterize the organic compounds in geological matrices. Raman spectroscopy is a very useful tool in detecting and characterizing organic matter. The data collected on-field and in the laboratory are analyzed and compared to reconstruct the composition of the analyzed samples. We will focus our efforts on any spectral signature related to the presence of biomarkers in the collected data since we know that the Ma\_MISS instrument can aid in detecting organics (Ferrari et al., 2023) in the Martian subsoil, which is one of the main scientific objectives of the Rosalind Franklin rover mission.

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## **Distinguishing geochemical signature of volcanic rocks using PRISMA satellite: the case study of Tenerife**

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*Keywords:* planetary science, petrology, spectral characterization.

Within the past few years, planetary exploration had an increasing interest, but direct access to other planets in the Solar System is still limited, except for a few rovers carrying out direct analysis on some planetary surfaces. Remote sensing techniques represent powerful tools and, in particular, spectral analyses are extremely useful to obtain information on the composition of soils on the surface of planetary bodies.

All terrestrial planets in the Solar System show evidence of past volcanic activity, sometimes similar to the one we observe today on Earth. Effusive igneous rocks are widely distributed on the surface of other terrestrial planets and can be distinguished by spectral analyses. Unlike other terrestrial planets, most of Earth's evolution is still dominated by plate tectonic which produces a wide variety of magma compositions, from ultrabasic to acidic, and from calc-alkaline to alkaline series, this makes the Earth an excellent natural volcanological laboratory where experiments with remote sensing techniques can be done and create a database of volcanic rocks' spectrum as models to be compared in the future with spectrum data from other terrestrial planets of the Solar System.

For this work, we carried out the spectral analysis in the Visible and Near Infra-Red (VNIR) region in Tenerife island with the use of PRISMA satellite (PREcursore IperSpettrale della Missione Applicativa) which is a medium to high-resolution hyperspectral imaging mission of the Italian Space Agency, ASI (Agenzia Spaziale Italiana) developed since 2008 (Zinzi et al., 2023.). The primary aim of this work is to identify the most abundant volcanic rocks cropping out at Tenerife island. Tenerife is a volcanic island where volcanic rocks are well exposed, in particular in the central part, where there are the Pico-Teide volcanic complex and the Cañadas Caldera there is no presence of vegetation and it offers a good range of chemical compositions that could reflect the geochemical compositions present on the other planets of the Solar System.

Results from this study are consistent with what is observable from the geochemical map of Tenerife, these new sampling and analysing methodologies can give new insight into the exploration and characterization of planetary volcanic regions during future missions of planetary explorations. As an example, CRISM (Compact Reconnaissance Imaging Spectrometer for Mars) which goes from 362 to 3920 nanometres, covers a wavelength in the visible, infrared and short wave range. These characteristics make CRISM able to study a wide variety of minerals on the Martian surface and it can be considered an analogous of PRISMA satellite (Pelkey et al., 2007).

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## **Integrating ASTER and Sentinel-2 Data for Detecting Potential Zones of Lead and Zinc Deposits Carbonate-Hosted Rocks: Case Study of Khan Khatun Area, Kerman, Southeast Iran**

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*Keywords:* carbonate-hosted mineralization zone, Sentinel-2, ASTER.

Multispectral satellite data play an important role in reducing the cost of exploration projects, especially in inaccessible areas, thanks to their free availability and to their increasing quality (spatial, spectral, and radiometric improvement over time) and. Indeed, the diversity of multispectral satellite data allows the user to provide more reliable results by identifying the spectral characteristics of rocks and minerals and simultaneously using multiple satellite data with different spectral capabilities. Various studies have proposed investigating the presence of iron oxides and dolomitization of rock units as two exploration keys in evaluating the mineralization potential of Pb-Zn using remote sensing satellite imagery (Sekandari et al., 2020; Rajabi et al., 2012; Molan & Behnia, 2013).

The present study aims to identify promising areas for Pb-Zn mineralization, by using and subsequently processing ASTER (Advanced Spaceborne Thermal Emission and Reflection Radiometer) and sentinel-2 satellite images acquired on July 21, 2001, and on September 4, 2021, over the Khan Khatun area, Kerman (southeast Iran). which is one of the parts of the Pb-Zn potential belt of Yazd-Anarak in Iran.

According to the study objectives, regarding the investigation of the presence of dolomitization and iron oxides using satellite data, it is useful to discuss the spectral characteristics of the identified targets (dolomitization and iron oxide). Consistent with their chemical composition, carbonate minerals can have different spectral absorption characteristics in the range of the electromagnetic spectrum. The results of characterizing iron oxides based on Sentinel 2 data are consistent with the location of dolomitized areas. Thanks to their higher spatial resolution, Sentinel-2 data highlight the mineralization zone more accurately, and due to the more recent nature of the images, some pixels are completely consistent with mining activities. It is interesting that in the output of the Sentinel-2 images, the place of accumulation of the extracted ore mineral is highlighted. The field reconnaissance has been carried out to investigate alteration zones in the area that have a high probability for Pb-Zn mineralization. Global positioning system (GPS) has also been used to determine the accuracy of the image processing method. To determine the quality and concentration of Pb-Zn, rock sampling and ran different laboratory analyses such as polish, thin section, ICP and XRD analysis have been conducted. The specification of VNIR (Visible and Near-Infrared) and SWIR (Shortwave Infrared) wavelengths provided by ASTER and Sentinel-2 displays that highly prospective zones of Pb-Zn mineralization in carbonate-hosted rocks are enhanced and approved by field survey. The results confirm this approach is useful for explorations in green and brown field areas of Pb-Zn mineralization.

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## Mineralogical characterization of the fusion crust of the Cavezzo L5 Chondrite

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Keywords: Cavezzo, meteorite, mineralogy.

On January 1st at 18:26:53 UT, eight stations of the PRISMA network detected a brilliant fireball, named IT20200101, in the skies of northern Italy (Gardiol et al., 2021). Thanks to the involvement of local people by an effective media campaign, two fragments were recovered, weighing 3.12 g (specimen 1) and 52.19 g (specimen 2), three days after the bolide was observed. In this contribution we describe the mineralogical characterization of the fusion crust of sample 2.

A thin section of sample 2, and a polished mount with several chips from the fusion crust have been studied by both optical microscopy and by FE-Scanning electron Microscopy.

Both Optical observations and micro-chemical analyses of the meteorite interior were consistent with published classification as a L5 ordinary chondrite (Pratesi et al., 2021). The fusion crust displays a complex texture of skeletal and acicular olivine, often with a rim richer in Fe than the core. The small size of most olivine crystal prevented to obtain an accurate composition for most of them. Magnetite dendrites are commonly associated to the olivines. Minor minerals found in the crust include euhedral chromites, ilmenites, plagioclases in aggregates with chromites (Pl-chr assemblages) and a nickel sulphide whose composition is close to Ni<sub>2</sub>S. One of the two Ni sulphides found display submicroscopic inclusions of metallic Ni. To our knowledge, Ni<sub>2</sub>S has never been reported before in chondritic material; thus, in order to confirm the composition and in order to determine the structure of this phase, we are planning to cut a slice of one of these grains by FIB and to study this phase by Transmission Electron Microscopy.

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## Highlighting hydrated minerals from orbital spectral data on Mars: potential through a colorized mapping method of sedimentary deposits

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*Keywords:* orbital spectroscopy, planetary exploration, sedimentary deposits on Mars.

We introduce a series of CRISM processing techniques that create visually appealing images which highlight the hydrated potential of the Martian surface. The processing includes: 1. a band ratio, 2. a new destripping method, 3. pixel group mode filtering, 4. slicing, 5. assigning a color gradient to the slices and 6. combining the result to the brightness channel of the original CRISM observation. These steps were tested on seven CRISM observations across two types of sedimentary deposits, the layered deposits in Bequerel crater and a delta in Shalabatta Valles.

A key indication of the presence of water is indicated by the relative absorption around 1.9  $\mu\text{m}$  of the  $\text{H}_2\text{O}$  molecule (Clark et al., 1990), thus a band ratio between bands 140 (wavelength 1.9149 – 1.9214) and 131 (wavelength 1.8555 – 1.8620) is applied to the observation and converted to greyscale. These bands were selected based from where the absorption is most intense (band 140) and just before the absorption begins (band 131) in the CAT library spectra of Gypsum LASF41A (Flahaut et al., 2015; Schmidt et al., 2018).

With the resulting image, a two-step normalization process is applied both across and along the pixel columns. Initially, mean and standard deviations are computed for each column. The pixels of each column are normalized by the central mean values and standard deviation of the group of eleven columns around it. Central mean and standard deviation were obtained by systematically eliminating the two columns with the highest and lowest mean and standard deviation values. Then, each pixel DN was corrected by a small factor proportional to the central means and standard deviations of the group of eleven pixels around it.

This destriped image is then sliced into several intervals which are then color coded. Slicing allowed the application of modal filtering to reduce local variability by substituting each pixel's DN by the most common value occurring within a circular area around it (2.5 pixel radius). A color is assigned to each interval/slice the resulting image is then color coded, (i.e. a color assigned to each interval/slice) and combined with the brightness channel (from the three channels: hue, saturation, and brightness) of the original CRISM observation. This combination allows the blending of the morphology and the color coded ratio which readily describes the surface of the coverage area. As a result, one can accurately observe the contrasting 1.9  $\mu\text{m}$  absorption intensity across the study area in what we refer to as an  $\text{H}_2\text{O}$  content map.

The proposed method has potential as an alternative to the summary parameters 1900 and SINDEXT of the CAT toolkit, and presents the band ratio in an intuitive way. The new destripping method is also a competitive alternative. Results can be used in combination with other datasets, ultimately aiding the geological interpretation of sedimentary environments on Mars and future mission target selection.

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## Elastic Thickness of Mercury's Lithosphere: Insights from the Topography of the Caloris Planitia Impact Region and the impeding Caloris Montes

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Keywords: Mercury crust, Caloris Planitia, planetary structural geology.

Aspects of the lithosphere of Mercury have become increasingly ascertainable, as recent work using data from the MESSENGER space probe has revealed the surface topography and mineralogy (e.g., Solomon et al., 2018). Although the mercurial lithosphere has been determined to be a silica-magnesium composition (Phillips et al., 2018; Solomon et al., 2018), its precise thickness and elasticity has yet to be established. Current estimates of the lithosphere thickness are  $35 \pm 11$  (Padovan et al., 2015) and varying regional thicknesses of  $19 \pm 11$  and  $50 \pm 12$  km (Beuthe et al., 2020), achieved by topographical analyses and partial melting laboratory experiments. However, by utilizing a Monte Carlo statistical approach of lithospheric flexure, these estimates can be constrained.

A large 1500 km diameter circular basin called Caloris Planitia has a complex geological history thought to have begun with a large impact event and subsequent infilling (Solomon et al., 2018). The basin is characterized by a sharp, radially asymmetrical, rim which has been retained in many places. Furthermore, the Caloris Montes east-west mountain range impedes the northern area of Caloris Planitia. This large basin and its surroundings have been examined and provide evidence of elastic flexural deformation, as well as significant vertical offset between the northern and southern basin rim.

By adopting equations for linear and central load flexure (Turcotte & Schubert, 2002) within the conditions of several parameters (i.e., Young's Elastic Modulus and Poisson ratio) for silicate-magnesium mixture, we can determine a specific range of values for the lithosphere elastic thickness, and the maximum vertical depression at the moment of impact. From these acquired values, an estimation of the load produced by the impact and the impact energy can be determined as well. The estimated impact energy in turn can provide a given range for the velocity, mass, and diameter of the impacting object at the moment of impact. Additionally, any resulting asymmetry of the flexural load can indicate the trajectory of the impacting body.

These equations were compared to the available topography along several selected radial profiles that crossed the basin, rim, and surroundings of Caloris Planitia. By utilizing multiple Monte Carlo-Convergent simulations, the best fit flexure surface was able to replicate the topography of the selected profiles within the aforementioned parameters. Although this work is currently ongoing, preliminary results provide a variety of information of the conditions at the time of impact. Furthermore, a 1000 km long section of the northern rim is approximately 2000 m below the southern rim and is aligned with the Caloris Montes mountain range, implying significant fault movement after the impact. This work aims to provide support to the upcoming arrival of BepiColombo. We gratefully acknowledge funding from the Italian Space Agency (ASI) under ASI-INAF agreement 2017-47-H.0.

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## Mapping structures and impact basins in Mercury's Discovery Quadrangle (H-11)

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Keywords: Mercury, multi-ring basin, planetary geology.

Mercury's Discovery quadrangle (H-11), located at southern mid-latitudes, contains the NE-SW trending Discovery Rupes, which is one of the longest and highest lobate scarps on the planet, with a length of 600 km and a height of 2 km. The quadrangle also hosts a probable multi-ring impact basin named Andal-Coleridge surrounded by a three- to five-ring system.

By using MESSENGER/MDIS imagery and the digital elevation model we produced a high-resolution structural map to evaluate the structural relationships among three main scarps (Discovery, Adventure and Resolution Rupes – DAR) and to define the multi-ring structure of the Andal-Coleridge basin.

We mapped more than 400 segments of contractional structures (lobate scarps, high-relief ridges, and wrinkle ridges) that are arranged in a circular pattern, approximately at the center of the quadrangle, with two NW-SE and NE-SW-trending linear systems. The mapped structures appear to surround an area of crustal thinning identified in the crustal thickness map that roughly coincides with a broad topographic low approximately centered in the Schubert crater.

The analysis of the scarp height (a proxy for the throw) along the fault lengths shows that the three structures represent segments of two different scarps, the Discovery Rupes and the Adventure-Resolution Rupes which appear to be kinematically soft-linked, since the cumulative throw falls approximately in the center of the system, consistent with typical fault growth patterns.

The strong arcuate trend and the circular pattern of the structures suggest the presence of an ancient multi-ring impact basin. The area of crustal thinning identified in the crustal thickness map could represent the transient crater or excavation cavity of the basin with a diameter of ~500 km. We recognized a four-ring system concentric to the crustal thinning area, interpreting the Discovery Rupes as the so-called "topographic rim". The Adventure-Resolution Rupes is not concentric to the basin here proposed but appears to be concentric to another area of crustal thinning close to the Rabelais crater, probably another impact basin.

These results mean that the two scarps formed as a result of two distinct local-scale processes, i.e., impacts, and were reactivated by Mercury's global contraction as a linked fault system. The concentric pattern of the structure could be due to the presence of the Andal-Coleridge multi-ring basin, which could have defined mechanical discontinuities in the crust, influencing the localization and orientation of thrusts that would have represented preferential weak zones along which the global contraction of Mercury acted.

**S31.**

**From facies to depositional sequences:  
experimental approaches and case studies on the analysis  
of sediments and sedimentary rocks**

*CONVENERS AND CHAIRPERSONS*

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*Luisa Sabato (Università degli Studi di Bari Aldo Moro)*

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## Neogene cold seep system reconstruction in the Crotona Basin (South Italy)

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*Keywords:* cold seep, conduit, pavement.

For the first time, the Neogene cold seep carbonate deposits of the Crotona Basin (south Italy) are described. These deposits form a carbonate body reaching a maximum length of 350 m and a thickness 40 m and are characterized by a conduit facies made of authigenic carbonates filling the previously active gas/fluid escape pipes and by a pavement facies consisting of early carbonate-cemented bioclastic and siliciclastic sediments. These latter are commonly colonized by chemosynthetic and non-chemosynthetic macrofauna which, however cannot be taxonomically defined since the majority of the shells and skeletons are dissolved or recrystallized. The conduit facies is characterized by the inward accretion of dark micritic laminae alternating with clear crystalline layers. The micritic laminae show a microbial peloidal to dendrolitic fabric, which commonly incorporates planktonic foraminifera and coprolites, whereas the crystalline layers are made of microsparitic and sparitic crusts made of prismatic zoned calcite crystals. The pavement facies shows a great variability since it is typified by laminated microbial boundstones, bioclastic bearing micrite, foraminiferal oozes and hybrid arenites. The foraminiferal assemblage, exclusively composed by planktonic forms suggests a deep-water setting occasionally affected by siliciclastic sedimentary flows. The pavement facies also shows common brecciation features, suggesting the establishment of post-depositional overpressure conditions due to the early cementation of the conduits, which triggered localized breakage and poorly energetic outbursts of the pressurized hydrocarbons. Stable isotopes analysis of the different facies reveals overall negative  $\delta^{13}\text{C}$  values (-6.82 to -37.39 ‰) and relatively positive  $\delta^{18}\text{O}$  values (-0.04 to 3.39 ‰), indicating the presence of a complex mixture of methane with other hydrocarbons, consumed by a consortium of sulphate-reducing bacteria and methanotrophic archaea via anaerobic oxidation of methane, and the possible destabilization of gas hydrates and/or dehydration of clay minerals.

## River instability during the Middle Ages in the Po Plain. Insights into mechanisms and rates of alluvial sedimentation

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Keywords: fluvial sedimentation, morpho-stratigraphy, Middle Ages.

The Early Middle Ages, also reported as Dark Ages, represent a period of political instability in Italy, subsequent to the fall of the Western Roman Empire. During this period, the loss of control of the drainage network and the contemporaneous increase in rainfall resulted in a phase of river instability (Cremonini et al., 2013) that persisted until the Renaissance, leading to a substantial reorganization of the river network. Natural-levee breaches and avulsions have been documented for many rivers of the Po Plain through geomorphological data (Castaldini, 1987). In a few locations, post-Roman sedimentation has been delineated based on the identification and lateral tracking of a buried paleosol dated to the Roman period (Bruno et al., 2013). However, no integrated geomorphological and stratigraphic studies have been undertaken to define a comprehensive model of fluvial sedimentation.

Through a morpho-stratigraphic approach based on the analysis and interpretation of (i) high resolution digital terrain models; (ii) satellite images; (iii) sediment cores; (iv) penetration tests and (v) pedological data, we reconstructed the post-Roman stratigraphy in the Po Plain between Po, Secchia and Panaro rivers, focusing on the Middle-Ages sedimentary evolution. The northward shift of the Po River created space for sediment delivered from three Apennine rivers: Secchia, Panaro and Reno. These rivers changed their course several times between 800 and 1500 AD and accumulated impressive volumes of sediment in crevasse splays and ribbon-shaped fluvial ridges and in the surrounding floodplains. The resulting morphology influenced human settlement in the area, with roads and villages aligned along topographically elevated areas. A detailed chronology based on radiocarbon dates and archaeological data, coupled with 3D mapping of sedimentary units confirmed the extremely episodic nature of alluvial sedimentation (Amorosi et al., 2017), with rapid variations of sedimentation rates (from 0 to 40 mm/yr) in a few km.

This study provides new insights into the mechanisms and rates of fluvial sedimentation in a well constrained chrono-stratigraphic framework. This type of research may help predict river behaviour during unstable climatic conditions and can be useful for decision makers in terms of land management, in a context of increasing extreme meteorological events.

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## On the Lowstand System Tracts (LSTs) as paleobathymetric indicators

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*Keywords:* paleobathymetry, lowstand systems tract, vertical tectonic movements.

Lowstand Systems Tracts (LSTs), formed in the transitional area between the continental shelf and upper slope during the sea level stillstand of the Last Glacial Maximum (LGM), were used to measure the magnitude and rate of Late Pleistocene-Holocene vertical tectonic movements (Casalbore et al., 2017; Fraccascia et al., 2013; Pepe et al., 2014). A literature review shows that different empirical methods have been used to derive the paleo depth of LSTs' formation. Consequently, the amount and rate of vertical movements calculated for different areas are not comparable.

Here, we present the first results of a quantitative analysis of oceanographic and geologic data to estimate the position of the paleo-sea level related to the depth of the LST. The dataset consists of high-resolution reflection seismic profiles, storm wave parameters (e.g., significant wave height, wave period) and grain-size data.

The comparison between the theoretical beach equilibrium profile, derived from the Bruun's method (Bruun, 1954), and the upper bounding surface of LST recognized in the seismic profile provides a depth of about 135 m of the paleo-sea level during the formation of the LST. The obtained value of the paleo-sea level combined with the depth of closure fits with the seaward limit of the active beach profile observed along the seismic section.

The results of the quantitative analysis integrated with the Holocene sea-level curves are used to derive the post-LGM vertical tectonic movements along the upper slope of the Southern Tyrrhenian Sea. The present study also provides a vertical tectonic movements chart of the southern Tyrrhenian Sea in the late Quaternary.

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## A geological model of the urban area of Palermo realized by a multidisciplinary approach

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Keywords: 3D modeling, geophysical techniques, constrained data inversion.

Geophysical techniques are becoming increasingly important in the reconstruction of geological models of the subsoil in urban areas. These surveys are fundamental considering that direct investigations are strongly invasive due to possible interference with the subservices of the urban networks. Moreover, carrying out a direct investigation, such as a drilling or a trench, requires several authorizations and complex and costly management of the yard. For these reasons active and passive seismic methods are nowadays widely used in urban areas.

Therefore, the geological modeling of an urban area requires working with a regular mesh of direct and indirect surveys. This approach is useful where local geology does not exhibit large lateral variations. Considering these stratigraphic contexts, several surface geophysical surveys can detail the geometry and volume of the deposits without the need to carry out further direct investigations.

From this perspective, the plain of Palermo is a natural laboratory of great interest. It is located in North Western Sicily and hosts the fifth largest city in Italy by population. In this work we present the reconstruction of a more accurate geological model of the plain close to the Oreto River, the main river crossing the urban area. This is produced by integrating several investigation techniques.

Firstly, a drill holes database property of the University of Palermo has been used. The database collects stratigraphic data from more than 2000 cores provided by several companies, freelance professionals geologists and engineers. These data have been collected since the early 2000 and have been homogenized and inserted in a consulting software (Giammarinaro et al., 2001).

Secondly, several microtremor acquisitions were considered. Noise recording stations have been located according to a regular mesh throughout the area and have been analyzed using Horizontal to Vertical Spectral Ratio (HVSr) technique (Nakamura, 1989). By inverting the HVSr curves, stratigraphic models were obtained, constraining the inversions with the nearest drill hole stratigraphic data and with shear velocity values obtained by Multichannel Analysis of Surface Waves (MASW) surveys (Park et al., 1999). These latter were carried out in the surrounding areas or within some previously studied sector of the plain in which the same lithologies outcrop (Martorana et al., 2018).

In addition, photogrammetric Digital Outcrop Models (DOMs) have been obtained on outcrops along the Oreto River. These will be used to develop qualitative sedimentological scenarios relevant for subsurface models, and possibly as training images for quantitative geostatistical models of coastal to alluvial facies geometries and spatial distribution.

Connecting all data available, a 3D model of the Oreto River area has been generated. Multidisciplinary data integration has resulted useful to describe the depth of the bedrock and the thickness variation of the near surface deposits.

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**Topographic control on turbidite deposition in foredeep and trench-slope basins:  
a comparison between the Serra Palazzo Fm. and the Tufiti di Tusa Fm.  
(Lucanian Apennines, Southern Italy)**

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*Keywords:* Serra Palazzo Formation, Tufiti di Tusa Formation, confined turbidite successions.

One of the key controls on turbidite systems is the presence of confining topography, with different basin configurations and evolution over time resulting in characteristic facies and architecture. In this study, two turbidite systems are compared: the Miocene Serra Palazzo Fm. (SPF) and the late Eocene-early Miocene Tufiti di Tusa Fm. (TTF), both cropping out along the outer border of the Lucanian Apennines in Southern Italy. The study area for the SPF is near the Campomaggiore village (central Basilicata region), where a c. 300 m-thick coarse-grained sandstone-rich succession crops out. This is compared to an about 230 m-thick muddy-sandy succession cropping out near the Rotondella village (SE Basilicata region). Detailed facies analysis based on high-resolution physical stratigraphy was used to infer basin morphology and evolution for both systems. The SPF outcrop is characterised by palaeocurrents directed towards SE, with flows moving parallel to the thrust front of the chain. This configuration suggests that the flows, after reaching the slope base of the foredeep basin, were deflected by the inbound slope and the proximal flank of the forebulge, and that they then travelled along the basin long axis. The sandstone to mudstone ratio (S/M) is relatively high (over 2) and it does not show any upward increase, suggesting that the succession was not fully confined and that did not experience any change over time in confinement. Sedimentary features, such as load casts, convolute lamination and mud-draped scours, observed at several different stratigraphic intervals, indicate that flows decelerated due to a reduction in gradient and the possible presence of morphological obstacles. The studied TTF succession lies unconformably on highly-deformed terrains of the Argille Variegate. Unlike the SPF, it shows a very high-dispersion of the palaeocurrent directions and an upward increase in the S/M ratio from 0.6 to 2.5, reflecting an evolution from a flow ponding phase to a flow stripping phase. Biconvex ripples with sigmoidal-cross laminae, hummocky-type structures and thick mudstone caps are widespread throughout the stratigraphy. This evidence suggests that the TTF was deposited in a fully-confined setting represented by a trench-slope basin. In conclusion, the studied outcrops represent two examples of turbidite systems controlled by different configurations of basin topography and the presented facies and architectures can help interpret turbidite systems in less well-exposed areas or in the subsurface.

## Pleistocene-Holocene stratigraphic architecture of the Po Plain

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*Keywords:* stratigraphic architecture, Quaternary, Po Plain.

Sedimentological and geochronological data (Radiocarbon, Infrared Stimulated Luminescence) from a recently drilled 176 m-long core (S15) and palynological, paleontological and geochronological (Radiocarbon, Electronic Spin Resonance and Magnetostratigraphy) data, from 22 cores published in recent decades, have been correlated to define the Pleistocene-Holocene depositional architecture of the Po Basin.

A 120 km long stratigraphic cross-section, striking from NNW to SSE across the central and eastern Po Plain, has been realized through the correlation of core and well data. The cross-section runs along the culmination of a thrusts-related fold, known in literature as the Mirandola Anticline, and to its eastward prosecution. Data beyond this section have been included into an additional SSW-NNE correlation panel.

Two Unconformity-Bounded Stratigraphic Units, the Lower and Upper Po Synthem (LPS and UPS, respectively), record the onset of continental deposition in the Po Basin since 870 ky BP. LPS and UPS in core S15 display an overall shallowing upward trend. The LPS is characterized by paralic deposits passing upwards to continental deposits. UPS is dominated by well-drained floodplain and fluvial-channel deposits. Within this overall trend a cyclic organization of facies can be observed in LPS and UPS deposits. In LPS each cycle is composed of lagoon or bay-head delta facies associations grading upwards into swamp and poorly drained-floodplain deposits. In UPS individual cycles include swamp and poorly drained deposits passing upwards to fluvial-channel sand bodies and/or paleosol-bearing well-drained floodplain deposits. These vertical repetitive facies changes are observed throughout the stratigraphic sections and permitted to subdivide the whole LPS and UPS succession in subunits (transgressive-regressive cycles) which are interpreted to reflect Middle-Late Pleistocene glacio-eustatic oscillations. This interpretation is corroborated by pollen data available in the literature, which indicate that the base of each subunit accumulated during interglacials whereas the upper part in glacial periods. Within each cycle, alluvial deposits grade eastward into coeval paralic and coastal deposits. From the oldest to the most recent cycle, a progressive eastward shift of facies and of maximum marine ingression coastlines is recorded. This trend possibly reflects the progressive filling of the basin, modulated by glacio-eustatic oscillations.

## Revising the western Hyblean sedimentary succession: an update from field mapping and integrated stratigraphic analysis

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*Keywords:* integrated stratigraphy, paleoclimatic variation, SE Sicily.

In south-east Sicily, the succession characterizing the western sector of the Hyblean Plateau is mainly composed of carbonate sediments interbedded with volcanic rocks, ranging in age from Late Cretaceous to Quaternary. This succession has recorded the important climatic variations taking place during their formation.

The field work carried out for the realization of the geological sheet 648 (Ragusa), in the framework of the CARG Project, has provided the opportunity to carry out a thorough review of the successions cropping out in the area, whose last update dates back to the late '90s. The outcropping sedimentary succession is mainly represented by the Ragusa, Tellaro and Palazzolo Formations, ranging in age from Oligocene to late Miocene. The review we are currently carrying out consists of an accurate field mapping accompanied by a series of stratigraphic logs and sampling for a set of stratigraphic analysis, consisting of integrated biostratigraphy (foraminifers and calcareous nannofossils), magnetostratigraphy and isotope stratigraphy.

The results have allowed to provide detailed ages for the different traditional members of the Ragusa Formation (Leonardo and Irminio), highlighting the presence of intraformational unconformities. Another important topic is the geometric stratigraphic relationships between the Ragusa and the overlying Tellaro Formation, generally consisting of a gradual vertical transition, but affected by a lateral transition. A marked sharp angular unconformity, postdating lower Miocene tectonics, is also present in the Ragusa High area. The Oligo-Miocene lithostratigraphic record helps to define a polyphase tectonic evolution, and a syn-sedimentary growth of structures along the Ragusa High hosting the Ragusa oil field.

**Inherited morphology control on basin evolution in Cretaceous-Paleogene carbonates.  
A case study of mass-transport deposit, Frasassi Area, Central Italy**

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*Keywords:* mass-transport deposits, basin evolution, inherited structures.

Mass-transport deposits have been documented in the deep marine marly pelagic carbonates situated in the Cretaceous – Paleogene Scaglia Rossa Fm., Northern Apennine, central Italy. The Umbria Marche sequence is characterized by Jurassic platform and basin carbonates overlaid by Cretaceous-Oligocene basinal limestones and marls. The mass-transport deposit in the Turonian-Selandian portion of the Scaglia Rossa Fm. are ubiquitous throughout the basins and can reach up to 10 m in thickness and more than 100 m of lateral extension. These deposits, predominantly slumps, are composed of folded and/or translated beds of pelagic wackestones, packstones and calcarenite grainstones. These deposits indicate a very short travel distance. The trigger and departure point of the mass-transport deposits could be controlled by (i) seismic activity, (ii) sudden larger sediment input, and/or (iii) tectonic tilting.

The investigated mass-transport deposit is situated near Genga, Northern Apennine. This slump level is Selandian in age and it is sandwiched between Campanian and Selandian marly limestones. The calcarenites underlying slump layers show a southwest and west direction of paleo flow (the source is hypothesized to be a buried carbonate platform to the NE), while the whole slump body is transported towards the east-north-east. We present this study in order to document the role of antecedent morphology and ongoing selective compaction between Jurassic carbonate platforms and basin deposits, together with the evidence of tectonic activity during this time period in the area.



## Provenance of the Pre-orogenic Lower-Middle Jurassic successions of the Prerif foreland basin (Rif chain, Morocco)

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Keywords: provenance, U-Pb zircon data, Morocco.

This study deals with the provenance of lower-middle Jurassic successions cropping out in the Prerif Foreland basin of the Rif chain (Morocco), by merging sedimentary petrology and U-Pb zircon geochronology on four stratigraphic successions to ensure a thorough new overview.

The analyzed sandstone suites have been collected from the lower-Middle Jurassic sandstones of Jbel Outita, Jbel Zerhoune, and Dhar N'sour sections accumulated in different depositional paleoenvironments evolving down-slope from proximal delta to bathyal and deep-sea basin. Both lithofacies belonged to the hyper-extended margin of the NW-Gondwana during the early-middle Jurassic time coevally with the earliest rifting-drifting stages of the western edge of the Tethyan Ocean.

Modal petrographic analyses show that sandstones are hybrid siliciclastic characterized by feldspathic litharenite, litharenite, and lithic arkose compositions. Detrital sandstone modes reveal a provenance from medium to high-grade metamorphic rocks namely of Transitional Continental block and recycled orogen.

Reliable new U/Pb zircon data (LA-ICP-MS) from sandstone outcropping in the Prerif Basin were carried out on two samples from Jbel Zerhoune and Jbel Outita. Concordant U/Pb zircon data yielded a Paleozoic zircon age that shows provenance from the exotic Sehoul Bloc, High Atlas, and Anti-Atlas chains (Tahiri et al., 2010). Neoproterozoic cluster ages with a dominant Ediacaran zircon population at the peak (612 Ma-598 Ma) corresponds to the Cadomian and/or the Pan-African orogens mainly of the "Sehoul block" exotic Terrane, Western Meseta, and Anti Atlas chains (El Haibi et al., 2020). Hence, rare Paleoproterozoic ages are less abundant with a peak age at 2.13 Ga, suggesting a provenance from the Anti-Atlas or probably from the Eburnean orogens of the West African Craton (WAC). (Pereira et al., 2015, Gärtner et al., 2013).

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## A revision of the depositional model for modern and ancient, tectonically-confined tidal straits

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Keywords: straits, tidalites, modelling.

In the last decades, the scientific interest in understanding geological processes of tidal straits has increased noticeably. That has mainly been due to the economic potential deriving from their strategic role as marine tradeways, heat transport, reservoir properties of their sand-rich deposits in the subsurface and paramount loci for production of renewable energy deriving from water movements. Therefore, their geological modelling is increasingly becoming crucial for planning human activities and assessing energetic potentials.

In 2013, a first depositional model was published, based on the cross checking of modern case studies and stratigraphic observations of outcrop examples exposed in southern Italy. The model suggested four depositional zones, laterally adjacent from the narrowest strait centre to its terminations. These zones are: (i) the strait-centre zone, associated with the tidal current maxima and where sediments are scarce or absent; (ii) the dune-bedded zone, where sediments form dune complexes due to tidal flow expansion; (iii) the strait-end zone, where currents decelerate accumulating thinly bedded, fine-grained deposits; and (iv) the strait-margin zone, where sediment mass-flows descend tectonically active, steep margins towards the strait axis.

After scientific sessions promoted in some major international congresses, thematic publications and field trips, studies on modern and ancient tidal straits have been encouraged worldwide among the scientific geological community. Worth mentioning are the sessions organized at the 34th IAS meeting of sedimentology, held in Rome, Italy, 2019, and at the 10th International Congress of Tidal Sedimentology, held in Matera, Italy, 2022. Here, valuable presentations provided novelties on modern and ancient straits, suggesting new aspects and terminologies. The results of these works have been recently collected in a special volume n. 523 of the Geological Society, London.

In this note, a revision of the 2013 first model on tidal strait is presented. The revision maintains the four-folded division into zones or environments, but suggests additional processes and bedforms, specifically for dune-bedded strait zone and the strait-margin zone and further sedimentological features. These include: (i) the dominance of prolonged net sediment transport produced by inertia-dominated but tidally-generated flows along sufficiently long areas, where contourite deposits may result as a direct effect of tidal strait amplification; (ii) the presence of large-scale bedforms, elongated in the direction of the dominant tidal flow, such as tidal sand ridges, including smaller tidal dunes on their top; (iii) additional erosional features, such as ‘comet marks’ in the vicinity of the strait-centre zone, but with a very low preservation potential in corresponding ancient lithofacies recording this type of environment.

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Dalrymple R.W. (2022) - A review of the morphology, physical processes and deposits of modern straits. In: Rossi V., Longhitano S.G., Olariu C., Chiocci F. (Eds.) Straits and Seaways: Controls, Processes and Implications in Modern and Ancient Systems. Special Volume n. 523 of the Geological Society, London, 17-83.

Longhitano S.G. (2013) - A facies-based depositional model for ancient and modern, tectonically-confined tidal straits. *Terra Nova*, 25, 446-452. <https://doi.org/10.1111/ter.12055>.

Rossi V., Longhitano S.G., Olariu C. & Chiocci F. (2023) - Straits and Seaways: Controls, Processes and Implications in Modern and Ancient Systems. Special Volume n. 523 of the Geological Society, London, 523 pp. <https://doi.org/10.1144/SP523>.

## **The impact of salt tectonics on the degree of preservation of the Middle Jurassic Garn Formation, Halten Terrace Norwegian Continental Shelf**

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*Keywords:* salt tectonics, Garn Formation, evaporite.

Salt tectonics is a process that has gained the interest of structural geologists and sedimentologists as it might facilitates the generation of hydrocarbon traps, impacts on the architecture of the reservoirs, and serves as a seal to prevent fluid leakage. The presence of salt-controlled structures can condition sedimentation locally by abruptly creating accommodation zones. In salt-controlled extensional basins, the impact of salt mobility on footwall uplift and the subsequent erosion of the footwall crest can represent a crucial aspect to be understood. The vertical and lateral migration of ductile subsurface evaporite layers can: (i) have significant impact on along-strike displacement variability of the cover strata, (ii) influence the development of new faults, (iii) modify the geometry of the sedimentary units, (iv) cause localized strain on footwalls, and (v) initiate sediment erosion leading to fault-scarp degradation along footwall crest.

In this study, we use high-resolution seismic data to document the impact of Triassic evaporite on the thickness variability of the Garn Formation - a middle Jurassic up to 120 m thick sand-rich succession accumulated in small grabens within the Halten Terrace (Norwegian Continental Shelf). Preliminary results reveal the dramatic change in the thickness of Garn Formation as a result of crestal collapse and partial erosion in areas controlled by Triassic evaporites. The plastic deformation of discrete units of Triassic units and the resulting additional uplift imparted on normal faults accentuated footwall uplift and consequent erosion. This process is invoked as one of the main factors for the absence of the Garn Fm and would contribute to interpret the thickness variations of pre-salt strata accumulated over a number of graben margins.

## The dinosaur tracksite of Molfetta: stratigraphy and facies analysis of the shallow-water carbonate succession hosting medium- to large-sized footprints

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Keywords: peritidal limestones, sea-level change, Albian.

The dinosaur tracksite of Molfetta (Apulia, southern Italy) was discovered in 2005 on a bed surface at the top of an about 10 m thick shallow-water carbonate succession cropping out in a disused quarry pit (the San Leonardo quarry) a few km south-west of the town of Molfetta in the northern Murge. Afterwards, the Molfetta tracksite has been the subject of in-depth studies aimed at: i) producing the geo thematic map of the whole track-bearing surface, by using digital photogrammetry (Petti et al., 2018); ii) describe the ichnological record, by using both traditional field standard ichnological methods and close-range photogrammetry to produce 3D models of better-preserved footprints (Antonelli et al. 2023). This work aims at defining the lithostratigraphy and biostratigraphy of the Calcare di Bari Fm. cropping out in the San Leonardo quarry and at performing a detailed facies analysis to clarify the depositional setting in which shallow-water carbonates formed. The carbonate succession cropping out in the San Leonardo quarry is about 9.5 m thick and can be split out in two distinct parts: i) the lower one (about 6 m thick) is dominated by coated bioclastic limestones showing a grain-supported fabric (packstones/grainstones); ii) the upper one (about 3.5 m thick) is mostly made up of biopeloidal limestones showing a mud-supported fabric (mudstones/wackestones). The track-bearing surface crops out at the top of the section. Microfossil assemblage is composed by the following index fossils: *Praechrysalidina infracretacica*, *Debarina hahounerensis*, *Pseudonummoloculina aurigerica*, *Pseudonummoloculina heimi*, *Vercorsella arenata*, *Vercorsella scarsellai*, *Cuneolina sliteri*, *Cuneolina pavonia*, *Nezzazatinella picardi*, and *Sabaudia minuta*. Based on this benthic foraminifer assemblage, the section is referred to the lower Albian.

Facies analysis showed that the lower part of the section consists of tabular cross-bedded packstones/grainstones made up of coated skeletal grains in association with intraclasts, benthic foraminifers, green algae, and peloids. The grain-supported textures and the presence of high-energy sedimentary structures permit to interpret the lower part of the section as deposited in shallow wave- or current-agitated open lagoonal environments where migrating shoals could form. The upper part of the section consists of strongly burrowed biopeloidal mudstones, and subordinately by microbial fenestral wackestones/bindstones, with benthic foraminifers, ostracodes, and peloids. Two distinct horizons of few m-thick intraformational breccias, showing a residual matrix, also occur in this part of the section. The muddy textures and the reduced biota are diagnostic criteria of low-energy peritidal environments subjected to ephemeral or prolonged subaerial exposure. The studied surface is placed at the top of a fenestral wackestone bed, suggesting that dinosaur footprints were produced on emerged peritidal limestones.

Antonelli M., Petti F.M., Conti J., Sacco E., Petruzzelli M., Spalluto L. & Wagensommer A. (2023) - Lower Cretaceous dinosaur footprints from the Molfetta tracksite (Apulia, southern Italy). *Cret. Res.*, 142. <https://doi.org/10.1016/j.cretres.2022.105388>.

Petti F.M., Petruzzelli M., Conti J., Spalluto L., Wagensommer A., Lamendola M., Francioso R., Montrone G., Sabato L., Tropeano M. (2018) - The use of aerial and close-range photogrammetry in the study of dinosaur tracksites: Lower Cretaceous (upper Aptian/lower Albian) Molfetta ichnosite (Apulia, southern Italy). *Palaeontologia Electronica*, 21 (3). <https://doi.org/10.26879/845>.

## **Modern fluvial sand composition and sediment production from the Crati River (Calabria, Italy): implications from provenance studies**

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*Keywords:* modern fluvial sands, sand generation indices.

Modern river sediments composition and texture reflect the provenance signals resulting from detrital contribution of each watershed and are therefore suitable to constrain erosion rates of several source rock lithotypes. The Crati River, is the longest and largest river of the Calabria region and is characterized by a narrow upper valley with high gradients, and an alluvial middle-lower valley with low gradients where it flows over Plio-Pleistocene deposits. The areal percentages of outcropping lithologies are predominantly sedimentary (67,74%) and metamorphic (26,07%), and minor plutonic (6,19%). The Crati River receives siliciclastic detritus inputs from tributaries draining multiple lithologies from the Sila Massif (granitoid and metamorphic), the Catena Costiera (metamorphic and minor plutonic) and the Pollino Massif (sedimentary). Petrographic composition of clastic detritus of the Crati River, and its main tributaries, provide an excellent tool for understanding what factors control sediment generation and transfer from the source region to sink areas. In order to compare the contribution of specific source rock types to the fluvial sand, several sub-basins were investigated and the contribution of the plutonic (granitoid), sedimentary and metamorphic source rocks was calculated according to the Sand Generation Index as first defined by Palomares and Arribas (1993), then modified by Vezzoli et al. (2004). Petrographic analyses of the modern sands sampled has been carried out through the polarizing microscope and morphometric analysis was made from a Digital Elevation Model using a Geographic Information System. Modal analysis of the modern fluvial sand shows that the Crati River main channel clastic detritus is litho-feldspatho-quartzose (mean value of  $Qm_{45,09}$ ,  $F_{32,55}$ ,  $Lt_{22,09}$  and  $Rg_{34,36}$ ,  $Rs_{4,45}$ ,  $Rm_{61,18}$ ), plagioclase dominant and rich in heavy minerals such as garnet and hornblende. The SGI indices, calculated for the Crati catchment area, indicate a SGI value of 5.5 for the Sila massif plutonites and of 2.4 for the Sila and Catena Costiera metamorphites, respectively. According to the SGI data, the Sila massif plutonites, which represent only 6.19% of the entire catchment, have the highest capacity of sand-sized bed-load production, owing to its granitoid lithotypes. It can also be observed that among the sub-basins of the Crati River considered, those draining the plutonites of the Sila Massif are those in which the erosive power is highest and therefore also those that provide a higher detrital input to the Crati River catchment area than other sub-basins draining the metamorphites of the Catena Costiera and the carbonate and siliciclastic units of the Pollino. This study thus shows that the composition of sandy sediments may be strongly influenced by the composition and texture of the source rocks and not by their greater areal spread in the drainage area.

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Vezzoli G., Garzanti E. & Monguzzi S. (1981) - Erosion in the Western Alps (Dora Baltea Basin): 1. Quantifying sediment provenance. In: Weltje, G.J., von Eynatten, H. (Eds.), *Quantitative Provenance Analysis of Sediments*. *Sedimentary Geology*, 171, 227-246.

## Diagenesis of carbonate density-flow deposits controlled by differential uplift of platform segments: examples from the Cretaceous of the Gargano Promontory (Italy)

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**Keywords:** isotope analysis, differential tectonic uplift, Apulia Carbonate Platform.

This study is based on thin-section investigation (polarized-light, cathodoluminescence and UV microscopy) combined with isotopic ( $\delta^{18}\text{O}$ ,  $\delta^{13}\text{C}$ ,  $^{87}\text{Sr}/^{86}\text{Sr}$ ) analyses of bulk carbonate samples to evaluate the diagenetic alteration of Albian-Cenomanian and Maastrichtian density-flow deposits off two segments of the Apulia Carbonate Platform in the Gargano Promontory. The data suggest a close relationship between differential platform uplift (Sælen et al., 2023), south and north of the Mattinata Fault (MF), and diagenesis of density-flow deposits during Albian-Cenomanian times. In both cases, the (i) abundant blocky cement and vuggy pores in clasts, and (ii) remnant blocky cement on allochems in the corresponding matrix samples with interparticle pores, indicate disintegration of early cemented deposits before failure into density flows. However, the  $\delta^{13}\text{C}$  compositions of the density-flow deposits south and north of the MF are different. Geochemical modelling, based on presumed marine and terrestrial  $\delta^{13}\text{C}$  compositions, indicates: (A) the  $\delta^{13}\text{C}$  values of deposits south of the MF suggest that the margin- and upper-slope deposits were subjected to predominantly marine-burial diagenesis before failure. Albian-Cenomanian Sr-isotope ages support this scenario where strontium was redistributed locally during calcitization of aragonitic allochems, and during precipitation of calcite cements. However, post-uplift precipitation of vadose cement in pores formed during marine-burial diagenesis has lowered the  $\delta^{13}\text{C}$  and increased the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio in many of the samples. (B) Twenty-five km north of the MF, the negative  $\delta^{13}\text{C}$  values suggest that oxidation of terrestrial plants supplied  $^{12}\text{C}$ -enriched  $\text{CO}_2$  to the pore-water carbon pool during subaerial exposure, thus lowering the  $\delta^{13}\text{C}$  compositions of the margin- and upper-slope deposits from values obtained during marine-burial diagenesis. This model requires that residual aragonitic and high-Mg calcitic allochems were available in the deposits during penetration of meteoric water. However, the Albian-Cenomanian Sr-isotope ages and the geochemical modelling support a predominantly marine-burial scenario, with intraformational redistribution of strontium during meteoric diagenesis. A similar diagenetic model is envisaged for the Maastrichtian density-flow deposits south of the MF, but the less negative  $\delta^{13}\text{C}$  and geochemical modelling suggest less influence of meteoric diagenesis before reworking. Most separate- and touching-vug pores likely formed during marine-burial prior to failure of the margin- and upper-slope deposits. The large range in porosity (4-31%) with predominantly interparticle pores are inferred to reflect varying degrees of compaction caused by variable overburden thickness as well as sedimentary processes. This study indicates that the geochemical imprint of meteoric diagenesis can be expected to vary in density-flows deposited along coeval segments of carbonate platforms in tectonically active regions.

Sælen G., Spalluto L., Grunnaleite I., Sande A.J.H., Jensen N.B., Svendsen P.O.E., Osso G., Paoli N. & Talbot M.R. (2023) - The impact of tectonic activity on carbonate density-flow deposition along two sectors of the Apulia Carbonate Platform. *Journal of Sedimentary Research*, 93(2), 88-117. <https://doi.org/10.2110/jsr.2021.031>.



**The Plio-Pleistocene Sant’Arcangelo Basin (southern Italy):  
a stratigraphic/sedimentologic review of the infill succession in its northern sector**

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*Keywords:* Pliocene-Pleistocene, Sant’Arcangelo Basin, stratigraphy.

Several different stratigraphic subdivisions have been adopted to describe the Plio-Pleistocene Sant’Arcangelo Basin infill (Basilicata, southern Italy), and often conflicting interpretations have been proposed both on the connections between surface and subsurface geology and on the structural setting (satellite vs piggyback vs wedge-top basin). The CARG Project was also unable to solve the correlation between lithostratigraphic data coming from different schools with various survey approaches (formation vs sequences vs synthems).

One of the most studied and debated areas of the Sant’Arcangelo Basin is the northwestern one, where some of the main tectonic structures crossing or bounding the basin and some regional unconformities cutting the infill successions can be detected. Our field data confirm the occurrence of some main discontinuity surfaces, in particular that one bounding the oldest infill unit (the Caliandro Unit) from the overlying one.

Depositional systems were coarse-grained in their western, proximal peripheries, whereas they pass basinward (eastward) to finer-grained lithofacies. This lithological partition records a complex of terrestrial depositional systems, including alluvial fans and fluvial braidplains, which passed seaward to deltas and to offshore environments. In particular, the observed deltas show continuous sub-horizontal succession of basinward-prograding, shelf-type sequences, indicating sediment dispersion in a shallow-marine receiving basin.

**Juxtapositions of load-and-flames, clastic diapirs and deformation bands  
as diagnostic tool for earthquake-induced liquefaction in mixed siliciclastic-carbonate  
successions of the Finale Ligure Basin (NW Italy)**

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*Keywords:* mixed siliciclastic-carbonate, Ligurian Alps, seismites.

The mixed siliciclastic-carbonate successions of the Finale Ligure Basin (NW Italy) features a terrigenous basal complex and a superimposing carbonate wedge. In wide parts, the siliciclastic and carbonate successions are characterized by heteropic sedimentation patterns. Moreover, individual sedimentary units are lithologically heterogeneous, as they display abrupt changes of lithofacies distributions and associated interpreted depositional environments. Essentially the interface between the terrigenous base and the carbonate wedge features a diverse suite of soft sediment deformation structures (SSDS).

In the course of this study we identified several deformed parts of stratigraphy, ranging from small size (cm- to dm-scale) load-and-flame structures, pseudonodules and ball-and-pillow structures, mini-slumpings to outsized (several meters in height) chaotic contorted and folded stratigraphic intervals, diapiric sand intrusions and tree-shaped water escape structures. Many of the SSDS are related to fast injection of overpressurized fluids after sand liquefaction. Arrays of deformation bands such as disaggregation and phyllosilicate dilational shear bands, carbonate filled veins and sandy dykelets accompany the cyclic repetition of these SSDS. In the case of the Finale Ligure basin the stratigraphic distribution and cyclic repetitions of SSDS-prone intervals indicate an earthquake-induced origin. We can also sustain that the contemporaneous presence of both dykes and disaggregation bands, moreover related to cyclicity and SSDS, serves as a reliable diagnostic tool for seismite identification in the field.

Since these particular SSDS reflect seismic activity in the area, they provide compelling evidence of previously unreported seismic activity in the Finale Ligure basin during the Miocene banding of the Ligurian area and the associated Corsica-Sardinia drift during the late stages of the opening of the Liguro-Provençal Basin.

**S32.**

**New advances in the tectono-stratigraphic evolution  
of the central and southern Apennines**

*CONVENERS AND CHAIRPERSONS*

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*Giovanni Luca Cardello (Università di Sassari)*

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*Domenico Cosentino (Università RomaTre)*

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## **Paleoenvironmental new constraints in upper Zanclean Benevento Valley deposits (Ariano Basin, southern Apennines)**

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**Keywords:** Southern Apennines, paleoecology, biostratigraphy.

In this paper, we provide a paleoenvironmental study of a wedge-top depozone succession of the Pliocene Foreland Basin System of the southern Apennines. In the Benevento area of Ariano Basin, upper Zanclean north-eastward alluvial progradational system (Ciarcia et al., 2006) and a gradual transition, from neritic to low-gradient nearshore facies, occur. In the pelitic facies, the sediments yielded mixed assemblages, including both very shallow (upper infralittoral) and open shelf (circalittoral) benthic foraminiferal and ostracod species. The paleoecological features of meiofaunal assemblages and the relationships between autochthonous ostracods and benthic foraminifera suggest a transgressive trend in a neritic platform environment, with paleobathymetric variations between infralittoral and circalittoral. Biostratigraphical analysis of these deposits highlights the presence of *Globorotalia puncticulata*, allowing it to be referred to the upper Zanclean (biozone MPI4a, MNN14–15/MNN16a partim, CN11b–CN12a partim; Ciarcia & Vitale, 2013).

Ciarcia S., Di Donato V., Mitrano T. & Torre M. (2006) - I depositi del bacino di Benevento (Pliocene inferiore, Appennino meridionale): nuovi vincoli stratigrafici e paleoambientali. *Bollettino della Società Geologica Italiana*, 125, 147-162.

Ciarcia S. & Vitale S. (2013) - Sedimentology, stratigraphy and tectonics of evolving wedge-top depozone: Ariano Basin, southern Apennines, Italy. *Sedimentary Geology*, 290, 27-46.

## **Miscano River: insights on sedimentation after the Messinian salinity crisis in the southern Apennines**

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*Keywords:* Southern Apennines, paleoecology, biostratigraphy.

We present a study of a Mio-Pliocene marine to continental clastic sedimentary succession belonging to the Foreland Basin System of the southern Apennines, well exposed in the Miscano River in the Irpinia sector. These well-bedded wedge-top basin deposits host a significant angular unconformity between a post-evaporitic succession (uppermost Messinian-lowermost Pliocene; Altavilla Group, Vitale & Ciarcia, 2018 cum bibl.), developed on top of the evaporite deposits related to the Messinian Salinity Crisis, and an overlying upper part of the upper Zanclean sediments. The unconformity witnesses a major orogenic stage of the southern Apennines characterized by out-of-sequence thrusting that involved the Mio-Pliocene wedge-top basin deposits. Meio-microfaunal and nannofloral fossil assemblages were analyzed to define the depositional environments and biostratigraphy of the two successions. In addition, benthic foraminiferal and ostracod assemblages were studied in detail, and their autochthonous/allochthonous provenience was discussed from a paleoecological point of view. The relative response of these assemblages to environmental parameters, such as salinity and paleobathymetry, allowed us to reconstruct the paleoenvironmental evolution of these wedge-top basin deposits.

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## **Lithiotid-coral deposits in the Lower Jurassic of the Apennine Carbonate Platform (Campania, southern Italy): new evidence from geological mapping**

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Keywords: geological mapping, stratigraphy, syn-sedimentary fault.

During the geological mapping of Sheet 430 Caserta Ovest of the Geological Map of Italy at the scale 1:50.000 (CARG Project), an outcrop was discovered that contains a peculiar association of lithiotid bivalves and corals. The area of interest is located in the Apennine Carbonate Platform, which consists of shallow-water carbonates that were deposited from the Late Triassic to the Late Cretaceous at the southern margin of the Tethys Ocean. The current setting is the result of a complex tectonic evolution involving compression phases (Miocene-Pliocene) and extensional and strike-slip phases (upper Pliocene-Pleistocene).

The studied outcrop is located near Leporano (CE) and belongs to the Calcarei a *Paleodasycladus* Fm. (Hettangian p.p. – Toarcian p.p. in Petti, 2007). It extends horizontally for ca. 30 meters and is characterized by limestone beds overlain by channelized marly limestones, containing the lithiotid-coral association. Overall, a shallowing-upward sequence is observed, ending with supratidal facies. The lithiotid shells in the channelized facies display an imbricated fabric. One of the channels sutures a syn-sedimentary fault, characterized by strata thickening near the fault. A pre-early Toarcian age can be inferred for the fault, based on the age of the upper part of the Calcarei a *Paleodasycladus* Fm., characterized by the high abundance of lithiotids (Posenato et al., 2018).

The co-occurrence of colonial corals and lithiotid bivalves has never been reported so far in the Apennine Carbonate Platform and in the classical localities of the Trento Platform (Broglia Loriga & Neri, 1976). Corals and lithiotids were considered to have different ecological requirements, with lithiotids favoring nutrient-rich turbid waters and corals favoring the blue waters of oligotrophic shallow-seas. However, recent studies have described lithiotid-coral reefal deposits from the Central High Atlas of Morocco (Brame et al., 2019). This work aims to contribute new data on the under investigated theme of these peculiar lithiotid -coral associations.

Brame H.R., Martindale R.C., Ettinger N.P., Debeljak I., Vasseur R., Lathuilière B., Kabiri L. & Bodin S. (2019) - Stratigraphic distribution and paleoecological significance of Early Jurassic (Pliensbachian-Toarcian) lithiotid-coral reefal deposits from the Central High Atlas of Morocco. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 514, 813-837. <https://doi.org/10.1016/j.palaeo.2018.09.001>.

Broglia Loriga C. & Neri C. (1976) - Aspetti paleobiologici e paleogeografici della facies a "Lithiotis" (Giurese inf). *Riv. Ital. Paleont. Strat.*, 82(4), 651-706.

Petti F.M. (2007) – Calcarei a *Paleodasycladus*. In Cita M.B., Abbate E., Balini M., Conti M.A., Falorni P., Germani D., Groppelli G., Manetti P., Petti F.M. (eds): *Carta Geologica d'Italia 1:50:000. Catalogo delle formazioni – Unità tradizionali (2) Fascicolo VII. Quaderni del Servizio Geologico d'Italia, Serie III, 7(7), 237-246.*

Posenato R., Bassi D., Trecalli A. & Parente M. (2018) - Taphonomy and evolution of Lower Jurassic lithiotid bivalve accumulation in the Apennine Carbonate Platform (southern Italy). *Palaeogeography, Palaeoclimatology, Palaeoecology*, 489, 261-271. <https://doi.org/10.1016/j.palaeo.2017.10.017>.



## **Plio-Pleistocene stratigraphic and tectonic evolution of a segment of the Sicilian Fold and Thrust Belt outcropping in the Sciacca area (south-western Sicily).**

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Maiorana M.G.<sup>1</sup>, Todaro S.<sup>1</sup>, Petrella F.<sup>1</sup>, Incarbona A.<sup>1</sup>, Agate M.<sup>1</sup>, Muraro C.<sup>2</sup> & Sulli A.<sup>1</sup>

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*Keywords:* synsedimentary tectonics, Gela Thrust System, CARG project.

During the analyses carried out within the CARG Project (Sheet 628 “Sciacca” - Geological Map of Italy) some relevant sedimentological, stratigraphic, biostratigraphic and tectonic features of the outcropping units were highlighted, with particular reference to the Pliocene and Quaternary evolution of this sector.

The study area, belonging to the Sicilian foreland-basin-system, corresponds to the outer sector of the Sicilian Fold and Thrust Belt (FTB) and the westernmost portion of the Gela Thrust System (GTS) (Catalano et al., 2013; Ghisetti et al., 2009). This part of the FTB is constituted by Meso-Cenozoic (Saccense and Sicilian Domains) south-verging tectonic units, unconformably covered by middle Miocene to Pleistocene deposits. The GTS in this sector is formed by late Miocene-lower Pleistocene deformed syntectonic successions. Both the FTB and GTS are covered by Plio-Pleistocene deposits that highlight continuous syndepositional tectonics of the Sicilian FTB evolution.

These Plio-Pleistocene successions are formed by:

- Trubi Fm. (TRB): alternations of white marly limestone, marls and sandy-marls, rich in planktonic fauna, evolving upward to grey-greenish silty-clay with resedimented calcarenites and thick bodies of breccias. These deposits, Zanclean-lower Piacenzian in age, outcrops in different sector of the study area and appear strongly deformed;
- Marnoso-Arenacea del Belice Fm. (BLC): hemipelagic clayey-marls and turbiditic sandy-silts and breccias, evolving to sands and resedimented calcarenites upward. This succession dated to the middle Piacenzian-Gelasian interval, represents different wedge-top basins, pointing out late Piacenzian-Calabrian compressional tectonic pulses;
- M.te Narbone Fm. (NAB): light grey marls and silty clays alternating with brownish clayey-marly levels (sapropel layers), with abundant planktonic and benthic fauna; dark gray levels with resedimented quartz, gypsum and reworked planktonic foraminifera are present in the middle and upper part of this succession. This succession deposited during the middle Piacenzian – early Calabrian (Santernian) age, well preserves sedimentary features of the wedge-top basins located in the GTS.
- Agrigento Fm. (AGG): slightly quartz yellow bio-calcarenites and sands, often with cross lamination and prograding geometry, alternating with bio-calcirudites, pelites and sandy marls. This formation, deposited during the lower and middle part of the Calabrian stage (Santernian - Emilian) in a coastal-inner shelf environment, unconformably covering different terms of the succession.

In conclusion, the sedimentological, stratigraphic and structural analyses, supported by the biostratigraphic constrain, makes it possible to decipher and well date the different tectonic events occurred during the Plio-Pleistocene and reveal that forward migration and inner deformation of GTS was largely coeval of the faulting and folding affecting the deformed foreland of Sciacca area.

Catalano R., Valenti V., Albanese C., Accaino F., Sulli A., Tinivella U., Gasparo Morticelli M., Zanolla C. & Giustiniani M. (2013) - Sicily's fold/thrust belt and slab rollback: The SI.RI.PRO. seismic crustal transect. *J. Geol. Soc. Lond.*, 170, 451-464.

Ghisetti F.C., Gorman A.R., Grasso M. & Vezzani L. (2009) - Imprint of foreland structure on the deformation of a thrust sheet: The Plio-Pleistocene Gela Nappe (southern Sicily, Italy). *Tectonics*, 28 (4).

## The reusing of the CROP11 seismic data: new insight on the stratigraphic and structural setting of the Fucino and Piani Palentini basins

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*Keywords:* refraction/reflection seismic, Central Apennines, Fucino Basin.

The long-offset seismic refraction/reflection data from CROP11-1999, which was harvested for deep seismic exploration, when reprocessed and integrated with other seismic reflection data, may give new insights into the main geological structures of the central Apennines.

The Piani Palentini and Fucino basins are crossed by a sub-transect of the CROP11 seismic profile, which we interpreted from a geophysical-geological perspective. An integrated approach based on the stacked refraction convolution section and refraction tomography was used to carry out a new geophysical interpretation. The reprocessing allowed us to obtain a high resolution (about 15 m in distance and depth) P-waves seismic velocity 2D model and to image the refractor interface of the basin down to the depth of the Meso-Cenozoic carbonate substratum. The refraction outcomes, combined with the interpretation of the CROP11 seismic reflection profile and of other commercial seismic reflection profiles available in the studied area, allowed us to highlight a complex basin-fill architecture and stratigraphy. On the basis of the reconstructed tomography model and the reflection analysis, and of a comparison with previous reconstruction and stratigraphic studies on the Fucino basin reported in literature (Cavinato et al., 2002; Patacca et al., 2008; Patruno & Scisciani, 2021), we propose four seismo-facies separated by several unconformities and characterized by different  $V_p$  velocity values. In particular, above a high velocity, high amplitude sequence, directly over the Meso-Cenozoic carbonate substratum, we identified two intra-Messinian unconformities. These unconformities delimit a low velocity sequence, likely composed by fine/medium-grained deposits (clays and silts), and an overlaid high-velocity sequence related to the presence of coarser deposits. Above these deposits, the reflectors are more regular and show a fan geometry against the well known San Benedetto-Serrone-Gioia dei Marsi normal fault. This latter sequence represents the Plio-Pleistocene post orogenic basin-fill deposit, controlled by the normal fault activity.

The obtained model constitutes a geophysical-geological informative base for future research on seismic wave propagation and site response studies at the large scale of the Fucino Basin, one of the regions of the Italian territory with a high seismic hazard.

Cavinato G.P., Carusi C., Dall'Asta M., Miccadei E. & Piacentini T. (2002) - Sedimentary and tectonic evolution of Plio-Pleistocene alluvial and lacustrine deposits of Fucino Basin (central Italy). *Sediment. Geol.*, 148, 29-59.

Patacca E., Scandone P., Di Luzio E., Cavinato G.P. & Parotto M. (2008) - Structural architecture of the central Apennines: Interpretation of the CROP11 seismic profile from the Adriatic coast to the orographic divide. *Tectonics*, 27. <https://doi.org/10.1029/2005TC001917>.

Patruno S. & Scisciani V. (2021) - Testing normal fault growth models by seismic stratigraphic architecture: The case of the Pliocene-Quaternary Fucino Basin (Central Apennines, Italy). *Basin Res.*, 33, 2118-2156. <https://doi.org/10.1111/bre.12551>.

## **Modes and geometry of drowning steps of an Upper Cretaceous-Paleogene carbonate platform**

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*Keywords:* platform drowning, Cretaceous-Paleogene, Central Apennines.

This paper is focused on the modes and geometry of the drowning phases of an Upper Cretaceous-Paleogene carbonate platform recognized in the north-west sector of the Latium-Abruzzi platform (Central Italy).

In the northern-central Apennines, the modes and geometries of carbonate platform drowning during the Lower Jurassic, with formation of basins and pelagic carbonate platforms are well known and studied for a long time. Carbonate platform drownings have also been recognized in other time intervals, such as in the Middle Jurassic or Cretaceous/Paleogene, but despite being younger, the driver-mechanisms of these drownings and their resulting geometries have not been yet fully elucidated.

The basal part of the Upper Cretaceous north-west sector of the Apennines carbonate platforms recorded a platform emergence before the drowning phase, followed by paraconcordant basinal sedimentation. This scenario is quite similar to that recorded during the Miocene transgression following the Paleogene gap.

Such an effect may be caused as a consequence of the formation of a very large-radius orogenic wave without evident brittle ruptures.

Since Coniacian-Santonian age and especially during the upper Paleocene, the definitive platform drowning is more markedly tectonic as it causes faulting and formation of tilted block-like geometries or relay-ramps. In contrast to the Jurassic drownings, there are no clear evidence of paleoescarpment formation except in the uppermost portions of the blocks at the hangingwall, sutured by the basinal Scaglia sediments (e.g. Scaglia Cinerea Fm.). Faults formed during drowning phase have often been preserved and locally strongly tilted by subsequent tectonics, especially Neogene compressional tectonics.

Drowning affected only the most marginal areas of the platform, so it must be assumed that the central part of the platform will continue to buckle and to emerge as direct consequence of a probable decrease of the curvature radius of the orogenic wave as the forming chain approaching. These movements, buckling and tectonic phases are related to the dynamics of South Atlantic Ocean opening and simultaneous closure of the Ligurian-Piedmont Ocean during the early stages of the Alpine orogeny.

By the onset of the Apennine orogeny, the drowned platform system is once again found to be buckled with a large curvature radius of the orogenic wave. Vertical movements without apparent faulting are still recognizable during the Oligocene and Early-Middle Miocene, evidenced by the different evolution of the carbonate ramp system existing in this time interval. In the Late Miocene, a new tectonic phase with important extensional faulting occurs with a new pronounced buckling on the edge of the peripheral bulge in front of the foredeep.

## Stratigraphy and structure of the Chaotic complex of the Volsci Range (central Apennines)

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*Keywords:* mélange, thrust sheets, inherited structures.

The Apennines are a fold-and-thrust belt also involving chaotic terrains, whose interpretation is crucial to decipher their forming processes and the regional tectonics. The structure of these terrains is often referred as a mélange, whose origin may be the result of the superposition of tectonic, sedimentary, and mud-diapiric processes, to which also the gravitative processes contribute incorporating both allochthonous exotic and autochthonous native blocks. Despite the subsequent tectonic overprint, occurring within highly-deformed units for example i.e. far-travelled thrust-sheets, their original succession and eventually structural heritage may be envisaged.

In this communication, we report on the stratigraphic and structural characteristics of the Chaotic complex of the northern Volsci Range, one of the less studied areas of the Apennines.

Atop the Meso-Cenozoic carbonate units, the Chaotic complex occurs as a mélange containing both native and exotic blocks, the latter being Cretaceous to Miocene basinal to distal ramp deposits. The deformed platform-derived native blocks involved within the Chaotic complex are stratigraphically comparable with the encrusted carbonates that are preserved at the articulated top of the Lower Volsci Unit, which was inherited by previous Tethyan passive margin tectonics.

Overall, the mélange blocks are wrapped within a sandy-clayey matrix that is alternated with shales, foliated brownish marl, greenish arenaceous beds with exotic lithic, and coarse-grained micro-conglomerate with carbonatic and crystalline elements. The matrix includes Paleocene-Eocene, Oligocene-early Miocene, middle Miocene, and also late Tortonian-Messinian (?) nannofossil assemblages.

In our interpretation, during Tortonian time, at the transition from ramp to flat, native blocks were scraped off from the Lower Volsci by the activity of thrust-sheets, whose erosive witnesses can be observed in the mountain backbone klippe, such as the Caccume mount. Consequentially, the pelagic deposits were squeezed off and juxtaposed as mélange units on top of the carbonate platform and within the Latina Valley.

To explain the abrupt thickening of the Chaotic complex east of the Caccume mount, we suggest that a growth structure was forming during the initial uplift of the Volsci Range front as testified by fault-propagation fold at the hanging wall of thicker Frosinone Formation (FFS). Following this interpretation, this process generated the glide of the Chaotic complex on top of the FFS units. Similar contexts were reconstructed for other mélange units at thrust fronts, where the remobilization of the formerly emplaced thrust sheets, allows the incorporation of the extrabasinal (exotic) lithologies within the foredeep. An alternative possible explanation to allow the juxtaposition of the Upper Volsci unit onto the FFS units, would envisage thrusting to occur during the uppermost Tortonian-earliest Messinian.

## Relations between structural-staking and clay minerals features across the regional decollement of the southern Apennines exposed at the Monte Alpi area of southern Italy

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*Keywords:* regional decollement, Southern Apennines, clay minerals.

The work aims at studying the main tectonic units across the high-strain decollement of the southern Apennines fold-and-thrust belt exposed at the Monte Alpi area. The analysis is conducted on both accretionary wedge terranes and terrigenous, Upper Messinian sedimentary rocks topping the Apulian carbonates (La Bruna et al., 2017). Detailed mesoscale and microscale structural investigations are performed along key outcrops and representative samples of the decollement. Laboratory mineralogical analysis was conducted by means of X-ray diffraction on clayish powder samples. The results confirm that the two investigated rock units were characterized by dissimilar tectonic evolutions until Lower Pliocene, when tectonic overthrusting took place. In particular, the accretionary wedge terranes derive from the Lagonegro succession, specifically from the Late Triassic-Jurassic Zia Santa Fm. (Cavalcante et al., 2023). These terranes are stacked into tectonic slices characterized by s-c and s-c-c' fabrics, which overthrust the tectonic melange and the Messinian sedimentary rocks. The mixed layers illite/smectite (I/S) are generally characterized by R3 long-range ordering with higher illite content (85-95%), thus pointing out to high diagenetic conditions (130-140°C) in accordance with a Kubler index of 0,6-0,7° 2 $\theta$  determined in the samples with higher illite discrete percentage. The estimate thermal maturity is in good agreement with fluid inclusions and vitrinite reflectance literature data (Corrado et al., 2005). Samples from the tectonic melange show a mineralogical assemblage comparable with the samples taken from the other structural levels. I/S R1, with 75-85% of illite, indicates a thermal maturity of the 120 - 130°C, in accordance with literature data (Corrado, 2005). The samples collected from shear zone show a long-range ordering I/S R3 with higher illite percentage (85-95), in accordance with the s-c-c' fabric. The samples of the lowest structural levels show I/S R1 order with 70-85% of illite percentage. In particular, the samples collected below the shear zone display 80-85 % of illite in I/S and s-c structure. The 70 - 75% range of illite in I/S is observed in samples collected away from the regional decollement. Also, note that the samples, collected from shear zone present amount of kaolinite very low (< 3%) contrary to what is observed for the other samples of the Messinian, where it is present in appreciable amounts (15-20%). The data show a good relationships between I/S features, strain amount and structural stacking. In particular, the higher strain and the thermal maturity recorded by uppermost Zia Santa Fm. is in agreement with the results commonly reported for accretionary wedges (Sciamanna et al., 2004). The higher strain, the illite percentage in I/S and the absence of kaolinite along shear zone of the Messinian sediment suggest a close-rock dominant system with probable overpressures that would have facilitated the decollement development.

Cavalcante F., Perri F., Belviso C., Lettino A., Prosser G., La Bruna V. & Agosta F. (2023) - Clayey sediments analysis as a useful tool to assessing the geodynamic evolution of fold-and-thrust belts: The case study of the Monte Alpi area (southern Apennines, Italy). *Marine and Petroleum Geology*, 151, 106204. <https://doi.org/10.1016/j.marpetgeo.2023.106204>.

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## The open question of the “Argille Varicolori” *Auctorum*: inferences on the geodynamic evolution of the southern Apennines

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Keywords: paleodomains, tectonic units, Southern Apennines.

In recent decades, the knowledge of southern Apennines geology had a significant impulse (e.g., Patacca & Scandone, 2007; Vitale & Ciarcia, 2013). Although a more accurate tectono-stratigraphic reconstruction has been carried out and a more detailed geodynamic evolution has been determined, many open questions remain still debated. Among these, many issues concern the origin, age and paleodomain attribution of the varicoloured clays known as *Argille Varicolori Auct.* (AV). In the central-western peri-Mediterranean orogenic chains, several pelagic successions include the AV. In the central and southern Apennines, the AV is part of the oceanic successions of the Ligurian Accretionary Complex (Parasicilide and Sicilide units) and it is included in several successions of the Lagonegro-Molise Basin. However, the similar lithostratigraphic features and the lacking of biostratigraphic, minero-petrographic and geochemical data caused a large uncertainty in their attribution to a specific tectonic unit (Cavalcante et al., 2003). In this work, we attempt to shed light on the correct stratigraphic attribution by sedimentological, meso- and microstructural analyses and minero-petrographic and geochemical characterizations.

Cavalcante F., Fiore S., Piccarreta G. & Tateo F. (2003) - Geochemical and mineralogical approaches to assessing provenance and deposition of shales: a case study. *Clay Minerals*, 38, 383-397.  
Patacca E. & Scandone P. (2007) - Geology of Southern Apennines, in: Mazzotti A., Patacca E., Scandone P. (eds.), Results of the CROP Project, Sub-project CROP - 04. *Bollettino Società Geologica Italiana, Special Issue 7*, 75-119.  
Vitale S. & Ciarcia S. (2013) - Tectono-stratigraphic and kinematic evolution of the southern Apennines/Calabria-Peloritani Terrane system (Italy). *Tectonophysics*, 583, 164-182.



## Field geology and cartography of the Muro Lucano, Bella and Castelgrande areas (Basilicata): revised stratigraphy, sedimentology and tectonics of the NW Lucanian-Apennines

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*Keywords:* Southern Apennines, geological survey, cartography.

New information on the stratigraphy and structural setting obtained during geological mapping of the 1:50.000 sheet n.469 Muro Lucano (CARG Project), in the NW sector of Basilicata (Southern Italy), are helpful to better understand the Mesozoic-Cenozoic stratigraphy and the Miocene-Pleistocene evolution of the Southern Apennines thrust and fold belt. New data have been obtained by means of a geological survey at a 1:10.000 scale recently undertaken in the area of the Bella, Castelgrande and Muro Lucano villages. Accordingly, a new detailed stratigraphic, sedimentological, and structural framework of the area is provided. Taking into account bio- and lithofacies analysis, the following tectono-stratigraphic units were recognised: (1) The Lagonegro Basin characterised by both the Rhaetian-Jurassic Scisti Silicei Formation (Patacca & Scandone, 2007) mostly consisting of jaspers with over than 1 m-thick silicified calcirudite beds in the lower portion, and the Neocomian-Aptian p.p. Galestri Formation (Patacca & Scandone, 2007) consisting of an alternation between marlstones and laminated calcarenites to calcilutites; (2) the Apenninic Carbonate Platform, made up of Hettangian-Toarcian fine-grained limestones with small thick-shelled pelecypods and *Palaeodasycladus mediterraneus*, Toarcian-Middle/Upper Jurassic oolitic limestones, Jurassic-to-Cretaceous alternation between fine-grained limestones and dolomitized limestones with fenestrae and calcilutites to calcirudites showing channel-shaped surfaces, and Cretaceous limestones with corals, rudists and gastropods; (3) sediments of the Castelvetere Formation (Pescatore, 1969), Serravallian-Tortonian in age (Patacca & Scandone, 2007 and reference therein), made up of coarse-grained sandstone to gravel, referred to settings ranging from channel to channel-lobe-transition zone, with intercalations at different stratigraphic levels of levee alternations from pelitic-arenaceous to arenaceous-pelitic, olistholits of the Apenninic Platform, and up to Km<sup>3</sup> olistostromes with matrix of deformed gray and red clays which can include olistholits; (4) deposits of the Pliocene Intrappenninic Basins (e.g., Servizio Geologico d'Italia, 2013), made up of deltaic pelitic-sandy, sandy and gravelly-sandy lithofacies with centimetric bivalves and ichnofacies. Improved stratigraphy and detailed field work has allowed mapping of a significant number of thrusts and high-angle faults. Moreover, structural measurements were carried out on significant fault planes, which were described in terms of orientation and kinematics. In the study area, syn-orogenic contractional deformation and post-orogenic extension are well testified respectively by (1) Cenozoic East-directed thrust/reverse faults and (2) Plio-Quaternary normal fault sets with E-W, NW-NE and NE-SW orientations.

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## The geological map of the Campania Region (southern Apennines) at 1:250,000 scale

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Keywords: Southern Apennines, stratigraphy, tectonics.

The Campania Region includes a large segment of the southern Apennines. Here, the orogenic chain is defined by the tectonic superposition of several thrust sheets made up of Meso-Cenozoic deep basin to shallow-water successions grouped in three main tectonic complexes: (i) Ligurian Accretionary Complex, (ii) Apennine Platform units and (iii) Lagonegro-Molise Basin units. The tectonic pile is unconformably covered by Mio-Pliocene wedge-top basin deposits and Quaternary post-orogenic sediments and volcanics (Vitale & Ciarcia, 2013; 2018; 2022). The complex tectonic architecture is characterized by in-sequence flat thrust faults bounding the main thrust sheets and by out-of-sequence ramp-dominated structures that crosscut the allochthonous units, including the wedge-top basin deposits. The chain is further crosscut by low and high-angle normal to transtensive faults formed during the out-of-sequence thrusting and the post-orogenic extension. Associated with the Pleistocene extension, several intramontane and coastal plains formed, and volcanism occurred on the Campania Plain (Vesuvius and Campi Flegrei volcanoes), Volturno River Plain (Roccamonfina volcano) and Gulf of Naples (Ischia and Procida islands).

We present a new version of the geological map of the Campania region, at 1:250,000 scale, with enclosed three geological cross-sections that illustrate the tectonic architecture of the chain and Campania Plain, a stratigraphic scheme and a sketch of the main kinematic complexes and wedge-top basin deposits.

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## **Surface and subsurface geological features at the boundary between the Bradanic Trough and Murge: a comparison with the Apulia Swell – Taranto Trench transition (Southern Italy)**

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*Keywords:* Apulia Foreland-Bradanic Trough transition, seismic profiles.

In southern Italy, the Apulia Foreland and the Bradanic Trough represents, respectively, the foreland and the foredeep of the southern Apennines orogenic system. The Apulia Foreland consists mainly of Cretaceous carbonates of the Mesozoic Apulia Carbonate Platform; these same rocks, faulted and downwards displaced toward the WSW respect to the foreland and covered by a Plio-Pleistocene sedimentary wedge, correspond to the bedrock of the foredeep. One of the most uplifted sector of the Apulia Foreland corresponds to the Murge, whose western margin is characterised by an important scarp, at the base of which the Plio-Pleistocene sediments of the Bradanic Trough extends. Close to the Murge, at the transition between the foreland and foredeep, in a few localities, the bedrock of the Bradanic Trough is exposed and this offers the possibility to verify in the field some of the features expected in the subsurface. One of these localities is the Gravina in Puglia town and surroundings where the only seismic profiles passing through the area are CD-3-84 from the ViDEPI project (2015) and two other lines provided by Eni S.p.A. The present work provides a first detailed interpretation of these seismic profiles (Cicala, 2023), with a first comparison between the here suggested geological interpretation and that one proposed by Cicala et al. (2021) in a comparable structural setting across the Apulia Swell.

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ViDEPI Project (2015) - <https://www.videpi.com>

## The Numidian sandstones of the southern Apennines: age and provenance analysis from the Molise domain

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**Keywords:** Numidian Sandstones, calcareous nannofossils biostratigraphy, U-Pb detrital zircon ages.

The Numidian sand event is one of the most widespread foreland-sourced sedimentary events in the orogenic systems of the Peri-Mediterranean Chain.

In this work, we analyze the Numidian Sandstones of the Guardiabruna section, which belongs to the Tufillo-Serra Palazzo Unit of the Molise Apennines (Trigno Valley, CH). The performed analyses allow us to define the stratigraphy, the depositional age, and the provenance of the super-mature quartz-arenites that reached the Molise domain of the southern Apennines. In the Guardiabruna section, the Numidian Sandstones are interbedded within medium to fine-grained bioclastic calcarenites and marls of the Tufillo Fm. Then, the super-mature detrital quartz arrived in a foreland basin setting, quite before the development of the foredeep domain (Agnone Flysch, early Messinian).

The quantitative analyses on the calcareous nannofossils allow us to refer the Guardiabruna stratigraphic section to the late Burdigalian-early Langhian. The provided deposition age for the Numidian Sandstones in the Molise Domain is quite similar to that in Sicily (upper Burdigalian), and it is slightly younger than that of the Maghreb Chain (lower Burdigalian).

The U-Pb detrital zircon ages from two quartz-arenites yielded 527 concordant zircon ages. They show age populations younger than the Precambrian, centered around 17, 200, 350, and 400 Ma, as well as large Precambrian age populations, centered between 500 and 700 Ma, and other populations at ~1000, 1700, and 2200 Ma. All zircons from the analyzed samples show oscillatory to sector growth zoning in CL images, which is typical of igneous zircons, suggesting a significant contribution from Neo-Proterozoic granitic rocks extensively present in the Western–Eastern African Craton.

Except for the U-Pb detrital zircon ages younger than Precambrian, the U-Pb detrital zircon ages from the Numidian Sandstones of the Molise Domain (Guardiabruna section) are analogous to the ages from the Numidian Sandstones in the Betics, Rif-Tell Chain, and Sicily. These data confirm an African provenance for the Numidian Sandstones of the southern Apennines. However, while the Numidian Sandstones of the Betics and the Maghreb Chain are sourced from the western African Craton and Hoggar, the Numidian Sandstones of southern Apennines and Sicily need detrital grains coming from areas of the northern African margin, containing both Precambrian igneous rocks (Saharan Metacraton and Nubian Craton) and Paleozoic and Meso-Cenozoic igneous rocks (e.g., Libya and Egypt).

Since the early Burdigalian supply of ultra-mature quartz grain deposits in the foreland domain of the Maghreb orogenic system have been related to the uplift of the Atlas intra-continental orogen, we suggest that differences in the depositional ages and U-Pb detrital zircon ages of the Numidian Sandstones could be explained by a west-to-east shifting of the Atlas uplift, due to an oblique collision between African and European plates.

## Mesozoic depositional architecture of the Mt. Sibilla-Mt. Priora area (Sibillini Mts) and its control on the orogenic and post-orogenic deformations

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**Keywords:** Jurassic inheritances, synsedimentary tectonics, orogenic deformation.

The combination of detailed field mapping, litho-biostratigraphic, sedimentological and structural analysis of carbonate rift basins has enormous potential to produce innovation on long-standing (paleo)tectonic issues. Fieldwork performed in the Mt. Sibilla-Mt. Priora area (Sibillini Mts., Marche) has allowed to identify the role played by the syn-sedimentary tectonics on the Mesozoic-Cenozoic depositional architecture, and to reconstruct the control exerted by the stratigraphic and paleotectonic inheritances on orogenic deformations. A Jurassic rift-related pelagic carbonate platform (PCP; Santantonio, 1994) characterizes the study area, displaying a plethora of peculiarities in both PCP-top and basin margin successions. Drowning unconformities occur between the pre-rift Calcare Massiccio and the overlying Jurassic *p.p.* drowning/condensed succession, accompanied by tilting of the fault blocks. Clinoforms of Calcare Massiccio representing the progradation of the shallow water carbonate platform into a young hanging wall basin occur along the horst-block margins. Three paleoescarpments bounding the PCP are spectacularly exposed in the high Tenna River valley, draped by epi-escarpment condensed deposits and overlapped by Sinemurian-Tithonian cherty pelagites. A km-scale scalloped morphology resulting from the backstepping of a steep fault scarp was mapped along the eastern escarpment of the PCP. The products of this dismantling are preserved in the basin-margin onlap succession, where Calcare Massiccio megablocks are embedded in basinal pelagites.

Evidence of Bajocian (?tectonically-triggered) gravitational instability is represented by mass-transport deposits embedded in the PCP-top condensed succession.

The Jurassic PCP-basin system and the overlying Cretaceous-to-Miocene pelagic deposits were deformed and displaced by the regional Sibillini Mts. Thrust. Rheological heterogeneities associated with the rift-related complex stratigraphic architecture steered the development of i) a box-shaped hanging wall anticline, reflecting the attitude of bedding of the PCP and its onlapping and overlying pelagic deposits, ii) tight and disharmonic folds (diffuse deformation) within pelagites onlapping the olistoliths, and iii) localized shear planes and cataclasites within the olistoliths, which acted as rigid rheological barriers promoting buttressing processes and steering strain localization.

Meso- and micro-structural analysis of the deformation zones, coupled with *in-situ* permeability, has allowed to identify the principal slip surfaces and associated S-C structures as efficient hydraulic barriers to sub-vertical fluid flows. The studied deformation zone can represent an outcrop analogous of present-day buried structures at hypocentral depth of extensional earthquakes. Hence, similar (paleo)tectonic and structural features at depth can play a key role for the fluid-assisted active extensional seismicity in the Central Apennines (Curzi et al., 2023).

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## **Reconstruction of the non-volcanic CO<sub>2</sub> migration pathway in the thermal springs of Contursi and Oliveto Citra sector (southern Apennines, Italy) through multidisciplinary investigations**

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*Keywords:* Southern Apennines, geophysical surveys, faults.

In this study, we analysed the area of Contursi and Oliveto Citra in the Sele River Valley (Vitale & Ciarcia, 2018; Vitale et al., 2020), where several CO<sub>2</sub> gas emissions occur. The area is characterized by the exposition of an oceanic succession (Parasicilide unit; Ciarcia et al., 2009) mainly formed by clays, pelagic limestones, marls and sandstones. Several vents are aligned along major faults, including the thermal springs of Contursi and Oliveto Citra. We performed different surveys, applying a multidisciplinary approach, including innovative methodologies, aiming to reconstruct the geometry of the shallow degassing pathways and investigate how the different geological and tectonic architecture influences the CO<sub>2</sub> seeping and surficial degassing processes. Electrical Resistivity (ERT) and Induced Polarization (IP) tomographies, combined with Self-Potential (SP), Magnetic (Mag), and pH mapping, have been performed in correspondence with the most degassing part of the study area. Results allowed us to construct different geophysical maps and geological cross-sections of the investigated area and develop a model of the degassing vents area, highlighting the role of reconstructed lithological and structural architecture in the shallow leaking processes.

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## **Geology of the Irpinia sector of southern Apennines: new data for the analysis of the tectono-stratigraphic evolution**

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*Keywords:* geology, tectono-stratigraphic evolution, Irpinia.

The Irpinia area, located between Sele and Ofanto river valleys, represents a key sector for analyzing the paleogeographic conditions and the tectono-stratigraphic evolution of the southern Apennine thrust belt. The geology of this area is described with new stratigraphic, petrographic and structural data. Subsurface geological data have been collected during the studies for the excavation works of the Pavoncelli bis hydraulic tunnel, developing between Caposele and Conza della Campania in an area that was highly damaged during 1980 Irpinia earthquake. Our approach includes geological, stratigraphic, structural studies, and petrological analyses of rock samples collected along the tunnel profile and in outcropping stratigraphic sections. Stratigraphic studies and detailed geological and structural mapping were carried out in about 200 km<sup>2</sup> wide area. The main outcropping units have been studied and correlated in order to document the effects of tectonic changes during the orogenic evolution of the foreland basin systems and related sandstone detrital modes variations. In particular, the presence of quartzolithic arenaceous successions with volcanoclastic composition, related to the Early Miocene arenaceous successions of the Corleto/Albanella Sandstone Formations, and quartz-feldspathic arenaceous successions, related to the late Miocene Castelvetere Formation, have been documented in an exhaustive way both in the outcrops and in the tunnel underground sectors. The multi-disciplinary and updated datasets have allowed getting new insights on the tectono-stratigraphic evolution and stratigraphic architecture of the southern Apennines foreland basin system and on timing of kinematic evolution of the Apennines tectonic units. They also allowed to better understand the relationships between internal and external basin units within the Apennine thrust belt and its tectonic evolution.

## **The nature of faults developed across a layered, pre-existing fault zone in dolostone rocks: insights from the Matese area (Southern Apennines, Italy)**

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*Keywords:* superposed fault zones, dolostones, fault rocks, Southern Apennines.

The mechanical stratigraphy of a layered sedimentary succession has been widely shown to guide the geometry and nature of faults deforming it. However, mechanic rock layering in carbonate rocks can also be developed as the result of brittle deformation in fault zones (i.e., layers with decreasing strain with departure from the main slip surfaces) and how this affects the nature of subsequent faults at an angle to it is still poorly investigated. Here, to explore this aspect poly-deformed Triassic dolostones in the Matese area of the southern Apennines (Italy), characterized by the superposition of at least two cross-cutting fault systems, were studied. These structures were analysed through detailed field mapping, in-situ mechanical tests, and optical and SEM analyses on collected samples. Results indicate the occurrence of an old, large-scale, extensional, N-S striking fault zone cross-cut by younger NE/SW-NW/SE-striking, conjugate, strike-slip faults. The old fault zone is associated with a well-developed layering defined by four structural units in which fault rocks are: i) Pulverised (Pu); ii) porous cataclastic (Cu); iii) High strained (HSDZ) and iv) Low strained (LSDZ). The in-situ sclerometer test indicates that Pu and LSDZ rocks have uniaxial compressive strength (UCS) values of, respectively, 60 to 100 and 170 MPa, while Cu and HSDZ rocks have lower UCS values ranging from 55 to 70 Mpa. The superimposed conjugate strike-slip faults developed as cataclastic shear bands (CSB) in LSDZ and HSDZ rocks, and as compaction bands (CB) in Pu and Cu rocks. In the LSDZ rocks, cataclasis is localized in meter-spaced, thick, tabular, and cemented CSB. In the HSDZ rocks, anastomosing clusters of CSB accommodate deformation through diffuse cataclasis and dissolution precipitation mechanisms. In Cu rocks, anastomosing clusters of CBs showing variable thickness (from a few centimetres up to decimetres), developed through pores collapse and dissolution-precipitation processes. In Pu rocks, compaction occurred by pore collapse and grain crushing developing a few centimetre-thick, narrowed, and highly spaced CB. A model is proposed for the poly-deformed fault zone evolution, in which the observed mechanical and textural characteristics of inherited structural units influence the strain accommodation mechanisms of the superimposed fault arrays. In detail, the stiffer LSDZ and Pu rocks accommodated strain in localized, and more brittle structures, while in Cu and HSDZ rocks, strain accommodation occurred in more diffuse and plastic deformation structures.

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## Multiple dolomitization events throughout the tectonic evolution of the southern Apennines from the passive margin to the mountain building stages constrained by new U-Pb dating

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Keywords: Southern Apennines, dolomitization processes, rifting events.

Dolomitization is a common phenomenon occurring in carbonates and can be associated with both early and late diagenetic events as well as with following deformation events. In the southern Apennines, dolostones are widely exposed, normally ranging from Triassic to Cenozoic in age (Iannace et al., 2011). Here we analysed and dated with the U-Pb method dolostones from the Matese and Sorrento Peninsula areas. Samples were initially studied by optical and scanning electron microscopes, which allowed us to identify different veins and cements that were then dated. The many sparry dolomite facies observed record well-known tectonic events that took place throughout the structural evolution of the southern Apennines from the passive margin to the mountain building stages. Results indicate a uniform Late Rhaetian age for all analysed dolomitic cements of the Matese area, whereas three different ages for the veins from the Sorrento Peninsula area: Upper Jurassic, Albian-Cenomanian boundary, and Eocene-Oligocene. The Rhaetian and Upper Jurassic dolomitizations are interpreted to relate to the rifting event that affected the Europe-Adria-Africa plates, migrating from east to west and leading to the development of the Neotethys Ocean and the dismembering of a wide shallow-water domain into several isolated carbonate platforms. The Cretaceous dolomitization is interpreted to be associated with the rifting event that affected the Africa and Adria plates with the emersion of part of the platform and the passage of several shallow-water sectors to margin-slope-deep basin environments (Vitale & Ciarcia, 2022). This extensional event was recorded in the whole Adria domain, including the Sorrento Peninsula (Tavani et al., 2013). Finally, the Eocene-Oligocene event is interpreted to relate to the onset of the contractional history, when warm fluids were flushed from the accretionary prism to the Apennine Platform, which was experiencing the synorogenic extension of the forebulge stage (Sabbatino et al., 2021).

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## **A multidisciplinary study of the “Bolle della Malvizza” mud volcanoes (southern Italy)**

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*Keywords:* Southern Apennines, mud volcanoes, faults.

In this paper, we provide an integrated study of the mud volcanoes of the Bolle della Malvizza, located in the Campania region of southern Italy (Vitale & Ciarcia, 2018). These volcanoes emit mud, salt water and gases (CH<sub>4</sub> and CO<sub>2</sub>). To shed light on the relationships between the mud emission and eventual faults, we performed different investigations, including stratigraphic and structural, topographic (photogrammetry by drone and construction of a Virtual Outcrop Model), geophysical (Self Potential) and geochemical (CO<sub>2</sub> flux and radioactivity). The host rock is formed by Upper Cretaceous-Burdigalian varicoloured clays with intercalations of calcareous turbiditic beds. The clayey succession is deformed by two shortening events. The last deformation recorded by folds and thrusts verging to E is shared with the overlying unconformable sandstones of the upper Tortonian-lower Messinian Castelvetero Group. Nine main groups of mud volcanoes are present in the area, varying in size (from a few centimetres to 13 meters) and height (from ca. 3 to 15 cm). These sedimentary structures are aligned along the directions ENE-WSW and ca. N-S. These trends are consistent with the main directions of the measured fractures in the host rock. The CO<sub>2</sub> flux, self-potential and radioactivity maps show anomalies in correspondence with the mud volcanoes highlighting the close relationships between tectonic features and upward migrations of fluids.

Vitale S. & Ciarcia S. (2018) - Tectono-stratigraphic setting of the Campania region (southern Italy). *Journal of Maps*, 14, 9-21. <https://doi.org/10.1080/17445647.2018.1424655>.

## **Geological, geochemical, and geophysical investigations of the CO<sub>2</sub> gas vent in the Solopaca area (southern Apennines, Italy): insights on the active Southern Matese Fault system**

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*Keywords:* Southern Apennines, nonvolcanic CO<sub>2</sub> vents, faults.

We present a geological study of the SE sector of the Matese Massif (Solopaca hills), where some nonvolcanic CO<sub>2</sub> gas vents occur (Vitale et al., 2023). The area is characterized by a margin succession (Sepino-Mt Moschiatturo unit) consisting of Maatrichtian-Paleocene calcareous breccias (Calcari Cristallini Fm) passing to Eocene-Lower Miocene Scaglia-type deposits, unconformably covered by upper Tortonian-lower Messinian sandstones and clays of the Castelvetere Group. We analysed the area through a multidisciplinary study, including stratigraphic and tectonic investigations, CO<sub>2</sub> flux and geoelectrical surveys. The structural study indicates that the youngest structures are NW-SE normal faults, well evidenced by the CO<sub>2</sub> flux anomalies map. These faults are the prolongation of the active Southern Matese Fault system bounding the SW Matese Massif and, such as the northern area (Ailano and Ciorlano gas emissions), these structures convey the CO<sub>2</sub> gas migration from depth to the Earth's surface, well-marked by the geoelectrical profile.

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## **Structural architecture and tectonic evolution of the west-central Campania-Lucania arc (Southern Apennines, Italy): constraints from seismic reflection profiles, well data and structural-geologic analysis**

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*Keywords:* seismic reflection profiles, structural evolution, Campania-Lucania Apennines.

The integrated analysis of largely unpublished seismic reflection profiles (commercial lines and a re-processed segment of the CROP-04 deep crustal line), exploratory well logs and geologic-structural relations among the lithostratigraphic units of the west-central Campania-Lucania Apennines (Italy), shed light on the structural architecture and tectonic evolution of this region.

Pre-orogenic, Mesozoic-Neogene carbonate platform, margin-slope and basinal units that frame the Picentini, Marzano and Alburni mountain ranges and the Irpinia hills were imbricated during Miocene thrusting. The imbrication led to the formation of an heterogeneous multilayer that controlled style and localization of both the late-orogenic Pliocene thick-skinned thrusting in the underlying Apulia platform and of the Quaternary transtension and extension.

We reinterpreted five exploratory well logs (Acerno, Contursi, San Fele, San Gregorio Magno and Taurasi) based on surface constraints and on the modern understanding of regional lithostratigraphy. Using velocity data from sonic logs, the well stratigraphy and the seismic signature were correlated through an accurate well-to-seismic tie, which, together with literature data, allowed to build a local velocity model for depth conversion of seismic profiles. Seismic facies analysis calibrated by the well-to-seismic tie led to identification of seven seismic units with distinctive reflections attributes, which were assigned to as many lithostratigraphic units logged in wells.

The analysis documents the stratigraphic-structural thickness and the depth distribution of the thin-skinned thrust sheets that form the Apennines fold-thrust belt. The Liguride Basin succession is characterized by a ~900 m thickness and is highly fragmented by later high-angle strike-slip and normal faults. The Apenninic Platform shows lateral thickness changes in correspondence with shelf (~3 km), margin (~2-2.5 km) and margin-to-slope (~1.5 km) facies successions that form as many imbricates within a coherent thrust sheet. The Lagonegro-Molise Basin rocks shows dramatic changes in structural thickness because of detachment of the Upper Mesozoic section (~500 m) from above the main Mesozoic section (~1-1.5 km).

The underlying Apulian Platform is characterized by a regional anticlinorium (~30-50 km wavelength) that, based on our new reconstruction, extends further to the west in the hinterland than previously known. The anticlinorium exhibits shorter-wavelength (<10 km wavelength) anticlines limited by NNE-verging thrust ramps. The ramps have a typical high (~45°) dip, suggesting they root in the crystalline basement of Apulia, and accommodate the thrust envelopment of the previously imbricated thrust sheets.

Analysis of the last ~15 years' seismicity reveals that most of the upper crustal seismicity falls within a crustal volume localized in the Apulia basement and broadly limited by the Irpinia fault and by its antithetic fault, both of which slipped during the Mw 6.9 1980 earthquake.



## The Late Paleogene volcanoclastic turbidite succession of the Candela Gorges (Southern Italy): new constrains for the Southern Apennines evolution

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*Keywords:* Central Mediterranean paleogeography, U-Pb detrital Zircon age, confined turbidite basins.

Stratigraphy, sedimentology and petrography of deep-sea deposits are conventional tools used to investigate timing and evolution of the Orogen. To date, several geodynamic models for the Apennines Chain have been provided, nevertheless some questions are still unsolved: i) beginning of the westward apenninic subduction; ii) type of synorogenic basin system; and iii) timing and distribution of calc-alkaline volcanic activity in the Central Mediterranean (e.g. Guerrera et al., 2019 and reference therein).

The Tufiti di Tusa Formation is one of the main turbidite successions belonging to the Southern Apennines inner paleogeographic domain. A recent lithostratigraphy and facies re-examination of its magnificent exposure, along the Candela Gorges (Rotondella village, Calabria-Basilicata boundary; Cerone, 2019), added new depositional details, and further petrographic, bio- and chronostratigraphic studies have yielded crucial information on the sedimentation age, sediment pathway and paleogeography.

The above section represents an eastward-migrating fully-confined succession, developed in front of the westward subducting oceanic/transitional Ligurian Tethys lithosphere (Gallicchio et al., 2023). The source area of deposits was represented by Hercynian and Alpine basements, Mesozoic sedimentary covers and Late Paleogene calc-alkaline volcanic centres. U-Pb spot ages, detected on detrital and euhedral zircons from syn-sedimentary volcanoclastic sandstones, is about 33±1 Ma (Fornelli et al., 2020); moreover, new calcareous nanofossils biostratigraphic data allowed to refer it to the Late Eocene–Early Oligocene. Accordingly, the succession can be correlated with other volcanoclastic turbidite ones of the Northern Apennines (Val d’Aveto, Petricciola and Ranzano Formations), and provides evidences of an eastward-migrating trench-slope system in front of a volcanic arc, discontinuously developed from south to north in the late Paleogene central Mediterranean Region.

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## Where is life? Preliminary biostratigraphic data on the Messinian-Zanclean successions from the CARG surveys in the Central Apennines

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**Keywords:** Messinian, Zanclean, biostratigraphy.

Preliminary biostratigraphic data based on calcareous nannofossil and foraminifers from successions sampled during the ongoing field mapping of the sheets 313 Camerino, 370 Guardiagrele and 379 Capracotta, are presented. In the aforementioned sheets, sedimentary successions ranging from the Messinian to the Zanclean encompassing the well-known Messinian Salinity Crisis (MSC) occur. As a consequence, biofacies attributed to the atypical association are present. About the calcareous nannofossils association: i) the pre-evaporitic Messinian is characterized by *Amaurolithus primus*, *A. delicatus*, *Nicklithus amplificus*, *Discoaster deflandrei*, *D. variabilis*, *Helicosphaera carteri* and *Reticulofenestra pseudoumbilicus* >7µm; ii) the post-evaporitic Messinian displays the absence of *Discoaster* genus and *R. pseudoumbilicus* >7µm (paracme), *Amaurolithus* genus and the occurrence of big *H. carteri*, *Triquetrorabdulus rugosus*, *Coccolithus miopelagicus*, as well as small placoliths that are considered as autochthonous fauna by Crescenti et al. (2002) and intact *C. pelagicus* coccospheres; iii) the Zanclean is marked by an increase in abundance of discoasters, the reentry of *R. pseudoumbilicus* >7µm, the first occurrence of *R. zancleana*, *H. sellii* and *D. tamalis* and small *Gephyrocapsa*. About the foraminifers, the pre-evaporitic assemblage is barren of benthic foraminifera or bears very few specimens of *Bolivina pseudoplicata* and *B. miocenica*. The planktonic assemblage is relatively diversified (mainly *Turborotalita quinqueloba*, *Neogloboquadrina acostaensis* and *Globigerinoides* spp.). The marker species *Globorotalia merotumida*, *G. miotumida*, *G. nicolae* and *T. multiloba* were recognised. This assemblage is characterised by generally small or very small specimens, typical of the interval preceding the MSC (deeper-water benthic foraminifera already disappeared at 7.167 Ma according to Kouwenhoven et al., 2006 and references therein). Planktonic assemblages are dominated by *T. quinqueloba* indicating cold eutrophic waters and hypersaline conditions (i.e. environmentally stressed conditions). The post-MSC is characterised by the Pliocene reflooding with a return to normal marine conditions, as testified by generally well preserved and very diversified foraminiferal assemblages (occurrence of *G. margaritae* and *G. puncticulata*). The Miocene-Pliocene boundary is characterized by autochthonal calcareous nannofossils, whereas foraminifers are almost absent or represented by very small planktonic species. The litho-biostratigraphic dataset coming from a wide area is statistically consistent (more than a hundred samples) and sheds new light on the Mediterranean Miocene-Pliocene paleoenvironmental reconstructions. In particular, our data indicate that the return to pure marine conditions in the post-evaporitic phase could have been occurred earlier than the Zanclean, as already reported in other Mediterranean areas (Pellen et al., 2017; Bulian et al., 2022).

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## **Bangiana beds from the Upper Cretaceous of Mt. Maro (Southern Apennines, Italy)**

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Keywords: *Bangiana*, Campanian, Teano.

As part of the biostratigraphic characterization of the carbonate successions within the CARG Project Sheet 417 Teano, we sampled a succession at Monte Maro (Caserta, coordinates: 41°12’26” N 14°04’43” E), a small relief located a few kilometers north of the Sparanise village.

The starting terms belong to the Upper Cretaceous Radiolitid Limestone Formation, whereas the uppermost to the Cusano Formation (CUS, Lower Miocene). Fifty samples were collected in two successive rounds. The succession is about 260 m thick and is composed of at least 160 m of the Radiolitid Limestone Formation, topped by some 10 m of mainly nodular limestone with *Bangiana*. These beds are overlain by stratified limestone referable to the Eocene Trentinara Formation for a thickness of about 25 m, capped by the Cusano Formation, about 65 m thick.

The terms underlying the “*Bangiana* beds” contain microfossils referable to the Coniacian-Santonian: *Cladocoropsis* sp., *Dicyclina schlumbergeri* (Munier-Chalmas), *Pseudorhapidionina mediterranea* (De Castro), *Nummuloculina robusta* Torre, *Decastronema kotori* (Radoičić), *Accordiella conica* Farinacci, *Dictyopselloides cuvillieri* (Gendrot), *Moncharmontia appenninica* (De Castro), *Murgeina apula* (Luperto-Sinni), *Rotalispira scarsellai* (Torre). The last meters can be referred to the Campanian (Moro et al., 2018) as they contain *Fleuryana adriatica* (De Castro, Drobne & Gušić).

*Bangiana hansenii* is a characteristic species of the Danian (Drobne et al., 2007). To our knowledge, this monospecific genus was never recognized in strata of this age. However, specimens that can be referred to *Bangiana* were depicted (as *Discorbidae* sp. B) by Chiocchini et al. (2012, pl. 147, figs. 2, 6, 8) from levels attributed to the upper Campanian. At Monte Maro the «*Bangiana* beds» may be referred to the lower Campanian because they still contain *Moncharmontia appenninica* as well as *Fleuryana adriatica*, and *Decastronema kotori*.

The limestones of the Trentinara Formation are referred to the lower Eocene for containing *Clypeina bucuri* (Barattolo & Romano), *Clypeina lucana* (Barattolo & Romano), *Pfendericonus makarskae* (van Soest), and *Cribrobulimina* sp.; they also contain charophyte gyrogonites, *Spirolina* sp., and rotaliids (Vecchio & Hottinger, 2007).

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## Apennines, what Apennines? The hidden orogeny

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*Keywords:* Northern Calabria, orogeny, Balearic stage.

Tackling the sedimentary/tectonic evolution of northern Calabria leads researchers into a slippery ground. The drift of the Calabria Peloritani Terrane (CPT) to its present-day position, and accretion to the “Apennines”, evokes the long lasting “Alps vs. Apennines” debate.

The core of our approach for untangling the polyphase deformation history of this sector of the CPT implies separating distinct orogenic wedges, which we identify as products of different geodynamic “engines”, in regions where they are disguised as one element. One major obstacle is a nomenclatural issue, intertwined with uncertainties regarding the age of thrusts and shortened sedimentary successions.

We elected to use a simple conceptual tool, based on firmly established geological constraints: 1. The known age of rotation of the Sardinia-Corsica Block (SCB) (late Oligocene – Langhian); 2. The halt of this rotation (ca. 15 My); 3. The opening of the Tyrrhenian Basin associated with jump of back-arc extension from West to the East of the SCB and drift to the SE of the CPT (post-Tortonian). Any orogenic wedge developed predating the inception of process #1 must be considered as “Alpine” (*i.e.*, N-S oriented shortening due to the Africa-Europe collision). The inception of process #1, with opening of the Ligurian-Provençal back-arc Basin, produced the rotation of the Alpine chain in Corsica with respect to mainland Italy, destroyed its physical continuity with the Betic Chain *via* the Northern Balearic fault, and welded the old chain with a new orogenic wedge, named “Balearic”. Process #1 ended with point #2. The inception of process #3 caused the dismembering of the Alpine and Balearic chains (now found at both sides of the Tyrrhenian Basin) and the growth of the Apennines. To the East of the Tyrrhenian Basin we therefore potentially find on land two or three welded orogens, according to where sea-floor spreading occurred.

If we follow this simple approach, it becomes evident that using the term “Apennines” is potentially misleading as it embeds two different orogens.

A recent field project in Northern Calabria, based on a multidisciplinary approach, revealed a latest Oligocene-Aquitian age for the thrusts shortening the Palaeozoic basement and the overlying Longobucco (Rhaetian to Early Eocene) basin, in good agreement with results recently obtained in other sectors of the CPT. This leads to consider Sila a Balearic orogen, with no signs of Alpine metamorphism. No Apenninic thrusting is seen on land in this northern sector of the CPT, rather back-arc extension with basins having a post-Langhian to Present age. The Balearic orogenesis is therefore responsible for the superposition of the Calabride Complex onto the Liguride Complex, which is exposed in the Alpine units of the Catena Costiera, facing the Tyrrhenian Sea.

Identifying the Balearic and the Apenninic orogens as two separate entities, their build up being separated by temporal gaps of variable extent, solves any issues with thrust propagation rates arising from computations based on the inferred continuity of the chain-building processes through the late Oligocene to Present, which would potentially produce unrealistic numbers.

While Northern Calabria proved a key region for testing our approach, we believe that it can be applied to other regions where a conceptual and physical divide can be placed based on the age of thrusting falling before or after the halt of SCB rotation.

## **Integrated investigation of the structural setting of the Val d'Agri oilfield (Basilicata, southern Apennines, Italy)**

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*Keywords:* active faults, seismicity, tectonic inversion.

The Val d'Agri oilfield is the largest reservoir in onshore Europe producing hydrocarbons, since the 1990s, thanks to the naturally fractured carbonates of the Inner Apulian Platform (API; Mazzoli et al., 2001). The oilfield is located in an area of the southern Apennines with high seismic hazard (historically struck by the 1857, M7 earthquake). It is featured by a Quaternary extensional tectonic basin resulting from the activity of two parallel and oppositely dipping normal fault systems bounding the basin on its western and eastern side, the Monti della Maddalena and the Eastern Agri Fault System, respectively (e.g. Maschio et al., 2005). The oil structural traps are provided by Pliocene thrust-related anticlines deforming the API carbonates, drilled at about 2-3 Km depth, and sealed by siliciclastic foredeep deposits and a thick tectonic mélange. ENI petroleum company is the main operator of the field, extracting oil and gas from about 25 wells with production rates of about  $7 \cdot 10^4$  barrels/day of oil and  $3 \cdot 10^6$  Sm<sup>3</sup>/day of gas. Since 2006, wastewater associated with oil production has been re-injected into a marginal portion of the reservoir by a high-rate well (Costa Molina 2, CM2).

Previous works highlighted a spatio-temporal relationship between micro-seismicity ( $ML \leq 2.2$ ) and wastewater injection (Buttinelli et al., 2016). Furthermore, some low-energy seismicity recorded in the southwestern sector of the field has also been associated with the Pertusillo Lake water level changes due both to the seasonal fluctuations and to the loading/unloading phases of the reservoir impoundment leading to interpret the earthquake clusters as reservoir-induced seismicity (Picozzi et al., 2022 and references therein).

The INGV (Istituto Nazionale di Geofisica e Vulcanologia), under the require of the Italian oil and gas safety authority (DGS UNMIG), is in charge of monitoring seismicity, ground deformation, and pore pressure variations, following governative guidelines, in areas where industrial activity involves subsoil exploitation. In this context, a working group has been assigned to study the main systems of active faults in Val d'Agri (Val d'Agri Active Faults Project, AFP-WG; Centro di Monitoraggio del Sottosuolo, <http://cms.ingv.it>).

In this study, the combined analyses of the local micro-seismicity recorded from April 2020 to November 2022 by public and private seismic stations; well data and seismic reflection profiles; electrical resistivity tomography together with the analyses of the stratigraphic and structural data collected at the outcrop scale; allowed us to highlight the active tectonics of the area, identifying potentially seismogenic faults with clear evidence for recent activity at the surface and to evaluate their relationship with the deep-seated faults dissecting the Apulian carbonates.

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## **The impact of Late Cretaceous-Eocene abortive rift in the carbonate platforms of the southern Apennines**

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*Keywords:* Southern Apennines, rifting, Adria.

Starting from the Late Cretaceous, a large part of the Africa-Adria domain, from Libya to Italy, was affected by an abortive rift event. In the Maastrichtian-Eocene interval, it had a significant impact on the palaeogeography, causing the dismembering of the pre-existing carbonate domains (Apennine and Apulian platforms). The rifting, accompanied by anorogenic magmatism and a severe extension, triggered the drowning of some shallow-water realms with the sedimentation of slope-to-basin deposits. Synchronously, the surrounding pre-existing slope-basin areas were the location of a widespread calciclastic supply. In this review, we described the stratigraphic records of this event in several key places of the southern Apennines. The reconstructed Maastrichtian-Eocene paleogeographic map shows remnants of the Apennine and Apulian platforms again in shallow-water conditions or forming emerged areas, surrounded by slope-to-deep-basin sectors. We propose a depositional model where the exposed Mesozoic carbonates were eroded, producing a calciclastic supply deposited in the drowned carbonate domains and the pre-existing surrounding basins. Along the slope, the calciclastic sediments deposited as aprons at the toe of fault scarps and as isolated debris and channel-fan deposits up to the deep basin. Scaglia-type successions are also present, characterized by a mix of calcareous and clayey sediments. Finally, calciclastic turbidites and isolated calciruditic bodies are intercalated with widespread clayey deposits in the deep basin.



## Paleocurrent analysis in the wedge-top basin deposits of Cilento Group and Monte Sacro (southern Italy)

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Keywords: Southern Apennines, paleocurrent analysis, wedge-top basin.

The Cilento area in southern Italy is characterized by wide exposition of oceanic successions (Ligurian units; Vitale et al., 2019) covered by unconformably wedge top basin clastic deposits of the Cilento Group and Monte Sacro Fm (Vitale & Ciarcia, 2018). The uppermost Burdigalian-lowermost Tortonian Cilento Group is characterized by siliciclastic and calciclastic deposits, including two turbiditic units: (i) the Pollica Fm encompassing thin beds of siltstones and sandstones at the base (Cannicchio Mb) and prevailing sandstones in the middle-upper part; (ii) the San Mauro Fm is formed by sandstones and conglomerates with some characteristic levels of marls (Fogliarina beds). These deposits are unconformably covered by the upper Tortonian-lower Messinian Monte Sacro Fm, a mainly conglomeratic succession corresponding to the widely exposed Castelvetero Group in southern Italy. The Cilento Group was deposited into a wedge-top basin developed onto the Ligurian accretionary wedge during the first stage of Apennine belt construction (Vitale et al., 2011; Ciarcia et al., 2012), whereas the Monte Sacro Fm formed in an extensional stage that affected the whole thrust-sheet orogenic wedge. To obtain information about the source areas of the sediment supply and, consequently, constraints about the geodynamic evolution of the tectonic wedge, a paleocurrent analysis was performed on these clastic deposits. Due to the intense folding that affected these deposits during an out-of-sequence thrusting (Vitale et al., 2020), paleocurrent measurements were restored, backing the bedding surfaces to the horizontal. Results indicate a complex pattern of the paleocurrents consistent with a source supply from different sectors of the overriding plate/accretionary wedge/down going plate system.

Ciarcia S., Mazzoli S., Vitale S. & Zattin M. (2012) - On the tectonic evolution of the Ligurian accretionary complex in southern Italy. *Geological Society of America Bulletin*, 124, 463-483. <https://doi.org/10.1130/B30437.1>.

Vitale S., Ciarcia S., Mazzoli S. & Zaghoul M.N. (2011) - Tectonic evolution of the 'Liguride' accretionary wedge in the Cilento area, southern Italy: a record of early Apennine geodynamics. *Journal of Geodynamics*, 51, 25-36. <https://doi.org/10.1016/j.jog.2010.06.002>.

Vitale S. & Ciarcia S. (2018) - Tectono-stratigraphic setting of the Campania region (southern Italy). *Journal of Maps*, 14, 9-21. <https://doi.org/10.1080/17445647.2018.1424655>.

Vitale S., Ciarcia S., Fedele L. & Tramparulo F.D.A. (2019) - The Ligurian oceanic successions in southern Italy: The key to decrypting the first orogenic stages of the southern Apennines-Calabria chain system. *Tectonophysics*, 750, 243-261. <https://doi.org/10.1016/j.tecto.2018.11.010>.

## Volcano-tectonic deformation during caldera collapse and resurgence of the Ischia Island

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*Keywords:* Caldera, resurgence, volcano-tectonics.

Ischia Island is a volcanic caldera characterized by a resurgence in the centre (Mt Epomeo). The oldest rocks (150 ka) are located outside the caldera rim, along the southern seacoast. The volcanism of the island develops as a volcanic field mainly formed by monogenic edifices mainly made by trachyte (Sbrana et al., 2018). Starting at 61 ka some ignimbrite eruptions formed a caldera and thick deposits of tuffs, including the 56.5 ka Mt Epomeo Green Tuff. Subsequently, a resurgence occurred characterized by an asymmetric uplift of the northern side of the caldera centre. The young Ischia Island is affected by gravitational instabilities triggering several landslides, including that occurred in 2023 on the northern side of the Mt Epomeo slope causing several deaths and damages to the Casamicciola town. We analysed several outcrops along an N-S transect from Mt Epomeo down to the town. The lowermost exposed deposits are pre-caldera marine sediments characterized, in the lower part, by rhythmites. These fine deposits stunningly recorded the deformation associated with the calderization by the development of reverse faults and associated folds. On the other hand, these deposits and the overlying tuffs recorded the deformation associated with the resurgence through dominantly normal faults with associated cataclasites.

Sbrana A., Marianelli P. & Pasquini G. (2018) - Volcanology of Ischia (Italy). *Journal of Maps*, 14(2), 494-503.

## **Middle-Late Pleistocene volcano-tectonic activity in carbonate mountains (southern Apennines, Italy): evidence of tectonic control on dike emplacement**

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*Keywords:* Southern Apennines, rifting, dike intrusion.

We performed stratigraphic and structural investigations on a magmatic dike hosted in Mesozoic carbonates exposed in a quarry to the North East of Roccamonfina volcano, southern Italy. A system of magmatic dikes composed of a principal structure and minor segments crops out for over 250 m, with thicknesses ranging between 2-30 meters. A meters-thick recrystallized calcareous aureole is present in the lower part of the exposed dike. In the upper part of the quarry, we described a stratigraphic succession made up of a series of pumice-lapilli layers of the White Trachytic Tuff (WTT) eruption of Roccamonfina (330-230 ka) and paleosols, which are in turn overlain by the pyroclastic products of the feeding dike. These products consist of meters of strombolian pyroclastic sequence characterized by scoriaceous juvenile material, spatters, and lava flow units. Structural data indicate that the major dike is characterized by a segmented contact with the hosting carbonates showing a dominant E-W direction and a secondary NE-SW direction. The dike, propagating obliquely from north to south, intruded within an E-W fault zone. A pre-existing NE-SW fault zone controlled the lateral dike trajectory before reaching the surface and feeding a fissure eruption. The dike and pyroclastic sequences are furtherly dislocated by N-S and E-W trending faults, marking an important tectonic extensional phase that drove the late development of the Garigliano and Formicola grabens resembling the pattern of rift-related extensional pulses. This diking event has to be considered independent of the dynamics of the nearby Roccamonfina volcano. Our results allow us to constrain this rift-like tectonic pulse and related monogenetic activity to the latest stage of the Roccamonfina evolution in the Middle-Late Pleistocene.

## Unravelling the geometry of poly-deformed allochthonous units in the Southern Apennines: geological map and 3D model of the left side of the High Agri Valley

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*Keywords:* high Agri valley, 3D model, throw profiles.

The Southern Apennine fold and thrust belt (ftb) is the result of the tectonic collision between the African and European plates, followed by migration of an allochthonous wedge with NE vergence on the autochthonous Apulian carbonates. Finally, NW-elongated tectonic depressions formed in the axial portion of the chain due to Plio-Pleistocene transtensional to extensional deformation. The superposition of different deformation phases produced a complex tectonic setting which is difficult by means of 2D cross-sections, which are generally used for depicting the geometry of the fold and thrust belt (e.g., Menardi Noguera & Rea, 2000). Therefore, we applied static 3D modelling to the allochthonous units exposed in the axial sector of the Southern Apennine ftb, in order to recognize along-strike structural variations and to define the role of the major structures in shaping the architecture of the ftb.

The High Agri Valley area has been selected as study area, due to the presence of good exposures of a thick pile of tectonic units making up the Southern Apennine ftb. Moreover, the allochthonous units cover the largest hydrocarbon reservoir in continental Europe and, therefore, have been deeply investigated during exploration activity. The 3D model was realized by using a new geological map constructed at a 1:25.000 scale, obtained through careful field mapping, combined with subsurface data. Data allowed to obtain 44 geological cross-sections which have been used for the construction of the tectonic and stratigraphic surfaces by means of the Move™ software.

Significant attention was paid to transvers faults, nearly perpendicular to the axis of the ftb, have been more deeply analysed. These latter structures do not appear to be related to the opening of the valley. Their maximum throw exceeds 1,500 m, thus allowing to consider these faults as first-order structures at the scale of the entire ftb.

Throw profiles were derived from the analysis of cut-off lines of formational tops, cut by selected faults obtained from the 3D model. The geometry of the throw profiles for most of the transverse faults appear to be typically bell-shaped, with greater displacement in the central part. In contrast, the throw profiles of structures parallel to the direction of the chain axis appear related to growth by linkage of initially isolated segments.

The analysis of throw profiles in faults developed within highly deformed allochthonous units can be considered as a new approach that can be proposed for further studies in fold and thrust belts. Transverse faults could in some cases night be interpreted as tear faults connecting fault segments parallel to the chain axis. However, the evident bell-shaped throw profiles suggests that along-strike fault propagation was inhibited by pre-existing NW-trending structures. This study could be important in relation to the seismicity of the area as well as in the study of the circulation of groundwaters in the allochthonous units.

Menardi-Noguera A. & Rea G. (2000) - Deep structure of the Campanian–Lucanian Arc (Southern Apennine, Italy). *Tectonophysics*, 324, 239-265. [https://doi.org/10.1016/S0040-1951\(00\)00137-2](https://doi.org/10.1016/S0040-1951(00)00137-2).

### 3D Structural model of the Sibillini Mountains area, Umbria-Marche Apennines, Italy

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*Keywords:* balanced geological sections, fold and thrust belts, 3D model.

The area of the Sibillini Mountains corresponds to a complex fold and thrust belt built-up as result of three main tectonic stages: a pre-orogenic Jurassic extension, a Mio-Pliocene compressional activity, and a recent extensional regime. These tectonic events affected both the Jurassic-Cretaceous carbonate Umbria-Marche sequence and the siliciclastic foredeep Mio-Pliocene deposits.

The Sibillini Mountains and the nearby area have been widely studied due to their structural complexity, still debated deformational style (e.g., Barchi & Tavernelli, 2022), and their significant historical and recent seismic activity (e.g., 2016-2017 seismic sequence, Civico et al., 2018). The structural models of the area have been traditionally based on surface geological maps, and low-quality geophysical data which put in evidence the need of validation through restoring and balancing of integrated geological models. The most recent outcomes of the current geological national mapping project at scale 1:50000 for the Sibillini area (Sheet Visso-325) generate an opportunity to review and propose new alternatives for the unsolved issues related to the geological complexity of the area.

This study proposes a 3D representation and a validation of the structural and stratigraphic settings to obtain a comprehensive geological model of the Sibillini Mountains in agreement with the most recent geological and geophysical dataset.

Our methodology involved the integration of a variety of techniques including surface geological mapping, seismic interpretation, cross-section balancing and restoration, and gravimetric modeling. To characterize the complexity of structural style and stratigraphic variations of the area, we constructed thirteen balanced cross-sections using a 10 m-cell size Digital Elevation Model and the latest version of the geological map in a 3D environment. The 3D geological model offers a detailed representation of the geometrical arrangement of the geology in the study area including major faults and key horizons (including base and top Calcare Massiccio Fm, top Maiolica Fm, top Scaglia Rossa Fm, top Bisciaro Fm.). The proposed model helps to describe how Jurassic extensional structures and the lithological competence contrast influence and affect the Mio-Pliocene thrust tectonics, the depositional setting of the basin and how older structures promotes recent extensional fault growth. It also provides a new insight for future seismic hazard evaluation for this sector of the Umbria-Marche Apennines.

Barchi M.R. & Tavernelli E. (2022) - Thin vs. thick-skinned tectonics in the Umbria-Marche fold-and-thrust belt: Contrast or coexistence? In: Koeberl C., Claeys P. & Montanari A. (eds) From the Guajira Desert to the Apennines, and from Mediterranean Microplates to the Mexican Killer Asteroid: Honoring the Career of Walter Alvarez. [https://doi.org/10.1130/2022.2557\(05\)](https://doi.org/10.1130/2022.2557(05)).

Civico R., Pucci S., Villani F., Pizzimenti L., De Martini P.M., Nappi R. & Open EMERGEO Working Group (2018) - Surface ruptures following the 30 October 2016 M w 6.5 Norcia earthquake, central Italy. *Journal of Maps*, 14(2), 151-160. <https://doi.org/10.1080/17445647.2018.1441756>.

## **Quaternary evolution of the southern Apennines (Italy): a foreland-basin perspective**

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*Keywords:* Quaternary, south Apennines, foreland basin.

Outcropping wedge-top and foredeep Quaternary successions of the foreland-basin system can contribute to decipher the history of the south-Apennines orogen (Italy). These successions are mainly characterized by shallow-marine deposits, either siliciclastic, or carbonate, or mixed in origin. The stratigraphic architecture of these deposits reveals a complex response to relative sea-level changes, the latter induced, with an eustatic imprinting, by foredeep subsidence, foreland uplift and chain-front migration.

A review of available data is proposed.



## Did Bradyseism drown the Roman city of Baiae?

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*Keywords:* Campi Flegrei, bradyseism, geoarcheology.

The active Campi Flegrei caldera in southern Italy has a remarkably long history of coexistence between volcanism and human settlements, and it is famous for its peculiar slow ground movement called Bradyseism, i.e., episodes of inflation and deflation of the caldera floor due to magmatic and/or hydrothermal processes. This natural phenomenon has interacted with the civilization that inhabited this strategic and fertile area, especially in Roman times when the sinking of the coast hindered the flourishing of Puteoli and Baiae coastal towns. The drowning of a large part of Republic-early Imperial Roman coastal buildings, west of the modern Pozzuoli town, is classically used to illustrate the Bradyseism activity. In this work, we investigate the spatial variability and the role of this phenomenon, demonstrating that the caldera deflation alone cannot account for the submersion of Roman facilities in the western sector where the harbour structures of Portus Julius and luxury villas of the Baianus Lacus presently lie beneath sea level (Vitale & Natale, 2023). On the contrary, the sinking of this area is mainly the result of the activity of volcano-tectonic faults. First, we restored the topography to 100 BCE using archaeological and high-resolution topographic data. Results show that the several meters of vertical displacement recorded in the Baia area in the last 2100 yr were mainly produced by the activity of normal faults and secondarily by caldera deflation, the former including the long-lived Baia Fault and the younger normal faults associated with the Monte Nuovo eruption at 1538 CE.

Vitale S. & Natale J. (2023) - Combined volcano-tectonic processes for the drowning of the western coastal Roman settlements at Campi Flegrei (southern Italy). *Earth, Planets and Space*, 75(1), 1-15. <https://doi.org/10.1186/s40623-023-01795-7>.

## Late Miocene-Early Pliocene out-of-sequence thrusting in the southern Apennines (Italy)

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*Keywords:* Southern Apennines, out-of-sequence thrusting, wedge-top basin.

We present a structural study on late Miocene-early Pliocene out-of-sequence thrusts affecting the southern Apennine orogenic belt. The analysed structures are exposed in the Campania region (southern Italy; Vitale & Ciarcia, 2018). Here, thrusts bound the N-NE side of the carbonate ridges that form the regional mountain backbone. In several outcrops, the Mesozoic carbonates are superposed onto the unconformable wedge-top basin deposits of the upper Miocene Castelvete Group, providing constraints to the age of the activity of this thrusting event (Vitale et al., 2017, 2020a, 2020b). The kinematic analysis of out-of-sequence major and minor structures hosted both in the hanging wall (Apennine Platform carbonates) and footwall (Castelvete Group deposits and Lagonegro-Molise Basin units) indicates the occurrence of two superposed shortening directions, about E-W and N-S, respectively. We associated these compressive structures with an out-of-sequence thrusting event defined by frontal thrusts verging to the east and lateral ramp thrusts verging to the north and south. We related the out-of-sequence thrusting episode to the positive inversion of inherited normal faults located in the Palaeozoic basement. These envelopments thrust upward to crosscut the allochthonous wedge, including, in the western zone of the chain, the upper Miocene wedge-top basin deposits.

Vitale S., Tramparulo F.D.A., Ciarcia S., Amore F.O., Prinzi E.P. & Laiena F. (2017) - The northward tectonic transport in the southern Apennines: Examples from the Capri Island and western Sorrento Peninsula (Italy). *International Journal of Earth Sciences*, 106, 97-113. <https://doi.org/10.1007/s00531-016-1300-9>.

Vitale S. & Ciarcia S. (2018) - Tectono-stratigraphic setting of the Campania region (southern Italy). *Journal of Maps*, 14, 9-21. <https://doi.org/10.1080/17445647.2018.1424655>.

Vitale S., Prinzi E.P., Tramparulo F.D.A., De Paola C., Di Maio R., Piegari E., Sabbatino M., Natale J., Notaro P. & Ciarcia S. (2020a) - Late Miocene-early Pliocene out-of-sequence thrusting in the southern Apennines (Italy). *Geosciences*, 10(8), 301. <https://doi.org/10.3390/geosciences10080301>.

Vitale S., Prinzi E.P., Monda M., Tramparulo F.D.A. & Ciarcia S. (2020b) - Structural and Stratigraphic Setting of Campagna and Giffoni Tectonic Windows: New Insights on the Orogenic Evolution of the Southern Apennines (Italy). *Geosciences*, 10, 405. <https://doi.org/10.3390/geosciences10100405>.

**S33.**

**Processes of volcanoclastic sedimentation: analytical,  
experimental and modelling approaches for stratigraphic  
record and modern environments**

*CONVENERS AND CHAIRPERSONS*

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## **Towards a spatial database for estimating the ash-fall pyroclastic deposit (APD) thickness in southern Italy: A tool for multi-hazard assessment in the landscapes impacted by active volcanoes**

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*Keywords:* thickness of pyroclastic deposits, explosive eruptions, geohazards.

Explosive volcanoes can generate huge pyroclastic density currents (PDCs) and propel considerable quantities of ash into the atmosphere. The PDCs rapidly propagate along the ground and the ash plume is subject to wind-driven dispersion and may deposit over thousands of square kilometers, depending on the magnitude of the eruption. In south Italy, the observed PDCs and ash-fall pyroclastic deposits (APDs) in the stratigraphic records demonstrate the history of tephra-producing eruptive events, being important for assessing volcanic hazards. APDs also play a critical role in geo-hydrological hazards (e.g., landslide and erosion) because their geotechnical and hydraulic properties are usually different from the underlying bedrock (mainly carbonate rocks, flysch sequences, tuff and lava in southern Italy). For estimating the thickness of APDs and PDCs, the interaction of the ash deposited during eruptions (APD<sub>0</sub>) with denudational processes needs to be considered. The main aim of our work is to conduct a literature review to collate a complete database of APD<sub>0</sub> thickness (i.e., the areal isopachs proposed by researchers for showing the ash dispersal pattern during a given eruption) associated with the major eruptive events in Campania. Then, the spatial distribution of cumulative APD<sub>0</sub> thickness is computed in southern Italy, mainly comprising Campania, Molise, Basilicata, Puglia, and Calabria regions.

After preparing a list of major tephra-producing eruptions of the Phlegrean Fields, Somma-Vesuvius and Roccamonfina volcanoes, the corresponding syn-eruptive ash dispersal patterns are retrieved from previous publications, digitized in ArcMap 10.8.2 and the cumulative APD<sub>0</sub> is calculated. It is evident that the volcanic ash released into the atmosphere during eruptions is generally transported towards the east (except for the southward dispersion of the ash in a couple of Somma-Vesuvius eruptions) and mostly deposited in Campania region (cumulative APD<sub>0</sub> thickness > 10 cm), being consistent with the distance from volcanoes. The 40-ka Campanian Ignimbrite and 26-ka Masseria del Monte large-magnitude eruptions are mostly responsible for APD<sub>0</sub> outside Campania region. The spatial cumulative APD<sub>0</sub> thickness is under 70 cm in south Italy, except for Campania and north-west Puglia. The results show approximately 2.5 m cumulative APD<sub>0</sub> thickness at Somma-Vesuvius volcano which declines to about 0.95 m in Phlegrean Fields area. The central and northern sectors of Campania are characterized by cumulative APD<sub>0</sub> thickness greater than 0.3-0.4 m.

The present dataset of major tephra-producing eruptions facilitates developing techniques for APD thickness spatial modeling, depending on the available field measurements, to have an idea of erosion and landslide processes during heavy rainfall events and the related hazards.

## Multidisciplinary research at the Campi Flegrei geothermal system: mineralogical and petrophysical characterization and geochemical modeling in the small coastal depression of the Volturno alluvial plain (Campanian Plain, Southern Italy)

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Keywords: Basin Routing System, Campi Flegrei, hydrothermal alteration.

Basin Routing System is a geological framework integrating erosion, landscape modifications, sediment transfer dynamics and the evolution of sedimentary environments. Its study bases on the analysis of the sink to identify the source so that sediment compositions are essential to describe and quantify the processes determining the formation and evolution of sedimentary basins (Caracciolo, 2020).

The Campi Flegrei (CF) is a volcanic depression generated by two giant eruptions at 40 and 15 ka in the Plio-Quaternary graben of the Campanian Plain an alluvial basin west of the southern Apennine in Italy. It can be therefore considered a peculiar sink zone for sediments from the erosional engine hinterland chain located 40 km far.

The caldera, wide 8 km, is mostly infilled by the Campanian Ignimbrite and later erupted pyroclastic deposits, overlying Quaternary marine and continental sediments filling the Campanian coastal plain (e.g., Piochi et al., 2005). It a small distinct basin in central coastal area of the Volturno alluvial plain.

Our research focused on the San Vito area due to its closeness to the Solfatara tuff cone, the highest and stable temperatures (up to 400°C) and the concentration of recent hydrothermal activities.

The objective of this study is to define a geochemical model, calibrated with actual data, to simulate the hydrothermal circulation and alteration at San Vito area, thus providing information on sediment evolution in a basin subjected to hydrothermal circulation. To achieve this goal, a comprehensive multidisciplinary research was developed, which included: 1) a review of available literature data; 2) new petrographic and MICP analyses of cores; 3) the development of a representative stratigraphic succession and geochemical conceptual model; 4) the implementation and calibration of thermodynamic and kinetic dataset.

Geochemical simulations were performed considering variable  $PCO_2$  and different temperatures after model validation by results comparison with water sampled at the Tennis Hotel, considered the most representative of the shallow hydrothermal reservoir in the San Vito area (e.g., Piochi et al., 2021 and reference therein).

The built model correctly reproduced the alteration of primary minerals and precipitation of zeolites and clay, although some discrepancies were present. Simulations of the Campanian Ignimbrite formation, the most important deposits in the case study area suggest that the observed mineral alteration is due to the fluid-rock interaction with  $PCO_2$  ranging from 1.2 and 0.4–0.3 bars. Moreover, the simulated aqueous concentrations best matched the Tennis Hotel values within 10 years of simulation, hinting that geochemical reactions and fluid circulation toward the surface are quite fast as confirmed also by the high gas flows sampled at fumaroles (Tamburello et al., 2019) and from soil exhalation.

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## Possible volcanic origin for “mounds” of the Hypanis fan system, Mars: magmatic vs sedimentary

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Keywords: volcanism, Mars, astrobiology.

Mars is one of the most studied planets in our solar system, although at present day many uncertainties remain about its geological history and evolution through time. One of these is the presence of sedimentary volcanism manifestation on the surface: the level of knowledge and remote sensing dataset we have today are not sufficient to prove, without any doubt, if such a phenomenon happened on Mars. Moreover, the problem of equifinality (different geological processes produce similar landforms (Komatsu, 2007)) made the research even more complicated. Being able to confirm the presence of sedimentary volcanism would be extremely important: it can help understanding the processes of sedimentation, water saturation, fluid and gas movement in the crust (Komatsu, 2014), and also probing the subterranean environmental conditions of Mars, more suitable for life or biological activity than the hostile surface. Furthermore, detailed remote sensing study for identification of “potential” sedimentary volcanism features is a necessary step in order to make a proper selection of promising future landing sites (Komatsu & Brož, 2021; Komatsu et al., 2016).

This work can be considered as a geological investigation on the area of Hypanis fan system in the western Chryse Planitia, with the purpose to give useful insight about origins of hundreds of meters to kilometers wide mounds discovered there. The first step is to focus on collecting available data and making objective observations regarding the geology of the zone, then the second step is the interpretation and formulation of hypotheses that fit with the geological context using the multiple hypotheses approach. The aim is to analyze the possible sedimentary volcanism genesis of the Hypanis mounds, from remote sensing observations to the building of plausible hypotheses, in order to achieve interesting considerations about an area potentially important from both geological and astrobiological points of view. Equifinality’s issue is taken into serious account, as a guidance on how to investigate and approach the scientific problem: there are many possibilities, crucial in terms of reasonable comparisons, which could form the base of discussion regarding the mound formation. Indeed, two main hypotheses prevail over the others: sedimentary and magmatic/phreatomagmatic volcanism. Due to the poor high-resolution and spectral data coverage of the zone, we suggest that further studies should be performed. Dataset improvements would be required for better understanding the nature of mounds and give a more solid base for the interpretation

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## Reconstruction of the sand transport pathways and provenance in Moreux crater, Mars

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*Keywords:* Moreux crater, aeolian bedforms, provenance.

Aeolian bedforms analogous to terrestrial features have been widely observed under the present atmospheric conditions on Mars from the orbiter and in situ instruments. Among all these, the sand dunes related to the aeolian processes, are the common widespread aeolian features on Mars (Hayward et al., 2007), suggesting that near surface winds commonly interact with dark mobile sediments (Chojnacki et al., 2014). In this study, we reconstructed the sand pathways within Moreux crater located in the northern mid latitudes of Mars. We use a multi-resolution imaging such as HiRISE images combined with CTX ones and spectral data, as CRISM from the Mars Reconnaissance Orbiter mission to better characterize local and regional aeolian sediment production and transport. HiRISE, coupled with a Geomatica tool, and CTX images are used to model the wind circulation which formed the dunes based on a geomorphic map of the dunes and ripple crests or wind streak orientations. CRISM dataset, performing a spectral mapping of the mineralogical composition are characterized to constraint the provenance of the aeolian sediment. Specifically, a dominant basaltic composition showing an olivine and clinopyroxene mixture characterize most of the dunes within Moreux crater, with a dark dunes in the northern sector of the crater showing an enrichment in Mg-olivine. This composition is similar to that detected in the central peak bedrock suggesting that central peak erosion contributes to the formation of the northly dunes. On the other hand, recent northeast wind flows and Moreux topography influence the wind circulation and determine the formation of the sand transport pathways within the crater. The slight variation of the dunes composition may be related to changes in the grain size as already observed in Gale crater. These results are consistent with the hypothesis that aeolian sands are generally sourced locally on Mars.

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Chojnacki M., Burr D.M., Moersh J.E. & Wray J.J. (2014) - Valles Marineris dune sediment provenance and pathways. *Icarus*, 232, 187-219.

## Volcanogenic turbidites in marine sediment successions off Stromboli island

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*Keywords:* Stromboli canyon, volcanogenic turbidites, component analyses.

Volcaniclastic turbidites preserved in the sedimentary record provide a unique opportunity to investigate the recurrence, dynamics and magnitude of past sector collapses in coastal volcanic areas. Twenty-two sediment cores were recovered in the area facing the Sciara del Fuoco scar, off Stromboli island, during the 2018 GEOMAR POS-522 cruise aboard R/V Poseidon. The cruise was aimed at gravity coring sediment sequences containing turbidity current deposits co-genetic to potential landslides associated with flank collapses of Stromboli volcano (Di Roberto et al., 2011). The cores contain hemipelagic sediments with intercalated multiple, variably thick volcaniclastic layers, possibly emplaced by turbidity currents co-genetic to volcanic landslides of Stromboli, and tephra layers crucial for the correlation and synchronization of the sequence (Albert et al., 2012). We initially selected four cores recovered in the Stromboli Canyon and in the area facing the Sciara del Fuoco, on the right bank of the Stromboli Canyon, covering a distance from the island comprised between 29 and 47 km. Fifty-two samples of volcaniclastic deposits were analyzed for grain-size and textural and geochemical characteristics of volcanic glass.

Grain-size analyses indicate that the volcaniclastic deposits of more distal (>40 km) cores comprise a higher mud/sand ratio and bear clasts characterized by low angularity with respect to more proximal (<30 km) samples. The volcaniclastic components of the silty-clay layers increase progressively from the distal to the more proximal samples (with respect to the non-volcanic extrabacinal and intrabacinal components), reaching 100% in proximal cores. Volcanic fragments are represented by: i) monomineralic grains of plagioclase and pyroxene, with minor olivine; ii) porphyritic and microlite-rich glassy fragments (tachylite); and iii) low-vesicularity, almost aphyric glass shards (sideromelane). Light-coloured, aphyric, highly vesicular pumice and glass shards also occur in minor amounts, reaching 50% in samples from the more distal cores. Tachylite glass always prevails on the sideromelane component. Results suggest a dual source area for the volcanic component: highly-vesicular, light pumices and shards suggest an origin from Lipari island (Monte Pilato and/or Gabelotto cycles), whereas mineral grains, porphyritic tachylite and sideromelane fragments are indicative of provenance from Stromboli. The increase of aphyric pumice and shards in the distal cores north of Stromboli and the increase of volcanic components in the finer fraction suggest their origin from local fallout reworking.

Albert P.G., Tomlinson E.L., Smith V.C., Di Roberto A., Todman A., Rosi M., Marani M., Muller W. & Menzies M.A. (2012) - Marine-continental tephra correlations: Volcanic glass geochemistry from the Marsili Basin and the Aeolian Islands, Southern Tyrrhenian Sea, Italy. *JVGR*, 229-230, 74-94.

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## Composition and potential provenance of aeolian deposits in Sera crater, Mars

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*Keywords:* aeolian deposits, mars, mafic minerals.

Sera is a ~30 km diameter, about 1 km deep, impact crater in central Arabia Terra, an equatorial region of Mars which shows a wide geological variability (Di Pietro et al., 2023). and widely hosts layered sequences known as Equatorial Layered Deposits, which also contain sulfates.

Sand sheets and dunes fields are the most recent indicators of a long history of erosion and deposition attesting to the ongoing wind activity in the study area. We analyzed hyperspectral data acquired by the CRISM instrument onboard Mars Reconnaissance Orbiter and found out these aeolian deposits show a difference in composition: the sands sheets reflect to be enriched with iron oxides and low-calcium pyroxenes, while the dark dunes represent an olivine-enriched material. This compositional differentiation likely reflects different source areas which may be placed either inside or outside the crater. This study contributes to the understanding of the regional provenance of these aeolian deposits and further detailed evidence are shown.

Di Pietro I., Schmidt G., Tangari A.C., Salese F., Silvestro S., Fairén A.G., Marinangeli L. & Pondrelli M. (2023) - Groundwater-controlled deposition of Equatorial Layered Deposits in central Arabia Terra, Mars. *Journal of Geophysical Research: Planets*, e2022JE007504.

## The volcanoclastic succession of Spiaggia di Pollara Formation (Salina Island, Aeolian Archipelago)

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*Keywords:* epiclastic deposits, syn-eruptive reworking, Upper Pollara eruption.

The volcanoclastic succession of Spiaggia di Pollara Formation, located in the north-western sector of the island of Salina (Aeolian Islands) has been object of a multidisciplinary study, including stratigraphic and sedimentological observations, grain size and component analysis, petrography and clast micromorphology. These investigations were aimed at reconstructing the main transport and depositional mechanisms and the temporal relationships with the primary eruptive activity in that area.

The Spiaggia di Pollara Formation is a 80 m-thick lentiform volcanoclastic succession cropping out along a NE-SW-oriented cliff in the Pollara bay. This succession is mostly constituted of epiclastic products derived from the reworking of the deposits of the Upper Pollara Formation, related to the youngest eruptive event on the island (15.6 +/- 0.4 ka), as testified by the interlayering of epiclastic and primary deposits of this eruption. This relationship is also established on the basis of the recognition of distinctive Upper Pollara juvenile fragments (white, gray, or banded pumices), crystals (pyroxene, plagioclase, minor amphibole, and biotite) and abundant lithic clasts from the base to the top of the Spiaggia di Pollara succession.

The succession is mostly made up of a complex alternation of massive to weakly stratified beds of tuffaceous sandstones and tuffaceous-breccias with a variable content of sub-rounded pumice lapilli and lithics, showing variable thickness, poor sorting and limited lateral continuity, at places interlayered by metre-thick planar-convex lobes and sometimes separated by localized erosive surfaces. Reworking in a water-rich environment is particularly visible at the base of the outcropping succession, in the occurrence of layers with load structures and plastic deformation. Lenses exclusively made up of pumices are interlayered in the intermediate part of the succession. Primary ash-rich beds are recognized in the intermediate-top part of the succession, showing massive to stratified lithofacies with traction structures and abundant ash aggregates. The succession is closed by a metre-thick massive, poorly sorted deposit of pumice and lithic fragments set in a whitish ash matrix that is related to subaerial reworking of the previous deposits.

Overall, the Spiaggia di Pollara succession is interpreted as the result of sin-eruptive reworking of the Upper Pollara pyroclastic deposits by means of a complex low-order system of streams along the steep slopes of the older Monte dei Porri and Corvo volcanoes and the flanks of the Pollara crater. The alternation of primary pyroclastic products and reworked equivalents accumulated in a morphological depression located between the outer slopes of the Pollara crater and the pre-existing volcanoes, on the bottom of which a shallow body of water of seasonal origin could occasionally be present.

## The use of mineral interfaces in sand-sized volcanic rock fragments to infer durability

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*Keywords:* durability, epiclastic fragments, interfacial boundaries, breakage.

The use of mineral interfaces, in sand-sized rock fragments, to infer the influence exerted by durability on the generation of sediments, has been determined for plutoniclastic sand (e.g., Heins, 1995). For volcanoclastic sand, it has received much less attention, and, this is the first attempt to make use of the volcanoclastic interfacial modal mineralogy of epiclastic fragments, to infer durability control at modern beach environment. Modern volcanoclastic sand was collected along five beaches developed on five islands (Alicudi, Filicudi, Salina, Panarea and Stromboli) of the Aeolian Archipelago, whereas one was sampled near the crateric centre of Stromboli volcano. Each sample was sieved and thin sectioned for petrographic analysis. The modal mineralogy of the very coarse, coarse and medium sand fractions was determined by point-counting of the interfacial boundaries discriminating 38 types of interfaces categories, both anisomineralic and/or anisostructural (e.g., phenocryst/glassy groundmass) and isomineralic, inside volcanic grains with lathwork and porphyric textures. A total of 47386 interfacial boundaries have been counted and, from the highest to the lowest durability, can be grouped as follows: a) ultrastable interfaces, categorized as Pl (Plagioclase)/Glgr (Glassy groundmass) >> Px (Pyroxene)/Glgr >> Ol (Olivine)/Glgr >> Op (Opaque)/Glgr >> Hbl (Hornblende)/Glgr >> Bt (Biotite)/Glgr >> Idd (Iddingsite)/Glgr >> Rt (Rutile)/Glgr; b) stable interfaces, categorized as Pl/Migr (Microlitic groundmass) >> Op/Migr >> Px/Migr >> Ol/Migr; c) moderately stable interfaces, categorized as Op/Px >> Op/Hbl >> Px/P >> Ol/Pl >> Bt/Op; and d) unstable interfaces, categorized as Pl/Pl >> Px/Px > Ol/Ol >> Op/Op >> Hbl/Hbl >> Bt/Bt. Volcanoclastic particles, if affected solely by abrasion, developed a rounded and smoothed form, with prevailing anisostructural interfaces such as Plagioclase/Glassy groundmass, Pyroxene/Glassy groundmass and Olivine/Glassy groundmass interfaces. Volcanoclastic particles that during transport process suffered fracturing and percussion have a sharp and angular form: this combined transport mechanisms produce mainly isostructural interfaces such as Plagioclase/Plagioclase, Pyroxene/Pyroxene, Hornblende/Hornblende, and, to a lesser extent, Biotite/Opaque and Biotite/Glassy groundmass interfaces. Thus, we should be aware that, especially for volcanoclastic particles of the stratigraphic record, interfaces types abundance and diversity are controlled by pre-burial transport processes that bias compositions towards glassy-rich volcanoclastic interfaces, and with an underestimation of the isomineralic ones.

Heins W.A. (1995) - The use of mineral interfaces in sand-sized rock fragments to infer ancient climate. Geological Society of America Bulletin, 107, 113-25.

## Petrography and provenance of Santa Maria Island shelf sand, Azores

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*Keywords:* volcanoclastic sand petrography, volcanic island sedimentation.

Santa Maria is the oldest island of the Azores Archipelago with late Miocene to  $\approx 2.8$  Ma onshore volcanism (Ramalho et al., 2020). Source rocks outcrops consist mainly of mafic subaerial pyroclastic and lava flows, and less abundant submarine lava flows, with minor sedimentary rocks, constituting a multiple provenance assemblage for the terrigenous sediment of the island shelf (Ramalho et al., 2017). The insular shelf that surrounds the island is wider and deeper on the northern side than on the other sides (Ricchi et al., 2020). The Pico Alto volcanic complex, constitute the main source rocks along the island's northern, southern, and eastern shelf sectors whereas the western shelf sector is mostly carved in the Anjos volcanic complex. The Pico Alto volcanic complex is largely composed of effusive submarine sequences at the base and subaerial flows at higher elevations. The Anjos Volcanic Complex is overwhelmingly subaerial in nature and dominantly composed of ankaramitic lava flows. The Touril Volcano Sedimentary complex corresponds to a dominantly clastic sequence intercalated by hydromagmatic tuffs and submarine effusive products (Ramalho et al., 2017), exposed on both northern and southern parts of the island. 32 shelf sand samples from Santa Maria were selected for petrographic inspection. On average, these sands constitute a volcanolithic petrofacies. The sand from the northern shelf of Santa Maria is composed mostly of black and brown glassy volcanic particles exhibiting microlitic, vitric and lathwork textures. The concentration of orange glass particles in the shelf sand is higher on northern, eastern, and southern shelf sectors than in the western shelf sector. These orange glassy textures have been sourced from the submarine volcanic products of the Pico Alto Volcanic complex. Also, exotic pyroclastic rocks, especially abundant in the northern shelf sedimentary archive have been recorded by the aphyric colourless pumice fragments, and likely sourced from nearby islands (e.g., São Miguel), given that volcanic rocks at Santa Maria are mafic and did not produce pumice sequences. A very small percentage of altered labile grains such as olivine and the paucity of altered volcanic lithics reflect the weathering-limited erosion regime of the island. The sedimentary record of Santa Maria's shelf, therefore, mainly reflects the composition of the source rocks exposed along the immediately adjacent eroding coastline, suggesting very little lateral sediment transport between shelf sectors and limited contributions by stream sources from the interior of the island.

Ramalho R.S., Helffrich G., Madeira, J., Cosca M., Thomas C., Quartau, R., Hipolito A., Rovere A., Hearty P.J. & Avila S.P. (2017) - Emergence and evolution of Santa Maria Island (Azores) - the conundrum of uplifted islands revisited. *Geol. Soc. Am. Bull.*, 129, 372-390.

Ramalho R.S., Quartau R., Hoskuldsson A., Madeira J., da Cruz J.V. & Rodrigues A. (2020) - Evidence for late Pleistocene volcanism at Santa Maria Island, Azores? *J. Volcanol. Geoth. Res.*, 394, 106829.

Ricchi A., Quartau R., Ramalho R.S., Romagnoli C. & Casalbore D. (2020) - Imprints of volcanic, erosional, depositional, tectonic and mass-wasting processes in the morphology of Santa Maria insular shelf. *Mar. Geol.*, 424, 106163.



## Searching for large magmatic events signature in the sedimentary record: a mineralogical, geochemical and isotopic study of the Bonarelli level (Gubbio, Italy)

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*Keywords:* mercury anomalies, LIPs, Bonarelli level.

Throughout the Earth's history, large magmatic events have had a strong impact in triggering dramatic paleo-environmental changes. The emplacement of the Large Igneous Provinces (LIPs), occurred between 250 and 50 Ma, has been proved to be coeval with Phanerozoic Oceanic Anoxic Events (OAEs) and large mass extinctions (Takashima et al., 2006). These events leave a signature in the sedimentary record, both at local and global scale, that can be detected by geochemical anomalies (Sanei et al., 2012). The Bonarelli level, a ~0.9-m thick layer made up of organic matter-rich shale exposed at Valle della Contessa section in Gubbio (Italy) within the pelagic limestones of the Scaglia Bianca Formation, is a marker of the OAE2 (Cenomanian-Turonian, ~93 Ma, e.g., Tsikos et al., 2004). This event is considered to be linked with submarine volcanism of the High Arctic and Caribbean LIPs, although clear evidence is missing at present. Geochemical tracers such as mercury (Hg), are proxies for large eruptions in sedimentary rocks worldwide (e.g., Grasby et al., 2019), and allow to correlate LIPs with oceanic anoxic events. At this aim, a detailed multidisciplinary study was conducted combining X-ray diffraction, petrographic and geochemical (Total Organic Carbon,  $\delta^{13}\text{C}$ , Hg concentration, trace elements, Hg, Sr and S isotopes) analyses on samples collected from both the Bonarelli level and the Scaglia Bianca Formation.

Results show that quartz (from 30 to 70 wt. %), phyllosilicates (from 20 to 60 wt. %), sulphates like baryte and jarosite (up to wt. 7%), and pyrite (up to 20 wt. %) are the mineral phases present in the Bonarelli level. Two sharp Hg anomalies up to ~1600  $\mu\text{g}/\text{kg}$  are here observed that correlate positively with chalcophile elements like Cu, Ni and Fe and with the total content of sulphate and sulphide, likely the main Hg host-minerals. We excluded a major effect of organic matter accumulation on the observed Hg anomaly looking at the Hg/TOC ratios (up to 220 Hg ( $\mu\text{g}/\text{kg}$ )/TOC wt. %). Isotopic analyses indicate a (deep) magmatic source for Hg ( $^{199}\Delta\text{Hg}$  ranging from -0.05 ‰ to 0.02 ‰) and a continental source for Sr ( $^{86}\text{Sr}/^{87}\text{Sr}$  of 0.70812-0.70978). Our results suggest that the Hg anomalous concentrations supported by Hg isotopic data have a mantle origin.

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## An update on numerical modeling of Vulcano Island

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Keywords: volcano modelling, volcanic risk.

The hydrothermal activity results in the heating and pressurization of hydrothermal fluids, which in turn induces changes in different geophysical parameters. Monitoring the geophysical observables, which are the surface expressions of processes that are not directly accessible, and developing modeling tools for their interpretation are the keys to opening up new perspectives in the exploration and monitoring of hydrothermal areas. In particular, pressure, temperature and density changes induced by fluid circulation are computed using the TOUGH2 numerical code, a well-known multi-phase multicomponent software for simulating fluid flow and heat transfer in porous media for a two-phase flow, which incorporates the equations of state for supercritical water extending the working range of the commercial version of TOUGH2 by using IAPWS97 formulation for water properties in the temperature and pressure range 0–1000°C and 0–100 MPa, respectively. Subsequently, the obtained variations referred to the values achieved at the steady-state, are used to compute the related ground deformation and gravity changes by a specifically thermo-poroelastic solver developed under the software COMSOL Multiphysics. The two codes, TOUGH2 and COMSOL Multiphysics, are linked by programming new specific subroutines for automatic sequence execution and data transfer. Devising multidisciplinary computational experiments enable us to learn how the hydrothermal system responds to unrest and which fingerprints it may leave in the geophysical signals. In view of the recent success in modeling the 2005 unrest with fumarole temperature increase up to about 400°C (Stissi et al., 2021), we are improving the Vulcano numerical model in full 3D settings with the aim to include not only the fumarolic duct and the crater fumarolic field but also the NNE main fracture related to the recent CO<sub>2</sub> degassing at Vulcano (Federico et al., 2023). Our attempt to simulate the cyclic episodic unrest at Vulcano island (Diliberto, 2011) shows the important role of permeability transients within the highly fractured crater area in controlling fluctuations in gas emission and temperature. The implementation of an extended 3D numerical model that will be linked to detailed geochemical and geophysical prospecting is needed to better define the spatial distribution of fractures that may compromise the integrity of the rock layers and consequently strongly control CO<sub>2</sub> degassing. For a better characterization, conventional prospecting methods could be complemented by the use of high spatial density strain measurements (Jousset et al. 2018; Currenti et al., 2021, 2023) and then included in the numerical model, that will become a “live” and useful tool for a better understanding of the Vulcano system.

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## **Volcano-tectonics and hydrothermal dynamics enhancing landscape modifications and sediment generations in a small scale basin routing system: the case of the northern Monte Epomeo at Ischia, Southern Italy**

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*Keywords:* erosional processes, slope stability, hydrothermal alteration.

Active volcanic environments can be considered a typical setting to generate sediments due to their rapid processes of growth, deformation and alteration, and heterogeneity of volcanic structures and local stress distribution as well. Ischia is an active volcanic island within the Gulf of Naples, characterized by the steep relief of the Monte Epomeo (787 m asl), a volcano-tectonic horst located in the central area of the island. Its complex volcanism began prior to 350 ka and continued, with phases of quiescence, until the last eruption (AD 1302). A caldera-forming eruption occurred 55 ka ago, followed by a resurgence process generating a net uplift of about 900 m since 33 ka (Sbrana et al., 2009).

Weathering, transport, hydrodynamics and hydrothermal alteration contribute to variability of the processes of volcanoclastic sedimentation and affect the slope stability, as well documented in the western and in the northern areas of the island (Selva et al., 2019). The Monte Epomeo can be considered a sort of basin routing system at a small scale, since it is the main source of sediments due to denudation processes and surface erosion enhanced by the recent volcano-tectonic dynamics and hydrothermal alteration. Our study focus on the erosional processes which affected the northern Monte Epomeo and we present a multidisciplinary research combining mineralogical, petrological, geochemical investigations with UAV photogrammetry techniques. The investigated area is Montagnone-Monte Cito, a hydrothermalized area close to Casamicciola town, which was the epicenter of the seismic event which occurred on August 21, 2017, with magnitude 4.0 (Piochi et al., 2019; Selva et al., 2021), and was destroyed by a powerful landslide on November 2022.

Mineralogical and geochemical analysis (X-ray diffraction, electron microscopy with energy dispersive microanalysis, and portable X-ray fluorescence) were performed to characterize altered deposits and were repeatedly carried out in the area. These data were correlated with geomorphological modifications obtained by comparison between 3D point cloud acquired in March and July 2022. The comparison between the two photogrammetric surveys shows a general loss of outcropping deposits. Major loss of material is observed along a steep valley running in the NNE - SSW direction and along a EW direction within the alteration area. Furthermore, volume's loss is evidenced along an alignment with a NW SE direction, probably related to unmapped fracture, with a trend parallel to faults characterizing the area further upstream. The identified structural features are preferential routes for the surface water flow and affected by erosion enhanced by the diffuse hydrothermal alteration processes. Our multidisciplinary approach contributed to evaluate evolution and rock fall susceptibility of solfataric terrains affected by hydrothermal dynamics, for a better understanding of erosional processes.

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## Field, mesoscopic, mineralogical, geochemical and textural features of a lithified tephra intercalated in the post-evaporitic Messinian level (5.5 Ma) of the Central Apennines in Italy

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Keywords: tephra, texture, deposition.

Tephra indicates pyroclastic materials along stratigraphic successions; they can be primary if pyroclasts erupted are directly settled in subaerial or submarine environments, or secondary if remobilised by sedimentary processes. However, such discrimination is challenging, especially for old, lithified and limitedly exposed deposits. Here, we investigate several sections of an endured tephra dated at 5.5 Ma and largely widespread in the central Apennine to further highlight its salient features (Trua et al., 2010; Cosentino et al., 2013; Potere et al., 2022).

Field- and mesoscopic-scale (on polished oriented surfaces) observations do not evidence an erosive basal contact, intra-basinal clasts and gradation at the sampled scale. As a function of the site, this tephra is mainly made of massive horizons with minor plane-parallel, curvilinear, cross laminations and local soft-sediment and fluid escape structures.

XRPD and SEM show that magmatic minerals (quartz, feldspar, biotite) are low, sedimentary crystals (sheet-silicates and carbonates) are variable and the amorphous (volcanic glass shards) phase is abundant. Bulk geochemistry unveils that the tephra is SiO<sub>2</sub>-rich and MgO-poor, while H<sub>2</sub>O<sup>-</sup>, H<sub>2</sub>O<sup>+</sup> and CO<sub>2</sub> ranges are comprised between 0.9-5.6, 5.6-7.2 and 0.03-3.44 wt.%, respectively; SiO<sub>2</sub> is inversely related to CaO + CO<sub>2</sub> reflecting the abundance of sedimentary carbonates. EPMA points for a calc-alkaline and almost constant rhyolite composition of pyroclasts, with SiO<sub>2</sub> > 70 wt.%, MgO < 0.2 wt.% and Na<sub>2</sub>O + K<sub>2</sub>O 5.5-7.5 wt.%.

2D-image analysis on micro-photographs obtained at the SEM furnishes the abundance of phases (area%) plus the area, length, width, aspect ratio and perimeter of each pyroclast; length and area of pyroclasts were used to construct 2D grain-size distributions and related parameters (M<sub>Z</sub>, σ<sub>i</sub>, SK<sub>i</sub>, K<sub>G</sub>). Glassy pyroclasts are the most abundant fraction in all samples (45 to 98 area%), carbonates are present only at some stratigraphic height (up to 40 area%) and magmatic minerals are invariably low (< 5 area%). The sampled shards have sizes between 10 and 200 μm (lengths < 100 μm are the most abundant), are very highly sorted, exhibit blocky and platy shapes with bubble-wall edges and are poorly vesiculated. Lengths of pyroclasts are not preferentially oriented. Roundness, elongation and angularity of pyroclasts are typical of primary fallout or pyroclasts with limited or absent abrasion and/or comminution; however, the presence of minor horizons in some sites with curvilinear and cross structures could be also indicative of remobilisation unable to alter the primary textural features of pyroclasts.

All these aspects support the deposition of the tephra from a large (and still unknown) eruption, possibly with limited syn-sedimentary remobilisation within the basin, from a volcanic-arc context active at 5.5. Ma in the Euro-Mediterranean region. The tephra is useful like chronostratigraphic level.

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## The Messinian monomagmatic turbidites in the Central Apennines: sedimentological and petrographic features from volcanoclastic layers in the new Amandola section (Marche, Italy)

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*Keywords:* monomagmatic turbidites, volcanoclastic deposits.

An Upper Miocene volcanoclastic interval, up to about 2.5 m thick, is exposed at several locations along the deep-water foreland basin system of central Apennines. Geochronological dating converges to indicate that these volcanic sediments were deposited at about 5.5 Ma (e.g., Odin et al., 1997), whereas mineralogical analyses indicate that the component strata comprise 80% of blocky and vesicular glassy shards and that the mineralogical phases represent the remaining 20% (Potere et al., 2022). These features, and the observed silica and alkali content, suggest that the volcanoclastic layers can be considered as the product of a calc-alkaline rhyolitic magma (Guerrera et al., 1986; Potere et al., 2022; Trua et al., 2010). In order to determine transport directions and depositional processes, in this study the volcanoclastic strata exposed on a recently made road cut near the town of Amandola (FM) have been investigated. At this new outcrop, the volcanoclastic horizon is 1.90 m thick and it comprises twenty-three beds, each recording a discrete density flow depositional event. Individual beds are characterized by sedimentological features typical of the product of turbidity currents, such as: i) flame structures along the contacts; ii) overall normal grain-size grading formed during temporal flow deceleration; and iii) the occurrence of a massive (i.e., “structureless”) Ta division overlain by plane-parallel and cross-laminated Tb and Tc divisions, with the massive division indicating deposition at rates of suspended load fallout high enough to suppress tractional transport and the laminated divisions indicating final flow stages, in which flow density and velocity are sufficiently low for bedform development to occur. The absence of laminated Tb and Tc divisions in some of the beds can be explained by the narrow grain-size distribution (i.e. the presence of well-sorted sediment) or by the post-depositional erosion of these divisions by succeeding sediment gravity flows, thus forming a set of amalgamated, top-truncated Ta beds. Principal paleocurrent directions indicate deposition from NE- and NW-directed paleoflows. Collected samples have been investigated via optical microscopy, SEM and EPMA, through which both petrographic and chemical composition are described. Microscopic observations result in glass shard morphologies description (i.e., bubbles' walls, vesiculation and stretched shapes). The high glass shard content, the glass coating of biotite and feldspar phenocrysts indicate an original primary deposition. The homogeneous composition of the volcanoclastic beds and the absence of interbedded hemipelagic marls is strong evidence that these turbidites were fed by a single eruptive event and that they may have originated either from flow transformation of pyroclastic flows, or rapid remobilization of stored volcanoclastic material.

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## Grain size analysis of modern beach sands in El Hierro and Tenerife islands (Canary Islands, Spain)

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Keywords: Canary Island, grain size, provenance.

The Canary Islands archipelago is located 100 km off the east coast of Africa and includes seven volcanic islands, with a total area of almost 7,500 km<sup>2</sup>. Among the islands, El Hierro, Tenerife and La Palma are the only active volcanoes.

El Hierro (1.1 Ma) is the smallest and youngest island in the archipelago, with a surface area of 269 km<sup>2</sup>. It has a total subaerial and submarine volume of ca. 5,500 km<sup>3</sup> and rises about 5,500 m from its submarine base to a depth of 4,000 m (Schmincke, 1990). Islandic eruptions have been mainly basaltic in nature, and accumulated thick lava flows and a large number of scoria and cinder cones across the island (Carracedo et al., 2001). In addition, very rare volcanic sequences on the island, trachytic in composition, have been documented (Guillou et al., 1996). Tenerife (11.9 Ma), is the largest (2034 km<sup>2</sup>) and highest island in the archipelago (3718 m). It is the emerged part of a large pyramid-shaped volcanic stack that rises from a depth of 3,000 m to its highest elevation, the Pico del Teide, at 3,718 m. It was built by the accumulation of volcanic and volcanoclastic sequences of different geochemistry over several million years. The southern Tenerife pyroclastic area preserves thick ignimbrite deposits, as well as ash and pumice fall layers of the Las Cañadas caldera, together with lava flows and landslide deposits, interspersed with palaeosols (Brown et al., 2003). Many are, again, the cinder and scoria cones preserved on the island. Nineteen beach sediment samples were analyzed: nine samples came from El Hierro and ten samples from Tenerife islands, respectively. Sediments were then mechanically sieved using  $1\Phi$  intervals (from  $-1\Phi$  to  $4\Phi$ ) in order to obtain grain-size distribution. All beach sediment samples exhibit unimodal grain size distributions, dominated by the sand fractions. The beach sand from El Hierro island ranges from very coarse to very fine sand, whereas most Tenerife beach samples are characterized by coarse sand, with only one sample of fine sand.

Grain-size distributions of the sand delivered to El Hierro and Tenerife beaches seem to be mainly controlled by the texture and composition of their source rocks under elaboration, weathering and/or erosion. The very coarse to fine beach sand of El Hierro are supplied by island instability and re-laboration of cinder cone deposits, with a less contribution of direct erosion of lava flows sequences, whereas the coarse sand of Tenerife is mainly linked to a provenance from basaltic lavas, and, to a lesser extent, trachibasaltic and phonolitic in composition, ignimbrites and pyroclastic flows contribution. Climate plays another important role in sediment production, because both islands have different microclimates, more humid in the north-northwestern side of the islands, more arid and windy to the south and southeast.

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## Aeolian processes on Mars, present and past

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Keywords: Mars, dunes, ripples.

The action of the wind was, and is at present-day, one of the major force shaping the Martian surface. Vast active dune fields and aeolian ripples, together with yardangs and wind streaks are abundant on the surface and have been observed by orbiters and landers. Here we focus our attention to depositional features, dunes and ripples. Dunes on Mars are dark-toned in orbiter images, reflecting a basaltic composition and are mostly accumulated around the north polar cap (Olympia Undae field, 470000 km<sup>2</sup>). Dunes source from the upwind sand-rich polar layered deposit with seasonal processes (CO<sub>2</sub> ice covering) controlling sand supply and availability. Repeating targeting by the HiRISE camera onboard the NASA Mars Reconnaissance Orbiter (images at 25 cm/pixel resolution) show moving dunes with high fluxes (Chojnacki et al., 2021). Dunes in equatorial/tropical areas of Mars are mostly accumulated inside impact craters, especially in the highly cratered southern highlands. In Gale Crater, the landing site of the NASA Mars Science Laboratory, they have been directly imaged by rover cameras (Lapotre et al., 2016). Even visible from orbits, it has been shown that dunes are sculpted by large, meter-scale, sand ripples which are in turn overlaid by more regular cm-scale ripples. The origin of these features, and the superposition of three bedform classes (dunes, large ripples and cm-scale ripples) is a matter of debate in the scientific community (Lapotre et al., 2016; Sullivan et al., 2020). Together with dunes and sand ripples, a particular class of ripples called “megaripples” or “coarse-grained ripples” was observed. These features are bright-toned and can be active when associated with dunes, or static. Bright megaripples have been observed in situ in all the landing sites and form complex patterns suggesting regional changes in the wind regime in different geological epochs (Fenton et al., 2018). Static megaripples (or dunes) have been observed in the Zhurong landing site. Their inactivity is related to the formation of crusts that show polygonal fractures enriched in hydrated minerals. It was thus proposed that such a crust could be related to recent aqueous activity and atmosphere-surface water exchange on Mars. Locally, static or slowly-moving megaripples or dunes can seed the erosion of the underlying bedrocks in scalloped terrains forming the so-called periodic bedrock ridges (PBRs). PBRs have been studied in situ in Gale Crater and were hypothesized to form during the exhumation of Aeolis Mons. Interestingly, PBRs have also been observed in Oxia Planum, the landing site of the future ESA ExoMars mission. Collectively, Mars hosts a wide variety of aeolian bedforms that can be used to reconstruct its present-day circulation and its past geological history.

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## **Pillow basalt, pyroclastic input and geomorphic processes on the genesis of the Monte Cerviero upland soils (Calabria, Italy)**

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*Keywords:* soil, pillow basalt, pyroclastic input.

The knowledge of soil formation processes affecting pillow basalt, in the mountainous environments of the central Mediterranean area is quite poor. This study provides new data of the genesis, evolution and geochronology of two representative soil profiles developed on alkaline pillow basalts in the Mt. Cerviero area (Calabria, southern Italy) using a multidisciplinary approach, including macro/micromorphological and chemico-physical pedological investigations, as well as petrographic, mineralogical and geochemical analyses. These analysis, also permitted us to discriminate the main features inherited from the hydrothermal alteration in a submarine environment from the chemical weathering processes under meteoric conditions. The radial weathering pattern of the bedrock appears controlled by the subspherical shape of the pillows and the outer concentric rims, affected by surface cracking, flaking and illuviation of Fe-Mn oxides and clay coatings. Irregular geochemical patterns and CIA values across the soil profiles and the pedological analyses indicate a lithological discontinuity between the bedrock and the topsoil horizons, which suggest a rejuvenation of the pedogenetic front, due to colluvial and erosive processes and allochthonous pyroclastic input. In accord with this, the soil profiles display an overall poor to moderate degree of development, despite the old ages of emplacement (Jurassic) and exhumation (Miocene) of the pillow basalts. Illuviation of clay and iron-manganese coatings in the Bt horizon of soil profile MC1 suggests an emplacement under warm-humid conditions probably during the last interglacial. The degeneration microtextures of the clay pedofeatures, caused by argilloturbation, bioturbation and/or cryoturbation processes, indicate their relict genesis. A Late Pleistocene to Holocene age estimated for both soils is supported by the trachytic composition of the volcanic glass fragments and micropumices, identified in the topsoils of both profiles which is consistent with a provenance from the explosive eruptions of the Campania province (Vesuvius and Campi Flegrei) or the Aeolian Arch (mainly Lipari and Volcano Islands). Therefore, this work demonstrates that the Andosol-like field appearance can be used as a potential indicator of cryptotephra, even when andic properties are not well-developed. This finding suggests that a possible contribution of fine volcanic ash to soil formation in soils of non-volcanic areas should be investigated in more detail, especially at the submicroscopic level, when andic properties or at least andic-like field features occur. This should lead to a partial reassessment of the volcanic versus non volcanic origin of certain Andosols worldwide and claims a good field work with detailed description of soil properties as a basis for choosing the best-suited laboratory methods, to fill the gap between ordinary lab and field results.

## Heavy minerals as indicators of coastal erosion processes: the Apulian coast case study

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*Keywords:* heavy minerals, coastal erosion, Ofanto river.

The heavy volcanic minerals occurring in the sediments of the Ofanto river, mainly represented by pyroxene, amphibole and melanitic garnet, witness the important contribution of Monte Vulture on the sediment production. This sediment is transported by the Ofanto river to the Apulia coast and dispersed northward by the main longshore current, and southward by the littoral currents of the Adriatic Sea. The result is that even the beach sands of the Adriatic coast of Apulia, from the Gulf of Manfredonia to the Otranto promontory, are locally made up of high amounts of heavy minerals concentrated in dark layers and placers, easily distinguishable from the lighter carbonaticlastic fraction.

The grain size of the sediments and the abundance of volcanic minerals are not constant along the coast. These variations could be attributed to differences in the coastal bathymetry and isobaths depths, but also to coastal erosion processes. In fact, during the last sixty years an important decrease of load of the Ofanto river has been recorded. This decrease is partly due to climatic variations but above all to the numerous dams built inside the drainage basins. As a consequence of the reduced supply of sediment, the Apulia coast shows a significant retreat, at places intensified as a consequence of anthropic works along the coast (harbours, piers etc). As the erosion mainly affects the light carbonaticlastic fraction, the stretches of coastline affected by the highest rates of erosion are also characterized by the highest amount of heavy volcanic minerals.

Also the grain microtextures of the pyroxene vary significantly along the coast, as a result of chemical and mechanical processes during their transport. At the Ofanto mouth most of the pyroxenes are angular or with poorly rounded edges. Mechanical fractures, collision pits, arcuate steps, straight steps and V-shaped pits are common. Chemical weathering features, as small chemical pits and some solution hollows, are rare. Only few crystals show an intense chemical weathering process producing numerous lenticular (almond-shaped) depressions. Moving northward and southward from the mouth the features related to chemical weathering and the roundness of the pyroxene crystals increase, testifying the longer transport. However, the high roundness and weathering of some crystals also close to the mouth could be the effect of continuous reworking, thus witnessing the decrease in the river sediment supply.

The results of the study demonstrated that there is a relationship between the presence, abundance and morphology of heavy minerals and the phenomenon of coastal erosion.

## **S34.**

### **Fluid-rock interaction and terrestrial heat for provenance analysis, traceability and sustainable use of natural resources**

#### *CONVENERS AND CHAIRPERSONS*

*Claudio Natali (Università degli Studi di Firenze)*

*Gianluca Bianchini (Università di Ferrara)*

*Cristina Pauselli (Università degli Studi di Perugia)*

*Massimo Verdoya (Università di Genova)*

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## The seismic imaging of the Nesjavellir (Iceland) geothermal production area

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*Keywords:* seismic imaging, Iceland, geothermal.

The Nesjavellir geothermal field is situated in South West Iceland. OR-Reykjavík Energy generates electricity and hot water for district heating at two power plants around Hengill: the Nesjavellir power plant, our target area, to the north and in Hellisheiði to the southwest. Volcano-tectonic processes, natural geothermal activity and geothermal production contribute to the seismicity recorded in this area.

This work aims to improve our knowledge about the medium of the Nesjavellir geothermal area and nearby. We aim to provide elastic and anelastic properties of the medium through 3D and 4D velocity tomography, scattering and absorption imaging, earthquake locations obtained in the new 3D velocity model, 3D b-value mapping, and almost 150 new focal mechanisms of  $M_L \geq 0.5$  seismic events.

Below Nesjavellir low  $V_p/V_s$  ratios and low b-values are observed at shallow depth (due to low  $V_p$ ). High  $V_p/V_s$  ratios and high b-values are observed between 3.5 and 6 km depths (due to high  $V_p$  and low  $V_s$ ), which is in correspondence with the deepest seismicity characterized by a higher percentage of small events. Our results suggest the coexistence of distinct mechanisms that control seismicity, highlighted also by the different focal mechanisms computed for shallower and deeper earthquakes (Amoroso et al., 2022). From 4D analysis we observe the evolution of seismicity and a corresponding variation in the elastic medium properties as a function of the depth.

This work has been supported by PRIN-2017 MATISSE project, No 20177EPPN2, funded by Italian Ministry of Education and Research.

Amoroso O., Napolitano F., Hersir G.P., Agustsdóttir T., Convertito V., De Matteis R., Gunnarsdóttir S., Hjörleifsdóttir V. & Capuano P. (2022) - 3D seismic imaging of the nesjavellir geothermal field, SW-Iceland. *Front. Earth Sci.*, 10. <https://doi.org/10.3389/feart.2022.994280>.

## **New data on Monterotondo Marittimo and Sasso Pisano geothermal areas: a focus on the carbon dioxide, methane and heat emissions (Tuscany, Italy)**

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*Keywords:* geothermal system, carbon dioxide, geothermics.

The Larderello-Travale geothermal area is located in the inner part of Northern Apennines, specifically in the Tuscan region, characterized by large-scale steam dominated system. In this particular area the reservoir temperatures exceed 350°C. This condition (high heat flow) is due to the presence of a thermal anomaly caused by the intrusion of a huge Pliocene batholith into the upper crust. It is possible to distinguish a geological setting that consist of Alpine tectonic units which overlaps the low-grade metamorphic basement (Granieri et al., 2022). In this work, the relationships between carbon dioxide and methane emissions and heat flow are investigated in the area between Monterotondo Marittimo and Sasso Pisano, located in the south-eastern sector of the Larderello-Travale geothermal region. CO<sub>2</sub> fluxes range from 0.1 gm<sup>-2</sup>d<sup>-1</sup> to about 20,000 gm<sup>-2</sup>d<sup>-1</sup>, while CH<sub>4</sub> fluxes, available for a lower number of points, vary between 0 and 637 gm<sup>-2</sup>d<sup>-1</sup>. Soil temperatures range from 8.0°C to 100°C, with an average of 37.8°C. CO<sub>2</sub> fluxes show a polymodal statistical distribution with (i) a background population characterised by an average CO<sub>2</sub> flux in the order of 20.9 g m<sup>-2</sup> d<sup>-1</sup> and (ii) anomalous population with an average CO<sub>2</sub> flux 741 g m<sup>-2</sup> d<sup>-1</sup>. CH<sub>4</sub> fluxes higher than instrumental sensitivity were measured only on measuring points belonging to the anomalous CO<sub>2</sub> flux population. The areas characterized by anomalous gas fluxes are alligned along an north-south narrow band and show an evident soil temperature anomaly (reaching values close to 100°C), suggesting that soil degassing (1) is controlled by a NE-SW main fault zone and (2) is associated to a significant process of steam condensation. In the anomalous areas, the CO<sub>2</sub>/CH<sub>4</sub> ratios by weight vary between 1.6 x 10<sup>-4</sup> to 1.0 x 10<sup>-1</sup> and fall in the range of variation observed for the geothermal fluids of the Larderello-Travale region (Truesdell & Nehring, 1978; Chiodini et al., 1991; Chiodini & Marini, 1998).

Assuming that the soil is heated by steam condensation, a thermal energy release associated to the degassing process of about > 300 MW is estimated for the study areas.

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## Understanding water-rock-biota interaction in the Critical Zone using stable isotopes: examples from Arctic to Mediterranean region

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*Keywords:* stable isotopes, critical zone.

The Critical Zone (CZ) is the lithosphere-atmosphere boundary, including the land surface and its canopy of vegetation, rivers, lakes, and shallow seas and extending through the pedosphere and groundwater zone, where complex physical, chemical and biological processes occur and control the transfer and storage of water and chemical elements. The study of the CZ requires investigations of earth-surface processes crossing time scales of seconds to that of millennia. To cross such scales requires measurements of today's fluxes (water and solutes) and the records of those fluxes in the geologic record (soils and sediments). Within the CZ, isotopic fractionation of elements is affected by multiple processes so that isotopes can enable fingerprint processes and quantify element fluxes over a broad range of compartments and timescales. This approach is particularly helpful when researchers use multiple isotopes in the same setting to explain complex systems.

Understanding the water-rock and biota interaction is a key issue for ensuring the CZ functioning and the geochemical characterization of different geological compartments. This understanding will help to predict the CZ evolution in response to environmental modifications due to tectonic, climatic or anthropogenic forcing.

Arctic regions, high mountains and wetland are heavily affected by climate change and the knowledge of present and past processes is fundamental to preserve these ecosystems and human communities. Here, three examples illustrate how elemental and stable isotopes are powerful tool to trace soil-water-vegetation interaction.

Climate-driven degradation of permafrost alters the water balance and hydrological processes as well as their seasonal dynamics within the cold region CZ. The Bayelva catchment (Western Svalbard-Norway) is an ideal site for surveys on hydrological response during active layer development in a dominantly mineral soil to understand how subsurface and surface waters interact.

High mountains are among the regions most affected by climate changes, which alter the complex network of interactions between climate, biological, and sociocultural structures in these regions. Soils are a critical in regulating many ecological processes that provide fundamental ecosystem services. Their formation factors may be operating at faster timescales than is typically considered in recently deglaciated alpine environments, yielding important implications for critical zone services (e.g., water retention, preservation of carbon and nutrients, and chemical weathering). Examples from Gran Paradiso site (Italy) will illustrate carbon storage processes in alpine landscape and biotic and abiotic interactions that drive soil development, nutrient release, and carbon storage.

Lacustrine and palustrine wetlands are one of the most important ecosystems, and play a key role in regulating runoff, mitigating floods, climate regulation and improving water quality and storage. As lake sediments collect most of the solid and dissolved fluxes from their catchment, they are invaluable and sometimes, underrated, archives for reconstruction of forcing mechanisms as well as reactions in the wetland CZ, both through the biotic and the abiotic compartments. Examples will describe carbon cycle in a Mediterranean lacustrine area in different compartment (sediment, water, gas) and how stable carbon isotopes can reconstruct the past history of the catchments.

## Stable isotopes as tracers of provenance in Holocene sediments from the Venetian-Paduan area (NE Italy)

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*Keywords:* Holocene sediments, tracers of provenance, stable isotopes.

This work reports an ab initio study on the carbon (C), nitrogen (N), and sulphur (S) elemental and isotope compositions of the Padanian Plain sediments collected in the Venetian-Paduan area (North Eastern Italy).

The investigated sediments were already characterized by previous research as Western- and Eastern-Alpine provenance, and were conveyed to the plain by Po and Adige River, respectively (Natali & Bianchini, 2017).

The sample group characterised by high Ni/Zn and Cr/Pb values conforms to modern Po River sediments, whereas a second group showing low Ni/Zn and Cr/Pb values conforms to the geochemical signature of modern Adige River sediments.

However, this work challenges these assertions observing that  $^{13}\text{C}/^{12}\text{C}$ ,  $^{15}\text{N}/^{14}\text{N}$ ,  $^{34}\text{S}/^{32}\text{S}$  are significantly different in Po and Adige River sediments. Our hypothesis is that the CNS geochemical signal is 1) mainly regulated by the inorganic and organic fractions included in the alluvial sediments, and 2) these organic fractions have in turn a specific composition in the distinct source catchments.

For carbon, the TC isotopic fingerprint depends on the OC and IC contents and their relative isotopic ratio. The difference cannot be related to a distinct fertilization history as proposed for other study-cases (Kanstrup et al., 2011) and must be interpreted as a distinctive natural character of the sediment source area, which is peculiar for every hydrological basin (Li et al., 2020).

In general, the  $\delta^{13}\text{C}_{\text{OC}}$  is controlled by the distribution of C3 and C4 plants, as according to their photosynthetic pathways ranges from  $-21\text{‰}$  and  $-35\text{‰}$  for C3 plants and from  $-9\text{‰}$  to  $-20\text{‰}$  for C4 plants. Moreover, in aquatic ecosystems the isotopic composition of the transported organic matter is also influenced by the autochthon growth of biomass constituted by algae and plankton. On the other hand, the  $\delta^{13}\text{C}_{\text{IC}}$  is controlled by the presence of lithogenic (i.e., primary) or pedogenic (i.e., secondary) carbonates, which have values close to 0‰ or negative, respectively.

We found out that the different CNS isotope fingerprint of Po and Reno River sediments is natural and not induced by anthropogenic contributions, but doesn't necessarily reflect a lithogenic signature, i.e., it is not solely related to different parent rock types in the Po and Adige River catchments. In fact, we infer that bio-geochemical processes, characterized by distinct ecological conditions in the Po and Adige River catchments, are recorded in the CNS isotopic signatures. Po River sediments are generally few hundreds of years older and pertain to a basin having a path of nearly seven hundred kilometres, much longer than that of Adige River. Consequently, soils developed on Po River sediments are comparatively more mature and record a more complete spectrum of biogeochemical processes that were more intense and affected nitrogen/sulphur compounds generating the distinctive isotope signatures.

More in general, the presented data increase the knowledge on the local elemental and isotopic backgrounds. This is important because many pollutants contain significant CNS concentration and specific isotope composition. Therefore, they serve as natural baseline and will provide a new tool to recognize possible anthropogenic anomalies in the studied area.

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## **Terrestrial heat-flow: a basic tool for the geothermal potential assessment**

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*Keywords:* heat flow, thermal data, geothermal resources.

The terrestrial heat flow, also referred to as heat flow density (HFD), is of great interest not only in studies on tectonics and geodynamics, but also in many aspects of energy exploration. In particular, the evaluation of the temperature field, the mode of heat transfer in the subsurface, and the assessment of the geothermal potential rely on HFD data. Defining temperature at depth to identify geothermal resources depends upon the evaluation of the HFD based on equilibrium temperature measurements as well as thermal conductivity and heat generation rate assessment. Unfortunately, the superposition of different biases can contaminate the heat-flow values. Uncritically contouring can thus lead to misleading thermal patterns. Moreover, the uneven spatial distribution of heat-flow sites and the differences in measurement techniques may cause additional interpretation difficulties. Depending on the possible targets (e.g., calculation of crustal geotherms, modelling or characterization of advective systems, evaluation of geothermal energy potential), ad hoc filtering should be applied to remove the different effects. Within the Global Heat Flow Data Assessment Project (2021-2025) framework, initiated by the International Heat Flow Commission (IHFC), we reviewed heat-flow data collected during several surveys since the 1960s in the Italian peninsula and surrounding seas. The data, extracted from the Global Heat Flow Database (GHDB) and national reports, have been processed by adopting the new standard for reporting and storing heat-flow data recently established by the IHFC. The new database format has some distinct key features, providing information for evaluating the HFD data quality and discriminating the thermal regime (conduction or convection-dominated). This can be useful to address geothermal exploration and make decisions about future research. The original data sources of the Italian peninsula and surrounding seas were carefully inspected to discern whether HFDs are affected by deviations from purely conductive, steady-state heat. Data were critically reviewed, validated and corrected for terrain effects. New heat-flow data from deep wells were also inferred through a minimisation technique accounting for temperatures, radiogenic heat production and the thermal conductivity variation with depth. The new picture of the heat flow pattern forms a basis for further studies for the geothermal potential assessment.

## **Favorability map for geothermal resources of Sicily with focus on Hyblean plateau area**

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*Keywords:* geothermal resources, Sicily.

Italy is considered a geothermal country as it is the fifth producer of geothermal energy in the world and the first to produce electric geothermal on an industrial scale. Geothermal energy makes a significant contribution to renewable energy in Italy, but its future potential has yet to be fully assessed. For geothermal exploration we follow a step-by-step analysis program that starts from regional surveys and develops up to detailed analysis. Despite the high Italian geothermal potential, to date, only two geothermal fields located along the Tyrrhenian coast are exploited.

This work therefore seeks to propose a work of analysis of geothermal pre-feasibility of the area of the Hyblean Plateau, in particular in the area of the concession Irminio, located between Modica and Ragusa, where within the drilling well Irminio were identified temperature gradients of 90 °C at about 2500 m depth, in order to identify additional potentially exploitable areas.

The proposed procedure is that of Index Overlay in Qgis environment that allows to analyse and correlate and integrate thermal gradient data, heat flow, carbonate roof depth, in order to create a map of geothermal favourability that classifies the study area in more or less favourable areas to be exploited by conventional geothermal systems.

The obtained map of favourability shows that the area under consideration has a medium- low geothermal favorability, but by extending the study interest to a larger area are identified areas of medium-high potential in the area to the north and north-east of the Hyblean Plateau.

It is specified that the method applied in this work is the first step of analysis in the geothermal field and that the results may present uncertainties, but when compared with results obtained from similar analysis work carried out with sensitive data, they show that the methodology adopted is correct and that it must be integrated with more detailed analyses in order to assess the real geothermal potential of the study area.

## Deep U-tube heat exchanger breakthrough: combining laser and cryogenics gas for geothermal energy exploitation

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*Keywords:* laser drilling, cryogenic gas, heat exchanger.

The disruptive technology envisioned in the “Deep U-tube heat exchanger breakthrough: combining laser and cryogenics gas for geothermal energy exploitation (DeepU)”. Project is expected to revolutionise the geothermal energy sector, increasing the accessibility of deep geothermal resources for low-carbon heating and power generation. The ultimate goal is to create a deep (>4 km) closed-loop connection in the shape of a U-tube exchanger by developing a fast and effective drilling technology. A laser drill head is combined with special drill strings sustaining the coupled action of laser and cryogenic gas, responsible for melting, evaporating and cooling even the hardest rocks. The fine particles are transported to the surface in the gas stream via the earth tube required for the geothermal heat exchanger. Specific temperature control analysis and innovative laser lenses convey the heat and sustain multilateral drilling. In addition, gases have to be kept cryogenic over a long distance. These innovations guarantee the liquefaction and vitrification of the rocks from the ground surface to significant depths. In case a glazed layer is formed on the borehole walls, the obtained systems are physically isolated from the surrounding rocks and ready to be developed immediately after drilling. A press container has been set to perform the first laboratory tests with the novel lightweight laser and gas processing drill head and was equipped with monitoring devices. The petro-thermo-mechanical phenomena affecting different rocks will be analysed on granite, limestone and sandstone samples, and the borehole wall vitrification and integrity will be assessed. In addition, constant rates of penetration (ROP) upwards of 20 m/hr have been achieved, with relatively low energy inputs and no component wear that would be associated with mechanical engaging drilling methods. The project will analyse the exploitation potential and economics of the developed drilling technology utilising numerical simulations calibrated by the laboratory data. Furthermore, the legislative aspects and environmental standards related to the proposed solution are also assessed. The high-risk innovation presented in DeepU has the potential to make geothermal energy systems accessible anywhere in a targeted and demand-oriented manner, offering a complementary approach and an alternative solution to traditional energy storage and production, decentralizing the power supply also in areas where this is currently deemed uneconomic.

This research is funded by the European Union (G.A. 101046937). However, the views and opinions expressed are those of the author(s) only and do not necessarily reflect those of the European Union or EISMEA. Neither the European Union nor the granting authority can be held responsible for them.

## A novel separation technique for thallium isotope determination via MC-ICP-MS

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Keywords: Tl isotopes, chromatographic separation, MC-ICP-MS.

Thallium isotopes (<sup>205</sup>Tl and <sup>203</sup>Tl) are emerging as a new tool for investigating petrological and geochemical processes related with environmental issue, and specifically in tracing the origin of Tl in polluted sites. Thallium is a contaminant of growing concern from an environmental perspective and human health threats, being listed among the 13 priority pollutants.

The available methods for Tl separation prior to MC-ICP-MS analyses requires the use of relatively dangerous reagents and typically not available in common laboratories, such as Br<sub>2</sub> and SO<sub>2</sub> gases (Rehkämper & Halliday, 1999; Wang et al., 2023). We developed a novel and simple experimental method to overcome this issue, which resulted also in shortening analytical times with respect to previously adopted procedures.

Our experimental method, after conventional acid digestion, needs NaClO addition to the digested samples to ensure a full conversion of Tl into the Tl<sup>3+</sup> form. Then the obtained sample solution was loaded in HCl into a tandem column separation, consisting of TBP (tributyl-phosphate) resin (1<sup>st</sup> column) and Sr-resin (2<sup>nd</sup> column). The first column makes use of the TBP, which has a strong affinity for Tl<sup>3+</sup> (Ghersini, 1975; Bragagni et al., 2023; Wang et al., 2023). After eluting the matrix in HCl, Tl is eluted in HNO<sub>3</sub> directly onto the second column. The Sr-resin is only used to ensure that Pb is fully separated from the Tl fraction, thanks to its strong affinity for Pb. Such a procedure resulted in procedural Tl yield of 99±1.3%.

Prior to MC-ICP-MS measurements, purified samples were doped with Pb (NIST SRM 981). The instrumental mass discrimination was corrected by internal normalisation to Pb and sample-standard bracketing technique (Rehkämper & Halliday, 1999). Reference materials (AGV-1, BHVO-1, BCR-2, G-2) are used to assess the precision and accuracy of the data.

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## Provenance of Holocene sediments from the Venetian-Paduan area (NE Italy) by elemental and Pb-Sr isotopes analyses.

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*Keywords:* water-rock interaction, sediments traceability, isotope geochemistry.

This study investigates a set of sediment samples from the easternmost sector of the Po Valley (north of the present-day Po River course), an area filled during the Holocene by alluvia from two interfering fluvial systems (Po and Adige). The investigated samples represent a subset of a wider collection already characterized through X-ray fluorescence (XRF) and classified for their provenance on the basis of the geochemical composition following the criteria reported in Natali & Bianchini (2017). In this work, these samples were analyzed for their trace elements composition by Inductively Coupled Plasma Mass Spectrometry (ICP-MS), and for lead (Pb)-strontium (Sr) isotope ratios by Thermal Ionization Mass Spectrometry (TIMS). The ICP-MS data show a lower dispersion and higher consistency with respect to XRF data, as highlighted by the distribution of siderophile and chalcophile elements, leading to a better discrimination of the sediments provenance for the two river systems (i.e., Adige and Po) in the study area, and a reclassification of some samples. The Sr and Pb isotopic composition of the investigated samples show a variability consistent with the provenance discrimination obtained by the ICP-MS data, and provide further information on the sediment's sources. The obtained isotopic ratios were compared with those of ore deposits from the whole Alpine arc (Giunti, 2010; Artioli et al., 2016) to find a link between different source lithologies and alluvial sediments. Sediments with Po River geochemical affinity show a Pb isotope composition consistent with that of ore deposits from western Alps, whereas sediments with Adige geochemical affinity show a Pb isotopic signature compatible with the Valsugana and Southalpine ore deposits.

Furthermore, the application at a regional scale of these new tracers, allowed to better constrain the geochemical and isotopic features of Po and Adige sources, and to identify further differences in Po affinity sediments settled in various sectors of the easternmost Padanian plain. In particular, sediments with Po affinity from the northern side of the present-day Po River course (Veneto region, this work) show intermediate geochemical features between those of Adige affinity and Po sediments collected from the southern side (Emilia-Romagna region, Ciarpaglini, 2021), the latter representing the Holocene sedimentary deposit with the most genuine signature of the Po River basin source rocks.

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## Reconstructing the thermal field of Sicily: development of numerical models for a small-to-large scale geothermal characterization of the island

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*Keywords:* thermal modeling, geothermal exploration, sustainability.

Evaluation of the thermal and mechanical nature of the lithosphere is a primary factor used to quantify the subsurface geothermal potential. In dynamic and complex tectonic settings, this strategy becomes even more relevant (Scheck-Wenderoth et al., 2021). In this sense, Sicily is an interesting case study due to its untapped geothermal potential trapped in a complicated geodynamic environment (Milano et al., 2020). This research attempted to reconstruct the present-day lithospheric state of Sicily to quantify its shallow and intermediate depth thermal regime. Starting from 3D lithospheric-scale gravity modeling, the main geological units and their lithology-dependent rock properties, consistent with available borehole and seismic datasets, have been defined (Florida et al., 2021). The constructed geological model with its lithology-dependent thermal conductivity and radiogenic heat production properties has been then used to obtain three conductive thermal models considering different boundary conditions (Florida et al., 2022). The modeling results have been validated against a shallow temperature public dataset. Results indicate that the thermal regional field at depths shallower than 10 km is largely controlled by variability in sedimentary thickness in the foreland and the orogen, while deeper temperatures are primarily controlled by the distribution of the heat transferred from the mantle, together with the radiogenic contribution of the deeper crustal layers. The thermal modeling portrays a rather heterogeneous Moho heat flow, locally higher than 80 mW/m<sup>2</sup>, revealing specific areas characterized by high-to-medium enthalpy geothermal potential correlated with particular geodynamic setting. The proposed 3D model of Sicily thereby allows to constrain areas with important geothermal anomalies, such as the volcanic zones of the Aeolian Island Arc, the Etnean area and the Sicily Channel Rift Zone, which could be suitable for the exploitation of medium-to-high enthalpy resources. The model also suggests that low-enthalpy resources are available over extended areas of the region, especially in the Caltanissetta Basin and the carbonate layers. To investigate the possible exploitation of shallow resources, a high-resolution exploitation scenario in a microdomain of south-eastern Sicily has been therefore simulated. All these aspects make Sicily a potential pilot region for fostering other geothermal exploration studies, with the same solid workflow, also for other areas of southern Italy. All the available data have been implemented into interactive thematic maps reproducing the thermal steady-state field at variable scales, which have been uploaded within a dedicated, expandable web portal that is a practical tool for the fast assessment of the geothermal condition of the Sicily subsoil. Optimization of the exploitation of this renewable resource can become an additional way to promote effectively the ongoing transition toward the green energy.

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## **Sr isotopes and Rare Earth Elements as tracing tools: the Tuscan Extra Virgin Olive Oil case study**

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*Keywords:* extra virgin olive oil, Sr isotopes and REEs, traceability.

The Extra Virgin Olive Oil (EVOO) is a primary and important component of our diet, therefore the provision of methods that testify its quality and authenticity represents an essential issue. The use of petrochemical parameters represents one of the most promising approaches to trace the geographical provenance of this precious product. Pelacani et al. (2017) and Techer et al. (2017) showed that the REEs and the  $^{87}\text{Sr}/^{86}\text{Sr}$  signatures are transferred from the bioavailable soil fraction (BSF) to the olive pulp, and then to the oil, without any significant elemental and isotopic fractionation. In this work, we therefore present a geochemical and isotopic study dealing with the REEs content and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of EVOOs and related olives, with the aim to establish a method for EVOO traceability. Samples of bioavailable soil fraction, olive, and oil were collected from Tuscan olive groves from the Chianti area, High Tiberina Valley, and Maremma. The selected localities are characterized by different geological and geomorphological settings, with minimal differences in climate, topography, and cultivar. Contrary to BSFs and olives, oils are characterized by low REEs and Sr content, which represents the main challenge in determining their elemental and isotopic content. Therefore, efficient pre-concentration is required to obtain reliable and precise results. To overcome these difficulties, we set up a procedure to extract REEs and Sr from olive oil and olives involving mechanical stirring and ultrasound-assisted extraction (Turk et al., 2019), followed by Sr purification using standard chromatographic techniques.  $^{87}\text{Sr}/^{86}\text{Sr}$  measurements in soil, olives, and olive oil were performed by TIMS, while the REEs content was determined by ICP-MS. Preliminary data on the whole (i.e., independent of the geological bedrocks) dataset show an appreciable variability of the  $^{87}\text{Sr}/^{86}\text{Sr}$  values among the bioavailable soil portion (0.7079 to 0.7117), olives (0.7081 to 0.7118) and EVOOs (0.7085 to 0.7097). In addition, oils from different foreign countries were compared to verify any possible isotopic and compositional differences with Tuscan EVOO.

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## Chemical and isotopic provenance study of Final Bronze Age glass artefacts from Central Italy

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Keywords: glass artefacts, Sr-Nd-Pb isotopes, provenance.

Glass is an amorphous solid found in nature, that Man has been manufacturing since ancient times mixing multiple components: a vitrifying agent, a stabilizer, a fluxing agent and a (de)colorant. Different elements come primarily from different components, therefore combining chemical and isotopic data, and comparing them with existing databases, it is possible to reconstruct the origin of the raw materials, and thus the provenance of the glass artifacts.

This study focused on the chemical (major, minor and trace elements) and isotopic (Sr, Nd, Pb) characterization of five vitreous samples dated to the Final Bronze Age – Early Iron Age (1126 a.C. – 897 a.C.) from the archaeological site of Paduli, lago di Piediluco (Rieti). The five samples were selected as the most representative among all glass samples found in the site during previous sampling campaigns.

One of the samples (blue vessel's fragment with white decorations) has chemical (i.e., Al<sub>2</sub>O<sub>3</sub>, Zr, Ti, REE) and isotopic (Sr and Nd) characteristics that point to a Levantine origin. Sr isotope ratios, as well as CaO, Sr, U, and Ba contents, indicate the use of aragonitic shells of marine organisms as stabilizer. Pb, probably used to favour glass matrix fluidity, has an isotopic fingerprint comparable to that of the Taurus ores (Turkey), known to be exploited in eastern Mediterranean glass production. The white decorations are obtained by the neo-crystallization of Ca antimonates, made with Sb of possible Caucasian origin.

The other four samples (two annular beads, one turquoise and one blue, a blue bichrome horned-impressed eye bead and a blue cylindrical bead with white decorations) are classifiable as *mixed alkali* glasses and present a composition that is typical of European vitreous materials. Chemical and isotopic fingerprint of these beads link them to Frattesina, a well-known glass production centre active during the Bronze Age. The differences among the samples derive from: i) the possible use of different types of stabilizers (CaO), recognizable through the absolute concentrations of Sr, Ba and U, as well as through the Sr-isotopic composition; ii) the use of sands (as a vitrifying agent source) with variable Nd isotopic composition, probably purified beforehand, and linked to Po River and Adige River; iii) the addition of colourants with different composition and origin. Pb isotopic ratios, characteristic of the source of colorant, suggest the use of metals coming from Trentino-Alto Adige ores for all samples except for the cylindrical bead, that seems to be linked to Austrian ores. Its white decorations are obtained through crystals of wollastonite.

Glass samples found in Paduli archaeological site seem therefore to originate from a well-known glass-making centres active during the Late Bronze Age (Frattesina and production centres in the Levant), suggesting that the site was an important trade centre between North Italy and the Eastern Mediterranean.

## Heavy metals and Pb isotopes as tracers in environmental matrices: the Valdinievole sub-basin river system (Tuscany, Italy) case study

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*Keywords:* environmental geochemistry, heavy metals, Pb isotopes.

Heavy metals distribution and behaviour in natural systems have been receiving increasing attention due to their impact on the environment and human health. These elements, indeed, can be essential for life, but also toxic when present in high concentrations causing critical diseases in the ecosystems. The geochemistry of trace and ultra-trace elements, coupled with Pb isotopic ratios, is a powerful tool for the discrimination of natural and anthropogenic sources and related geochemical processes. The geological matrices that constitute the riverine environment (water, suspended solid load, and sediment) are intimately linked and their simultaneous investigation allows to increase the knowledge of the trace elements mobility and distribution, as well as to distinguish between geogenic and human contributions to their heavy metal budget. The Valdinievole (Tuscany, Central Italy), is a secondary basin of the Arno River Basin and includes the Padule di Fucecchio, one of the most relevant Tuscan swampy zones. Besides, the Valdinievole sub-basin hosts a large number of important productive sectors such as paper mills, flora nursery farms, thermal spas, and tanning industries, thus representing an ideal study case to evaluate the impact on water, sediment and suspended solid load (SSL) of industrial and urban sewages. The water geochemistry highlighted a wide compositional variability, which ranged from  $\text{Ca}^{2+}(\text{Mg}^{2+})\text{-HCO}_3^-$  to  $\text{Na}^+\text{-Cl}(\text{SO}_4^{2-})$  and Total Dissolved Solids up to 6,390 mg/L. The relatively high contents of the reduced N-species, which were up to 6.2 ( $\text{NO}_2^-$ ) and 23 ( $\text{NH}_4^+$ ) mg/L, suggested the presence of a fresh and diffuse pollution. A few samples of water, SSL and sediment showed Cs contents up to 170  $\mu\text{g/L}$ , 57 mg/L, and 46 mg/L, respectively. The SSLs and sediments were characterized by high heavy metal concentrations, e.g., Pb, Cu, Zn and Cr up to 174, 766, 1,899 and 7,953 mg/kg, respectively, likely including a variable contribution from anthropogenic sources. This hypothesis is further supported by i) the Pb isotopic ratios, which allowed to identify a clear tendency from a geogenic to an anthropogenic signature and ii) the heavy metals Enrichment Factors, whose values are indicative of the significant impact exerted by local human activities on riverine environmental matrices. EFs of Pb, Cu, Zn and Cr, calculated using the world suspended solid load concentration averages, reached values up to 12, 163, 56 and 134, respectively, confirming the influence of the enterprises situated in the Valdinievole sub-basin on the geochemical abundances of heavy metals.

## Heat transfer From Shallow Magma intrusions: an Updated Study of the Thermal Evolution of the Monte Capanne Magmatic System

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*Keywords:* numerical modelling, pluton exhumation, paleo-geothermal.

Eastward migrating Neogene-Quaternary extensional tectonics affected the Inner Northern Apennines and triggered the emplacement of magmatic bodies at shallow crustal levels, producing a strong influence on the long wavelength thermal anomaly characterizing the northern Tyrrhenian area since middle-upper Miocene. Our case study, the Monte Capanne monzogranite (western Elba Island), is a late Miocene magmatic body emplaced within a NE-striking transfer zone and unroofed by low-angle extensional detachments. In comparison to the other exhumed felsic plutons belonging to the Tuscan Magmatic Province, the Monte Capanne granite is better constrained from a geological, petrological and geochronological point of view. Repeated magma injections are fundamental for the maintenance of long living geothermal systems, as demonstrated for the Larderello and Monte Amiata geothermal systems, still active in southern Tuscany. Consequently, the knowledge of the evolution of the Monte Capanne magmatic system makes this case study useful to properly model the long wavelength surface heat flow anomaly produced by the pluton emplacement, and to refine the geological evolution of the inner Northern Apennines (i.e. the Tyrrhenian area). In this presentation, we propose an updated 2D thermo-rheological modelling, that incorporates the effects of the pluton exhumation on the heat flow. The extensional tectonics and the associated magma emplacement have been reproduced in a numerical domain extending down to the base of the thermal lithosphere in order to: i) explain the present-day heat flux measured in the Elba Island sector (Italy); ii) properly quantify the exhumation rate of the pluton; and iii) understand how the exhumation rate of the monzogranite influences the intensity and timing of the conductive thermal perturbation.



## EMOTION and IRGIE two broad-scope projects to support the geothermal research

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Keywords: geothermal energy, geochemistry, geoscience.

The global energy demand is continuously increasing, arriving at a critical threshold that points the attention to the necessity for urgent development of a strategic energy plan to encourage low carbon technologies and energy autonomy. In this framework, the increase in the use of renewable energy sources represents a mandatory choice aimed at favouring independent energy management and a more sustainable use of the resources. In light of this, the development of geothermal energy can represent an important goal even though it has historically had a limited role in influencing global energy scenarios. Actually, its role at a local scale can largely satisfy the energy demand and boost the local economy through both direct and indirect uses. This concept is particularly relevant for the countries characterized by high-quality geothermal resources such as Italy.

In light of this, the geosciences and geoscientists can have a key role to increase the scientific knowledge about geothermal resources supporting geothermal exploration, but also leading dissemination actions dedicated to young and adult citizens in order to increase their awareness with respect to the useful role of geothermic towards a more sustainable life.

In this framework, INGV strongly supports research activities that move in this direction, and EMOTION and IRGIE Projects represent an example. These are two broad-scope ongoing projects, led by INGV.

EMOTION is a three-year project (2023-2026) funded by MUR (*Ministero dell'Università e della Ricerca*) in the framework of ten-year INGV PIANETA DINAMICO Research-Program. The project aims to provide a detailed geochemical characterization of the manifestations of geothermal interest (thermal springs, mineral waters and gas emissions) in central northern Italy and also to develop a solid and public web portal of all Italian geothermal manifestations, including those already studied in the central-southern part of the country.

IRGIE is also a three-year project that will end at the beginning of 2026, it is funded by *Regione Siciliana* and aims to develop an inventory of the geothermal resources of the Aeolian Islands (Sicily). In particular, the project aims to characterize the geothermal systems of the Aeolian arc providing also useful suggestions in terms of potential uses of the resources. Moreover, social acceptance analysis in respect of geothermal energy will be carried out jointly with specific on-site dissemination activities dedicated to both primary and secondary school students and adult citizens and stakeholders. The main goal of the IRGIE project is to facilitate energy independence and transition of the small islands, towards renewable energy choices. Aeolian islands are strongly dependent on fossil fuel and are not connected to the national power network, so geothermal energy could be a powerful way to improve their sustainability, providing a virtuous example to repeat in other small islands.

<https://progetti.ingv.it/it/emotion>

<https://progetti.ingv.it/it/irgie>

## Elemental and isotopic fingerprints during the life cycle of the manila clams *Ruditapes philippinarum* in the Goro Lagoon (north Adriatic Sea): tools for food provenance traceability and environmental studies

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Keywords: manila clams, traceability, isotopes.

In Italy, the production of manila clams (*Ruditapes philippinarum*, Adams and Reeve, 1850) is mainly localized in northern Adriatic lagoons of the Po River delta, where shellfish farming provides important economic revenue (Giani et al., 2012). However, the seafood market is threatened by fraudulent activities in which agri-food products, whose provenance is not certified, are sold posing a risk to consumers health. Multi-isotope ratios and elemental analyses are commonly used to trace the provenance of food products in different countries, included seafood and to assess their safety. However, the variability of geochemical fingerprints during the life-cycle of the manila clams where never investigated. In this study, the elemental concentrations and isotopic ratios in seeded manila clams (both shells and tissue) were monitored during mollusks growth at two sites of the Goro Lagoon (Emilia-Romagna). Tissues of juvenile (< 1.6 cm) and old (> 1.6 cm) organisms were analyzed with an elemental analyzer coupled with an isotopic ratio mass spectrometer (EA-IRMS) for total carbon, organic carbon, nitrogen, and sulphur elemental contents and the relative isotopic ratios ( $d^{13}C_{TC}$ ,  $d^{13}C_{OC}$ ,  $d^{15}N$ ,  $d^{34}S$ ). Shells of the same organisms were analyzed with a head-space analyzer coupled with an IRMS for carbon and oxygen isotopic fingerprints ( $d^{13}C$ ,  $d^{18}O$ ) and with an inductively coupled plasma mass spectrometer (ICP-MS) for the trace elemental compositions. Total Hg concentrations in manila clam tissues were also determined with a Direct Mercury Analyser (DMA-80, Milestone) according to EPA Method 7473 in order to assess contamination levels and potential risk for human consumption. The environmental conditions of the Goro Lagoon during shellfish sampling were also monitored through the *in-situ* measure of pH, temperature and electrical conductivity of the water. Anions and cations of water samples were measured with ion-chromatography. Finally, also sediment samples from the two sites were collected during the different sampling seasons and  $CaCO_3$  content measurements, grain size and geochemical (isotopes and elemental concentrations) analyses were performed. The obtained results complement earlier works on tracing the provenance of manila clams in the northern Adriatic lagoons (Bianchini et al., 2021; Brombin et al., 2022) by adding physico-chemical, elemental and isotopic parameters during the entire life-cycle of the mollusks. This will allow to test the reliability of the food traceability geochemical techniques. Finally, the outcomes of this work might help to monitor the resilience of these organisms to the effects of anthropogenic and natural factors (e.g. pollution, water circulation, nutrient supply, climate changes) occurring in the Goro Lagoon.

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## **Mapping the thermophysical properties of rocks: implications for the temperature state of the crust**

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*Keywords:* thermophysical properties, geothermal exploration.

This laboratory study presents thermophysical rock measurements of 31 carbonates outcrop samples from the main geological formations of Umbria (central Italy). Mineralogical analysis indicates that the formations under examination are mainly composed of calcite, with an abundance of quartz for some samples.

The conductivity and thermal diffusivity were determined with varying temperatures and both under dry and saturated conditions. Dry thermal conductivity measured with three different transient technique (optical scanning, transient plane source, transient hot wire method), differ by less than 10%.

At ambient temperature of 20 – 25°C, conductivity varies from 1.8 to 3.0 W/(mK) for samples with predominant calcite and show values greater than 3.6 W/(mK) for samples with larger quantities of quartz. For temperatures up to 200°C, conductivity for most of the samples decreases by about 30%.

Porosities reveal values of less than 5%. Theoretical mixing models based on the mineralogical composition and porosity were analysed to find the right fit with the measured values, with the possibility of extending the results to other parts of the world.

The results obtained from the study represent the basis for a more complete evaluation of the temperature trend with depth, useful for the evaluation of geothermal systems and for defining the rheological behaviour of the crust.

## **Carbon dynamics in the chestnut forests of Lazio (Central Italy): insights from the critical zone**

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*Keywords:* chestnut forest, carbon sequestration,  $\delta^{13}\text{C}$ .

Chestnut managed land is an agroforestry's good that plays an important role in the carbon cycle as well as providing habitats for a wide range of animal species, chestnut crop, timber and soil stabilization and preventing erosion.

Lazio region (Central Italy) is covered by 600.000 hectares of forests and 6% of those are chestnuts forest with a life cycle of ~30 years. The volcanic areas of Anticolana Valley and Cimino Hills are a fertile substrate that, developing a symbiosis with chestnut, increase the local carbon sequestration. Also for these reasons the abovementioned areas covered by chestnut forests were listed in the Natura 2000 network for the environmental protection.

In this study, a representative and georeferenced sampling has been carried out in the two areas to provide the evaluation of the physical and chemical characteristics of the soils, with the aim to delineate the soil quality as well as how the carbon sequestration occurs in the two involved domains. In particular, with a coupled elemental and isotopic ratio mass spectrometer analysis (EA-IRMS): total (TC), organic (OC), inorganic carbon (IC) and total nitrogen (N) contents and the relative isotopic signatures ( $\delta^{13}\text{C}_{\text{TC}}$ ;  $\delta^{13}\text{C}_{\text{OC}}$ ;  $\delta^{13}\text{C}_{\text{IC}}$ ;  $\delta^{15}\text{N}$ ) were measured to quantify in  $\text{Mg ha}^{-1}$  the Carbon stock and the Carbon dioxide equivalent ( $\text{CO}_2$  eq.).

## Soil Organic Carbon estimation in Ferrara (Northern Italy) combining in situ geochemical analyses, hyperspectral remote sensing and neural networks

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*Keywords:* organic carbon, remote sensing, neural networks.

The critical zone (CZ) is the uppermost portion of the Earth's crust, extremely vulnerable to human activities, and comprises plants, soil, air, water, rocks, and living organisms. In fact, anthropic processes such as agricultural practices involve the superficial CZ layer, exposing the soil organic matter to factors that lead to a variable depletion of the organic carbon pool. Obviously, organic carbon is a proxy of fertility and thus of soil health, therefore is a crucial element that must be monitored in the CZ. In this study, we investigated whether surface soil organic carbon (SOC) content could be measured using hyperspectral data provided by the Italian Space Agency PRISMA satellite. We collected 100 representative topsoil samples in an area of 30 × 30 Km<sup>2</sup> in the Ferrara province (Northern Italy) and estimated their SOC content by elemental analysis. We matched the soil parameters to the spectra of the sampled areas that were measured by PRISMA on April 7th 2020 and used this data to train and test an Artificial Neural Network (ANN) for SOC estimation.

Our research showed that this methodology can work also with few samples (100) in an area where the SOC concentration varies significantly (values from 0.7 to 9.3 wt%) over a spatial scale of just a few meters. The combination of geochemical analysis of in situ samples, hyperspectral remote sensing and neural network machine learning can thus be used in areas whose soils have a complex nature to reconstruct a detailed organic carbon distribution map. This can have a variety of practical applications, including monitoring the degradation of agricultural soils.

## Mapping of distribution of Soil Organic Carbon and CO<sub>2</sub> emissions in the Ferrara province: comparison of C contents in 1937 and 2022

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Keywords: soil, carbon, isotopes.

Global warming is accelerating soil organic matter (SOM) degradation and increasing the release of greenhouse gases (GHGs; e.g., CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O) into the atmosphere. In addition, unsustainable agricultural practices, agricultural land use and land cover change (LULCC) exacerbate the process and account for 20% of the total CO<sub>2</sub> emissions. In particular, over the last century LULCC have reduced SOM and released CO<sub>2</sub> in Northern Italy. Today the Ferrara province, located in the easternmost part of the Po River plain in Northern Italy, has soils with a large range of SOM content that include peatlands with very high SOM, which is the result of a wetland reclamation program of palustrine environment that started before the World War II and ended in the 1970s, increasing the agricultural production area by ~78000 ha. In 1937 Ferrari et al. (1937) conducted a survey of the soil of the entire Ferrara province to assess the physicochemical properties of the soils and the SOM content in the 0-30 cm topsoil layer. In this research we compared the SOM content data collected by Ferrari et al. (1937) with new topsoil geochemical data collected from the same sample locations in 2022. In particular, for each location the total (TC) and organic (OC) carbon contents and the relative isotopic signatures ( $\delta^{13}\text{C}_{\text{TC}}$ ;  $\delta^{13}\text{C}_{\text{OC}}$ ) of the samples obtained in 2022 were measured through an elemental isotope analyzer coupled with an isotopic ratio mass spectrometer (EA-IRMS). The distributions of C fractions of the samples collected in 1937 and 2022 were represented into maps and used to calculate the carbon dioxide equivalent (CO<sub>2</sub> eq) released in the atmosphere in 85 years. Comparison of SOC maps from 1937 and 2022 indicates that most of the Ferrara area suffered a significant SOC loss ( $\Delta\text{OC}_{85 \text{ years}}$  from 0.05 to 18.57 wt%), with the exception of northern areas in which the peat nature of the soil has been preserved with SOC up to 25 wt%. However, it is important to note that the highest decrease occurred just in reclaimed peatlands coupled with a strong CO<sub>2</sub> emission due to the conversion of the peatland into croplands and the unsustainable farming activities encouraged by the fertility of these soils. Finally, we also measured the <sup>13</sup>C/<sup>12</sup>C on the 2022 soil samples and generated a present-day map of the SOC isotopic ratios. The isotopic signature was used as a tool to evaluate changes in soil carbon stocks that had occurred over long time periods, and in the future it will be used as a benchmark to measure C changes. Works like this highlight the importance to create and to update OC content inventories in order to estimate the SOC stock loss after several years and to calculate the amount of CO<sub>2</sub> eq released in the atmosphere.

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## Geothermal potential assessment of fractured carbonate reservoirs through 3D thermal and structural reconstruction: a case study from the southern Latium (Central Peri-Tyrrhenian Italy)

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Keywords: geothermal energy, decarbonisation, geothermal potential assessment.

At national level, several studies and efforts have been made to investigate the medium and high enthalpy geothermal potential, mainly in areas characterized by high temperatures and high heat flux (Procesi et al., 2013; Tescione et al. 2021). In particular, in the Latium region, the main interesting geothermal areas are located in the northern part. On the contrary, the southern part of the region is still less explored (Giordano et al., 2014). Procesi et al. (2013) found that temperatures between 70 and 100°C should occur at the top of carbonates units at depths of 2000 m and 3000 m. In this framework, Quaternary magmatism can be identified as the source of a potential geothermal system whose reservoir is represented by the Apennine carbonates of the Mesozoic Tethys platforms.

The general objective of this study consists of an accurate characterization of selected geothermal systems in central Italy, defining their potential in terms of geothermal energy planning and elaborating a regional circulation model. The target is the development of a unifying and reliable map of the Geothermal Potential of the central peri-Tyrrhenian Italy and the identification of one or more case studies in the southern Latium.

To reconstruct the distributions of temperatures at depth we performed various operational data processing and elaboration projects in GIS environment. We used as input data the temperature values extracted from the isolines at 1000, 2000 and 3000 m depth reported in the UNMIG, CNR and AGIP 1988 database to extrapolate the isothermal surfaces from 50° to 350°C, every 50°C.

Preliminary results highlight and confirm some areas characterized by heat temperatures values in correspondence of : the Bracciano and Bolsena caldera lakes, Viterbo city, the south-western coastal area of Rome, and close to the Campi Flegrei and Vesuvius zones. Some minor geothermal areas could be correlated to magmatic bodies in southern Latium with a heat flow in the range of 40-100 mW/m<sup>2</sup>. Through the interpretation of public geophysical data (seismic reflection profiles and well log data), some structural carbonate highs were identified in the southern Latium, in particular in the Valle Latina area, at 1000 and 2000 meters of depth. The first ongoing step of the geothermal potential evaluation requires calculating the initial heat in place (HIP) (Muffler & Cataldi, 1978), related to the volume of the geological structure, and calculating values from the available database. Analysing the National Geothermal database by CNR, there are two main high thermal anomalies along the Valle Latina, highlighted by the 3D isothermal surfaces reconstruction.

The technical potential will be estimated for some identified carbonatic structures in the Valle Latina area, assuming a value for the recovery factor, the efficiency and the life span of geothermal plants.

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## Multiphase rifting and rivers: Geothermal energy in the West Netherlands basin

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Keywords: geothermal energy, rifting.

On the road to a sustainable planet, geothermal energy is considered as one of the main substitutes for heating houses, industry and agriculture. The Netherlands is one of the leading countries in Europe, with 25 producing geothermal projects, from which the majority (14 projects) can be found in the West Netherlands Basin. Located underneath a densely populated area with an extensive horticulture sector and the harbour of Rotterdam, there is an increasingly broad interest for geothermal exploitation in the area (Willems et al., 2020).

As a former hydrocarbon province, the West Netherlands Basin is covered by publicly available seismic 2D, 3D and well datasets. With a renewed seismic interpretation, our study uses the West Netherlands Basin as a case study for geothermal exploration in former rift basins. Development of the West Netherlands Basin happened during the Mesozoic in several rift phases (Van Wijhe, 1987). The renewed interpretation allowed us to reconstruct the rifting architecture of two rifting episodes in the Jurassic; the first one during the Early Jurassic and the second one, partly controlled by structures of the former, during the Late Jurassic.

This Late Jurassic rifting episode coincides with deposition of the main geothermal target in the West Netherlands Basin: the fluvial-deltaic Nieuwerkerk Formation. The multi-phase rifting during the Mesozoic led to the compartmentalisation of the Nieuwerkerk Formation. Its fluvial system was likely localised in the central portions of the several sub-basins (Gawthorpe & Leeder, 2000). Therefore, the targeted irregular deposited fluvial sandstones can best be exploited in those central portions.

Our case-study shows that the understanding of the rifting architecture can help reconstruct fluvial reservoirs. Also, multi-phase rift history can influence reservoir-seal thicknesses and integrity, and with that, the amount of MW that can be safely extracted from geothermal aquifers. Therefore, this study helps de-risk the planning of geothermal systems in basins with a multi-phase rifting history.

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**S35.**

**Groundwater sustainability and water-energy-food nexus**

*CONVENERS AND CHAIRPERSONS*

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## **New threats in the Trieste Karst (Italy): pollution by microplastics in groundwaters and springs**

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*Keywords:* microplastic pollution, karst, water.

Microplastic (MP) pollution in karst systems is still poorly studied, especially in underground environments and aquifers, despite groundwater in karst aquifers constitutes about a quarter of the global drinking water sources. In this preliminary study we collected and investigated different water samples from the Trieste Karst, Italy, considering three caves and a spring.

MPs were subjected to organic matter removal with 1:1 30% hydrogen peroxide solution and extracted from water samples by filtration. MPs on filters were counted and characterized by size, color and shape via visual identification under a microscope, with and without UV light, exploiting fluorescence given by fluorescent whitening additives contained in plastic materials. Finally, spectroscopic analyses were carried out on random particles observed on each filter.

The concentration of MPs in cave waters varied from 47.2 to 96 items/L, with a mean value of 75.3 items/L, instead, in the water of the spring it was of 50.9 items/L. Fibre represented the most abundant shape (68.8%), followed by fragment (26.8%), bead (pellet and sphere) (2.3%), film (1.8%) and foam (0.3%). Most MPs (79.6%) were smaller than 1 mm. The majority of the MPs were fluorescent under UV light (65%) and have 69.4% blue fluorescence, 17.7% green fluorescence, 6.4% red fluorescence and 6.9 % other colours. Most of fluorescent particles were transparent (57.4%). However, black (48.3%) and blue (23.0%) microplastics were more common among the non-fluorescent ones.

Our results highlight the presence of MPs in spring and cave waters of the Trieste Karst and provide useful information for future research. Karst aquifers are open systems, subjected to possible contamination by surface pollutants. The examined area is crossed by highways, roads and railways, therefore, most of the particles found in water samples could come from these sources of pollution, transported by water and or air. MPs in karst systems can be consumed by animals, damage ecosystems and contaminate water resources, therefore, surface and underground environments should therefore be monitored and protected. Analyses on a greater range of surface and subterranean waters are required and karst areas conservation should become a priority for the management of water resources.

## Soil permeability map of the Ferrara plain (Northern Italy)

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*Keywords:* soil permeability map, Ferrara plain.

The assessment of the intrinsic permeability of soils is a fundamental tool for territorial management and planning (agricultural, hydraulic, urban planning). This research has made it possible to build a map of soil permeability in the Province of Ferrara, whose estimate was mainly based on the granulometric distribution of the soils. In particular, the results of the granulometric analyses were plotted on Shepard's (1954) triangular diagrams. Based on the texture it is thus possible to distinguish three classes of relative permeability corresponding to i) permeable soils (sands, silty sands, clayey sands, sandy silts), ii) poorly permeable soils (silts, clayey silts, sandy clays, ternary mixtures of sands, clays and silts) and iii) impermeable soils (clays, silty clays, peaty clays). Additionally, in selected areas of the upper, middle and lower Ferrara area, representative of the geomorphological, hydrological and sedimentological evolution, a) new continuous core borings were carried out; b) the hydrolithological architecture has been defined; c) the spatial distribution of textural parameters and organic matter content was reconstructed in 3D; and d) the intrinsic permeability of the lithologies was calculated by applying empirical methods based on the soil texture. Finally, the map of the intrinsic permeability of the soils was created based on a geographic information system.

## **An innovative platform for water crisis management: WebGIS to support the emergency**

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*Keywords:* Web Gis, Drought emergency, water resources.

The water crisis is affecting more and more areas in Italy. Among the causes are the lack of rainfall, the persistence of high above-average temperatures (about 2-3 degrees above average for the period), and the sharp decline of snow in the high altitudes, which represent the “warehouse and storage in the mountains” of water. The effects, will affect not only agro-livestock, but also drinking and related use in hydropower generation. It follows, that now more than ever, sustainable management of the resource based on dynamic, timely and effective management of all information that may affect it will be essential. The main challenge will be to understand, by constantly monitoring the hydrological situation, the right balance between ‘civil’ and agro-livestock needs. In this regard, the use of WebGIS can be effective, as they allow not only to define risk scenarios and related forecasting and prevention models, but also allow their wider dissemination. Therefore, in this work an innovative platform is proposed for monitoring and restitution of all the main parameters that go into characterizing surface and groundwater bodies, both qualitative and quantitative. The platform will enable local authorities and companies to implement local adaptation strategies and action plans based on a better identification of different phenomena. The use of the platform will also allow any regional or local water crisis to be better addressed.



## **Salinization of water resources and urban regeneration processes in the delta Po area (Northern Italy)**

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*Keywords:* salinization, aquifer, urban regeneration.

About 50% of the world population lives within a distance of 60 km from the shoreline, while many coastal aquifers are affected by saltwater intrusion phenomena due to natural and anthropogenic causes. The salinization of these natural systems can lead to a severe and enhanced deterioration of the quality of existing fresh groundwater resources. In coastal aquifers, the hydrochemical recognition of the salinization processes is very complex due to superposition of different processes like the marine intrusion, the occurrence of continental salt- or mixed water lagoons and diverse pollution phenomena. The delta Po River (Northern Italy) is a good example of this general and worldwide problem. In particular, the humid area of the delta is a fragile ecosystem characterised by a high biodiversity extremely sensible to even small environmental changes. In order to define the hydrodynamic and geochemical processes of the coastal aquifer between the Volano branch of the Po River and the Reno River and especially the behaviour of the local unconfined aquifer, geomorphological, lithological, hydrogeological and geochemical data have been systematically analysed with the purpose of defining the conceptual hydrogeological and hydrochemical model. In the second phase, we focused on the definition of urban regeneration scenarios, for some inhabited centres located along the coastal area; with the aim of creating urbanised areas resilient to climate, environmental, demographic and economic changes.

## Karst Hydrology and Geomorphology of the Alburni Massif (Campania, Italy)

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*Keywords:* karst geomorphology, hydrological features, karst landform mapping.

Karst environments are peculiar settings characterized by a deep interaction between groundwater circulation and surface hydrology and landforms (Ford and Williams, 2007). Small- to large-scale morphological features typified karst terrains, such as ponors, shafts, dolines, poljes, caves, endorheic basins, etc. All these features play an important role in hydrological processes, as they control meteoric water runoff/infiltration, the transferring of water into the underground, and thus groundwater recharge (Bonacci, 2013). In this context, mapping the karst landforms, understanding their formation mechanism and hydrological role, combined with the analysis of geological and geomorphological data, are of crucial importance to fully characterize a karst system. In particular, this information represents the starting point for many investigations, including hydrological modelling of the surface runoff and groundwater recharge, delineation of protection zones for wells and springs, simulation of point source contamination, and artificial test planning. This contribution presents a map of the karst features of the Alburni massif (Campania, southern Italy), illustrating landforms of a typical karst relief from the hydrological perspective. The hydrological analysis of high-resolution Digital Elevation Models (DEMs) in a GIS (Geographic Information System) environment has represented the primary method used in map making, which has driven the identification of the dolines and poljes, first, and has allowed for the delineation of small- and large-scale endorheic areas, then. From the point of view of surface hydrology, an endorheic area constitutes a closed watershed with internal runoff, which conveys meteoric water toward ponors, dolines, and poljes, representing the most depressed points or areas of the watershed. Therefore, endorheic areas are peculiar parts of a spring catchment from which meteoric water cannot escape (Fiorillo et al., 2015). Visual inspection of various informative layers, including Google Earth images and DEM-derived contour maps and hill-shade, was carried out to support dolines delineations. In addition, ponors and cave entrances were mapped based on surveys of the Campanian Speleological Federation. Cartographic data were integrated with information derived from the morphometric analysis of karst features, climate analysis, and hydrological modelling of the aquifer recharge process. Furthermore, a schematic hydrogeological model across the Alburno massif was derived from reports concerning speleological surveys and artificial tracer tests, which illustrates the connections between the summit plateau and basal springs. This amount of data provides an overview of the hydrogeological and karst hydrological features of the Alburni massif and is of high significance in improving the knowledge of this karst system.

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## Characterization of aquifer recharge processes in the Laga Geological Formation of Marche Region through the permanent monitoring of the vadose zone

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Keywords: aquifer, vadose zone, water isotopes.

Carbonate aquifers represent the main source of drinking supply in central Italy (Lorenzi et al., 2022). Even in the Marche Region, most of the potable water is provided by the mountainous aquifers hosted in the carbonate rocks. However, considering the well-documented ongoing depletion of water resources caused by the recent climatic context, often responsible for very prolonged dry periods, the need of finding alternative or integrative groundwater resources has been growing. For this reason, the aim of this study is to characterize the recharge processes in the turbiditic succession of the Laga Geological Formation in Marche Region to quantify the sustainable exploitation of groundwater resources as an alternative water supply. In fact, turbidite successions can act as aquitards or aquifers depending on their lithological characteristics. Hence, these systems deserve detailed investigations on a local scale aimed at building reliable hydrogeological models (Rizzo et al., 2022). In this scenario, the balance between incoming precipitation and groundwater available remains a challenging aspect (Mammoliti et al., 2021) and the infiltration processes occurring in the vadose zone should be carefully assessed by continuous in-situ monitoring (Gaj et al., 2015). This study exploits a permanent field laboratory composed of a rain gauge connected to a buried rainfall collector tank, three lysimeters (30, 60, and 90 cm depth), soil temperature and moisture scanners (every 10 cm until 100 cm depth), and groundwater-surface water level monitoring probes installed within a small watershed. Through continuous monitoring of the infiltration processes, coupled with isotope hydrology techniques, it was possible to characterize the recharge processes occurring on the turbiditic succession of the Laga Geological Formation, enhancing detailed hydrogeological balance calculations in such lithological heterogeneous layers. The ultimate goal of this study is therefore providing the regional authorities and others a useful tool for water management in areas characterized by marked lithological variability, where sparse aquifers alternated with low permeability horizons occur.

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## Hydrogeological setting of the Monte Alpi carbonate massif, southern Italy, hydro-structural aspects and water budget calculations

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*Keywords:* fault network, groundwater recharge, water budget.

The Monte Alpi carbonate massif is located in the axial zone of the southern Apennines, to the east of the Sirino Mt., and in between the valleys of the Agri and Sinni rivers. Its hydro-structure is characterized by an irregular carbonate cusp surrounded by low permeability to impermeable allochthonous terranes tectonically overriding the carbonates. Such a geometry is consistent with a closure of the hydrogeological system along these tectonic contacts, which would constitute the buffer collar of the Monte Alpi aquifer. The modalities of water infiltration at surface, and of its underground circulation are significantly affected by the diffuse fracturing and high-angle, ENE-WSW and NW-SE striking fault zones crosscutting the carbonates. Together with the stratigraphic setting of the carbonates, these fault zones also control the geometry and distribution of the widespread karst-related cavities (La Bruna et al., 2017a, 2018b). Based upon the results of the ongoing hydrogeological monitoring of the area, we assess that a shallow water circuit occurs within the uppermost portion of the fractured carbonates or, alternatively, within the slope debris fans. Such a water circuit is characterized by a main horizontal component of flow feeding cold springs. The results are also consistent with a deep water circuit fed by water infiltrating the high angle faults, and then merging with the main aquifer at depth. These faults therefore act as efficient drains due to presence of 100's m-thick, highly fractured damage zones. Specifically, the ENE-WSW striking faults are interpreted as combined conduit-barrier permeability structures, in which the clayish fault cores act as baffles/impermeables for cross-fault fluid flow, whereas the carbonate damage zones as conduits for fault-parallel flow. Differently, the NW-SE striking faults are thought envisioned as diffuse fluid conduits because of their brecciated fault cores. In order gain insights into its hydrogeological setting, since 2017 we conduct the hydrogeological monitoring of the cold springs, and of the hypothermal springs located at the La Calda area, and computed the inverse hydrogeological budget of the Monte Alpi massif (Lerner et al., 1990). By working in a GIS environment, the average active recharge value is first computed for the whole Monte Alpi area, and then compared with the total amount of water discharge from both cold and hypothermal springs. Results show that the Monte Alpi carbonates form an isolated carbonate aquifer that feed that hypothermal springs characterized by a historical average discharge is about 0.5 m<sup>3</sup>/s, at a constant temperature of 22-23°C all year-long (Matinata, 1992). Results of this ongoing work will be essential to lower the vulnerability of the aquifer, manage and preserve the water resources for the next future.

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## Analysis and modeling of the complex recharge-discharge relationship of the Caposele karst spring (southern Apennine)

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*Keywords:* karst spring, recharge-discharge modelling, lumped parameter model.

Karst aquifers represent a major source of groundwater and provides drinking water to population in many regions of the World. Although several factors control the recharge-discharge processes within karst aquifers, precipitation and temperature are the primary drivers for groundwater storage and spring discharge variability. In particular, recharge-discharge processes occur and evolve over different time scales and strongly depends on the climate regime and its variability. Understanding the response of karst aquifers to the hydrological input is of great relevance for a better assessment of groundwater resource variability in response to climatic or anthropogenic factors and requires specific numerical modelling approaches (Jourde et al., 2018; Jeannin et al., 2021). Due to the complexity of karst hydro-systems and the lack of distributed information, physically based modelling of karst aquifers may result challenging. For these reasons, and also because the only available data often consist in discharge time series at spring, lumped parameter models are usually considered of rainfall discharge modelling.

The Cervialto karst system was investigated because of the absence of any anthropogenic disturbance and its peculiar hydrological and hydraulic behavior in response to the meteorological input (Fiorillo & Doglioni 2010). Unlike typical karst aquifers, this karst system shows a strongly smoothed and delayed response to the meteorological input.

The KarstMod modelling platform (Mazzilli et al., 2017) was applied to simulate discharge of the Caposele karst spring (Cervialto massif, southern Italy) on a daily scale and to better characterize recharge-discharge processes within this complex karst system.

Due to the articulated topography and spatial climate variability of the spring catchment, specific approaches were applied to estimate the meteorological input (rainfall, snow melting, and evapotranspiration). Successively, several model structures were tested, and model parameters were calibrated based on the daily discharge time series of the Caposele spring.

The calibrated model provided good performance and successfully simulated the smooth behavior of the Caposele spring on a daily scale, characterized by the complete absence of discharge peaks following intense rainstorms. Nevertheless, the analysis highlighted a general difficulty in calibrating models able to replicate both discharge peak amplitude and timing, which is probably due to the peculiar hydrological and hydraulic behavior of the Cervialto massif. Indeed, the surface features of the massif, characterized by a pyroclastic soil covering the karst slopes and filling karst depressions, and the absence of a well-developed and interconnected conduit network, probably delays the infiltration within the karst aquifers and thus partly explains the smoothed and dampened observed hydrological response the Caposele spring, rarely observed in regions of karst terrains. The calibrated model provides a powerful tool that might be consider in the future to investigate in detail the response of the Caposele spring to climate variability and change.

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## **Coupled soil water balance and isotopic approach to determine spatial and temporal distribution of groundwater recharge**

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*Keywords:* soil water balance, groundwater recharge.

The expansion of human activities such as agriculture has led to an over-exploitation and depletion of groundwater resources coupled with diffuse contamination. The spreading of pesticides and fertilizers has caused the release of varying amounts of chemical pollutants into the soil, which the leaching action of rainwater then carries into the water table. In these contexts, it is essential to quantify the aquifer's active recharge and assess the timescale at which this recharge occurs. When applying groundwater recharge methods, evaluation of potential amounts that can reach the water table is performed, but how long the water takes to reach it is usually neglected.

The Arborea Plain (Italy) has been designated as a Nitrate Vulnerable Zone since 2005, but despite the restrictive regulations imposed by the Nitrates Directive, the latest reports published by the agencies proposed for monitoring did not show any improvement in groundwater quality, but rather it was classified as being a low quantitative status.

In this study, the Soil Water Balance (SWB) code and the isotope soil pore water profile method were employed to evaluate both the amount of groundwater recharge in the Arborea NVZ and the time lag between infiltration and water table attainment. The SWB code utilizes a modified version of the Thornthwaite-Mather soil-water balance approach at a daily time step and incorporates spatially distributed soil, meteorological, and land cover data (Westenbroek et al., 2010). Soil pore water stable isotope analysis is based on the peak-shift method, according to which on the assumption that seasonal effects on the isotopic composition of precipitation are traced through the soil vertical isotopic profile.

An experimental approach combining hydrogeology, satellite remote sensing and soil analysis was used to estimate the data required for the application of the two methods by combining on-site, laboratory and remote data.

In this study, the application of the SWB model and the isotope approach proved to be useful and simplified tools in estimating the net water infiltration. An accurate estimation of spatial and temporal distribution of groundwater recharges contributes to better land management in terms of optimizing agricultural practices with the purpose of performing specific interventions that can reduce groundwater pollution.

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## Thermal conductivity and grain size in unconsolidated materials

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*Keywords:* thermal conductivity, unconsolidated materials, geothermal energy.

Renewable energies are becoming increasingly important in everyday life, not only for electricity generation, but also for heating and cooling of buildings. Geothermal energy, despite currently being underutilized, has significant potential. Specifically, low-enthalpy geothermal energy could play a fundamental role in the energy transition, as most CO<sub>2</sub> emissions in Europe come from heating and cooling of buildings (European Commission, 2016). The study of the subsurface at the hydro-thermo-petro-physical level, especially in the first few hundred meters, is extremely important to understand how to exploit the heat present beneath the surface. This methodology of study can be important in various fields such as geology for geothermal energy, CCUS, UTES, as well as other development areas such as engineering, ceramics, and agriculture. This work aims to highlight the importance and the role of selected parameters in terms of thermo-physical behaviour exploring possible relationships. In particular, thermal conductivity will be considered, which is closely related to grain size, porosity, bulk density, and water content. To achieve this goal, we measured the thermal conductivity of unconsolidated materials for numerous samples by exploiting the GeoTh laboratory (Rapti, et al. 2022) based on the guarded hot plate method. The analysed material was separated into specific size ranges (Wentworth, 1922) allowing to relate thermal conductivity and grain size through data analysis. The results were also compared with other petro-physical parameters. Analysed samples cover the range from gravel to clay. These materials were sieved and analysed to identify the present mineral phases, and then thermally tested at different saturation rates. The tested materials came from different areas of the Po Valley (Italy), Greece, and some areas of Canada. The results were processed using statistical techniques and compared with literature data and empirical relationships. Providing new and well constrained data and identifying trends among these parameters are the main objectives of the research that will improve our capacity of geothermal characterization of the subsoil and therefore facilitating the planning for new installations devoted to the heat exchange.

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## **Some consideration on the hydrochemical and isotopic composition of bottled mineral waters in the Mediterranean area**

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*Keywords:* bottle mineral water, isotopic and hydrochemical composition, Mediterranean area.

In the last decades, the bottled water industry is expanding and is steadily becoming a significant economic and public health factor. For example, in 2005, the estimated global consumption of bottled water was approximately 165 billion litres, which equates to a per capita annual consumption of 25 litres while during the last two decades bottled water consumption has increased dramatically. In particular, more than 25% of the world's bottled water is produced in the European Union, where 52 billion litres are consumed annually. Due to the fact that bottled mineral waters originate from groundwater aquifers, their chemical composition is initially determined by geochemical water-rock interaction processes. As water moves through the water cycle, the isotopic composition of oxygen and hydrogen in the water molecule may change. For example,  $^{18}\text{O}$  and  $^2\text{H}$  values in precipitation vary significantly with latitude and altitude. Determining  $^{18}\text{O}$  and  $^2\text{H}$  can thus help to characterize the source of bottled water and the natural conditions of the parent water body, of the recharge area, and the influence of various processes during infiltration and water flow within the water body. We will present and discuss the results of about 150 bottled water samples from different countries in the Mediterranean region in terms of hydrochemistry and  $^{18}\text{O}$  and  $^2\text{H}$  isotopic composition to define the possible relations between meteoric isotope data and isotopic composition of bottled water.

## Flow and transport numerical modeling for groundwater management: the Metaponto coastal aquifer case study (Basilicata, Italy)

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*Keywords:* coastal aquifer, Metaponto plain, numerical modeling.

In the Metaponto coastal plain (Basilicata, Italy), groundwater represents fundamental resources to the economic growth of intensive agriculture and tourism. Due to the agricultural vocation and the presence of residential settlements, tourist facilities, and natural areas (woodlands and wetlands), the plain is relevant for the entire Basilicata region. Human changes have adversely affected the hydrogeological system, threatening the groundwater availability/quality along the coastal plain and intensifying the potential seawater intrusion (SWI) risk. Currently, groundwater is particularly exposed to quantitative degradation, due to unfavorable climatic conditions exacerbated by climate change and the increasing demand for water, and to qualitative degradation also caused by SWI.

In this study, groundwater flow and variable-density transport numerical modeling was performed for the part of the plain with a higher propensity for SWI. The study area selection was based on the hydrochemical characterization, revealing a progressive mixing between freshwater and seawater, and the groundwater vulnerability to SWI assessment of the entire coastal plain (Muzzillo et al., 2022). Geological, hydrogeological, hydrological, and hydrochemical data were acquired to define the accurate conceptual model of the selected area, which was the first step for later groundwater flow numerical simulations and the SWI phenomenon modeling. The data of the PRISMAS project of the Basilicata Region focused on the Metaponto coastal plain were implemented for the numerical model calibration (Martinelli & Marchetti, 2000).

The numerical modeling of groundwater flow and the following variable-density transport were performed, in steady-state and transient conditions, through the Visual MODFLOW Flex 7.0 software (© 2021 by Waterloo Hydrogeologic).

Several scenario simulations were performed to examine the effects of the different pumping conditions and the impact of climate change on the aquifer recharge.

Numerical simulations allowed reasonably accurate simulation of the dynamic behavior of the aquifer system and, therefore, provided helpful insights for groundwater use and planning.

Groundwater modeling permitted thus the definition of the aquifer system's hydrogeological and hydrodynamic conditions and the understanding of the flow and transport mechanisms that govern groundwater resources. The numerical modeling outcomes can be used for the groundwater resources effective management in the Metaponto coastal plain aquifer.

The results obtained in the framework of the Ph.D. project (Muzzillo, 2023) are helpful for the definition of appropriate groundwater management and planning proposals finalized to preserve the groundwater resource from SWI. The findings may also provide effective support for groundwater quality and quantity protection and optimal directions for implementing criteria and strategies that address climate change and changes in water demand.

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## **Game-theoretical model for sustainable use of groundwater in the heavily stressed system of the Acque Albule Basin (Rome, Italy)**

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*Keywords:* groundwater, sustainable yield, game-theoretical modeling.

This study is aimed at identifying the sustainable withdrawal from the aquifer of the Tivoli Plain (Central Italy), where thermal springs with considerable flow (over 2 m<sup>3</sup>/s) emerge (or rather emerged) and supply a thermal plant. In the same plain, another profitable economic activity concerns the extraction of travertine. The withdrawal of groundwater from the quarry area, necessary to extract the travertine in depth, determined a significant impact on the water balance of the system. Specifically, under dewatering conditions from the quarry area, an increase in inflow from surrounding aquifers coupled with a decrease in storage and in natural discharge of the travertine aquifer result. Residual discharges towards the springs and river are very sensitive to quarries pumping flow rate according to an inverse linear relationship. These heavily stressed environmental conditions lay the basis for developing a game-theoretical modeling of the sustainable withdrawal from the quarry area in order to maximize the gain from the extraction of travertine in a cooperative way, and at the same time the springs flow rate must satisfy a sustainability constraint, while we also maintain the equilibrium between ground-surface water of the plain. In the game the quarry concession holders are the players, the strategy of a player is bound by the influence of dewatering on the water levels of the springs and the river, and the player's utility is proportional to the total quantity of travertine extracted. A special constrained Pareto optimal strategy choice is obtained which can constitute the conceptual foundations for a future sustainable management of groundwater in the plain.

## Groundwater age tracer challenges: a case study from the Muravera plain, Italy

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Keywords: dating groundwater, coastal aquifer.

Groundwater dating contributes to the characterization and management of groundwater systems, providing valuable information for establishing sustainable extraction rates and minimizing the impacts of groundwater contaminants.

However, interpretation of age tracer data can be a challenge because tracer concentrations are often affected by factors unrelated to groundwater age, introducing substantial uncertainty (i.e. mixing processes, contamination by geogenic sources, and degradation) (Beyer et al., 2014; Cook, 2022). This work reports a case study in which groundwater dating is applied in the Muravera coastal plain (SE Sardinia, Italy), which is characterized by significant seawater intrusion, focusing on the challenges of tracer data interpretation in salinized aquifers. Multiple tracers were used: <sup>3</sup>H, He, CFC, SF<sub>6</sub>, and noble gases. To reduce errors related to mixing with seawater, age tracer and noble gas concentrations were calculated for the freshwater fraction using estimated concentrations for the saltwater fraction of each sample. Recharge parameters were computed from the noble gas concentrations using the PANGA code (Jung & Aeschbach, 2018). The mean age of the freshwater fraction in each sample was constrained using the TracerLPM software assuming a BMM-PFM-PFM mixing model. The combined tracer results indicated that several samples were affected by geogenic source of SF<sub>6</sub> (possibly fluorite mineralization) as well as CFC contamination possibly introduced during the sampling. Furthermore, reliable <sup>3</sup>H/<sup>3</sup>He ages could not be computed due to elevated terrigenous He (He<sub>terr</sub>) concentrations and/or apparent loss of tritogenic <sup>3</sup>He for unknown reasons. However, despite these difficulties, the age tracers still provided valuable information. The seawater component has a high He<sub>terr</sub> concentration of over 4E-7 ccSTP/g, meaning that the seawater component is likely entirely premodern (recharged prior to 1953), as confirmed by the very low tritium value. Concentrations of this magnitude are typical for groundwater >1000 years old. The <sup>3</sup>H, SF<sub>6</sub>, and CFC results combined successfully provide a minimum mean age estimate for the freshwater component (40 to 70 years), in turn enabling a minimum mean age estimate for each sample (40 to >500 years). The spatial distribution of the minimum ages indicates age gradients within the aquifer, revealing groundwater flowpath geometry and likely recharge locations. Despite the processing difficulties, meaningful preliminary results were achieved through a combination of dating, isotopic, chemical, and hydrogeological techniques.

Beyer M., Morgenstern U. & Jackson B. (2014) - Review of techniques for dating young groundwater (< 100 years) in New Zealand. *Journal of Hydrology (New Zealand)*, 93-111.

Cook P. (2022) - Introduction to isotopes and environmental tracers as indicators of groundwater flow. *The Groundwater Project*.

Jung M. & Aeschbach W. (2018) - A new software tool for the analysis of noble gas data sets from (ground)water, *Environmental Modelling & Software*, 103, 120-130.

## **A new dynamic closed loop exchange for the exploration of shallow geothermal resources**

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*Keywords:* dynamic closed loop exchange, shallow geothermy, aquifer.

Theoretical research and real examples of successful applications of renewable and eco-sustainable resources represent an important support to the energy transition. At this regard, a new dynamic closed loop exchange for the exploration of shallow geothermal resources and an innovative monitoring system have been installed in a test site located in the northern alluvial plain of the Modena Province. Here, the lithostratigraphic sequences and the hydrogeological conditions have been strongly influenced by sedimentation processes and the recent tectonics activity of the blind structures. At the investigated site, we collected i) litho-stratigraphic, ii) hydrogeological, iii) hydrochemical and iv) thermos-physical data acquired by means of in situ tests and analysed them on the basis of an integrated approach. All these tests allowed us to properly define the hydrodynamic and thermos-physical behaviour of the local aquifers and the response of the subsoil to the thermal stresses potentially applied by a low enthalpy geothermal plant. Finally, the integrated and holistic analyses of all the data allowed us to evaluate the energy and environmental sustainability of these innovative dynamic closed-loop heat exchangers.



## **GeoTh: An experimental laboratory set-up for the measurement of the thermal conductivity of granular materials**

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*Keywords:* Geoth laboratory, thermal conductivity, geothermal energy.

Geothermal energy is a valuable source of renewable energy that can help us transition towards a more sustainable future. One of the ways geothermal energy can be extracted and utilized is by tapping into the heat stored in the subsurface. This can be done through the use of geothermal heat pumps, which can provide heating and cooling systems for homes, buildings, and other structures. The advantage of geothermal energy is that it can be harnessed 24/7 throughout the year, unlike other renewable sources such as solar or wind power that are dependent on weather conditions. To optimize the use of geothermal energy, it is important to have accurate measurements of the thermal properties of the subsurface materials. In particular, the thermal conductivity of granular materials such as soil, sand, silt, clay, or artificial composites needs to be determined. To address this issue, we developed an innovative laboratory apparatus called GeoTh (Rapti, et al. 2022), which is a new, simple, efficient, flexible, and low-cost apparatus. GeoTh enables the measurement of the thermal conductivity of granular materials. The laboratory has been designed for a one-dimensional steady-state thermal conduction configuration, which allows for the determination of the thermal conductivity of the samples. The apparatus allows for the contemporaneous measurement of up to 12 samples under ambient and constant temperature conditions. Its robustness has been tested by analysing and measuring numerous materials under different conditions. We also performed various tests varying the water content (between 0% and 100% water saturation) for gravel, sand, and clayey silt samples to calibrate and test the system's robustness and verify the repeatability of the experimental data. Finally, the obtained thermal conductivity values were compared with other datasets proposed in the literature, showing good correspondence.

Rapti D., Marchetti A., Andreotti M., Neri I. & Caputo R. (2022) - GeoTh: An Experimental Laboratory Set-Up for the Measurement of the Thermal Conductivity of Granular Materials. *Soil Systems*, 6(4),88. <https://doi.org/10.3390/soilsystems6040088>.

## Some considerations on the reuse of geopressurized deep aquifers as an energy resource

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Keywords: geopressurized deep aquifers, energy.

The show how abandoned oil wells could be exploited for thermal energy generation and thus contribute to the needs of the built environment. The possibility of using these wells is strongly conditioned by many factors, such as for example the geological and hydrogeological conditions of the subsoil, the operating costs and the distance from the final user of the thermal energy. In this context, the Malossa field (Bergamo, Italy) cultivated from 1973 until the end of the 1980s for the production of gas and condensates was taken into consideration and analysed. Production tests have shown a daily productivity of the reservoir of 500,000 Sm<sup>3</sup> of gas and 2,800 bbl of oil, as well as 943 mc/h of water. The field was cultivated using wells up to a depth of 6 km, while in the stretch from 4 to 6 km anomalous overpressures were measured which reach the maximum peak of 15,000 PSI (1,020 atm) at about 5 km. The analysis of the available geological, hydrogeological and thermophysical data allowed us to estimate and represent in 3D the porosity of the Dolomia Principale, Zandobbio and Maiolica formations, as well as the total permeability mainly attributed to the presence of discontinuities which characterize the rock mass. The analysis of the temperatures also made it possible to estimate, in the geothermal reservoir, compressed values between 150 and 165°C at a depth of about 6 km. The integrated analysis of these data constituted the starting point for the modelling and development of some scenarios aimed at evaluating the energy potential of the geothermal reservoir using a doublet system (withdrawal and reinjection well); as well as the analysis of the benefits and criticalities of the system.

## Unconventional pumping tests in carbonate, alluvial and complex aquifers, without interruption of drinking water exploitation

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*Keywords:* pumping test, carbonate aquifer, alluvial aquifer.

Pumping tests are very useful for aquifers characterization especially for exploited ones, but it is even important to provide drinking water without service interruption during tests’ execution.

In the Central Italy, the main groundwater resources come from the Apennines carbonate structures which feed the plain and where the main springs can be found. Another important area is the Periadriatic one, where alluvial aquifer can be observed.

In this study, three different case studies have been analysed, the first one is the Gran Sasso carbonate aquifer, the largest and most productive in the Apennines (Petitta & Tallini, 2002); its hydrogeological structure has been deeply studied since the middle of the last century for springs’ characterization for drinking purposes and for drilling of a motorway tunnel. The aquifer is characterized by secondary porosity, and an underlying impermeable marly complex, which represents the basal aquiclude.

Other tests have been carried out in the Vomano alluvial aquifer and in the Gole di Popoli area. The former is in the Abruzzo Periadriatic area, and it is characterized by gravelly and arenaceous bodies, which work as aquifer, over an aquiclude made by clayey deposits; groundwater is exploited in the portion of the aquifer where the permeable deposits are thicker (Rusi et al., 2004). The second, located in the Apennines area, is a complex aquifer and it can be described as a carbonate aquifer characterized by secondary porosity, under Quaternary deposits referring to alluvial and detrital deposits, marly deposits at the bottom of the permeable succession act as aquiclude (Di Curzio et al., 2018).

In carbonate and complex aquifers, it might appear inappropriate to characterize the hydraulic properties via pumping tests, as their reliability is proven in homogeneous and isotropic media. However, the high extent of this aquifer, the wells’ location, as well as the scarcity of information available and the lack of alternatives forced to estimate some hydrodynamic parameters as in porous aquifers and to test the aquifer experimentally, especially in conditions of maximum pumping even for the evaluation of the influence radius.

In all three, the aquifer testing was performed during the normal activities of abstraction and distribution, it was not possible to perform canonical tests, i.e. with only one pumping well and observing the adjacent wells.

Therefore, the step-drawdown test was obtained by turning on an increasing number of wells over time and keeping fixed the observation points. This kind of test, in addition to avoid interrupting the water supply, allowed:

- estimating hydraulic conductivity and transmissivity;
- estimating drawdown in pumping wells and in observation piezometers in operating conditions;
- evaluating the extension of the perturbation induced to the aquifer both at the test and stress discharges;
- evaluating flow directions in operating conditions.

Di Curzio D., Rusi S. & Semeraro R. (2018) - Multi-scenario numerical modeling applied to groundwater contamination: The Popoli Gorges complex aquifer case study (Central Italy). *Acque Sotterranee - Italian Journal of Groundwater*, 7(4), 49-58. <https://doi.org/10.7343/as-2018-361>.

Petitta M. & Tallini M. (2002) - Idrodinamica sotterranea del Gran Sasso (Abruzzo): nuove indagini idrologiche, idrogeologiche e idrochimiche (1994-2001). *Boll. Soc. Geol. It.*, 121(3), 343-363

Rusi S., Tatangelo F. & Crestaz E. (2004) - The hydrogeological conceptualisation and well fields management of the Vomano Valley (Abruzzo, Central Italy) using groundwater numerical modelling. *Geologia Tecnica e ambientale*, 4, 5-22.

## Water management in agro-industrial processes: successful case studies

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Keywords: water recovery, food wastewater, membrane technologies.

Water plays a crucial role in agro-industrial processes. It is one of the main ingredients in food, also used for heating, cooling, or preserving, or in cleaning operations on food, machinery, or production areas to guarantee food safety. The increase in food production to meet population growth causes a dramatic surge in water consumption in food processing.

Each type of commodity and food shows a water footprint that characterizes its sustainability regarding the water consumption necessary for its transformation and production. Furthermore, the more food is processed and handled, the greater its water footprint will be, as each processing step and co-product production (e.g., additional ingredients or packaging) may need water (Mekonnen & Gerbens-Leenes, 2020). The food and beverage industry has a strong impact on water resources, consuming almost 3% of the world's water supply.

Three ways to manage water for food production are possible: Reduce water consumption, Reuse and recycle wastewater, Use of alternative water sources. Various methods are available depending on water quality requirements, space, and budget constraints (Shrivastava et al., 2022).

Membrane technologies are an effective tool to recycle wastewater or make alternative water sources suitable for industrial processes. Membrane separation techniques allow the recovery of water otherwise lost, while concentrating and purifying valuable compounds (Pervez et al., 2021).

Membrane processes are included in the Best Available Techniques (BAT) (Joint Research Centre, 2018). They are mild, non-destructive, and energy-efficient methods, suitable to treat liquid by-products deriving from food processing, such as olive mill wastewater, dairy wastewater, brewery wastewater, and blanching water (e.g., from the almond, tomato, or potato processing industry). Micro-, ultra-, and nano-filtration can be used sequentially to separate and concentrate the solutes from the aqueous fraction. Reverse osmosis systems can intervene downstream of these treatments to obtain purified water.

The benefits of these treatments include the reduction of wastewater flows, freshwater costs, and the water footprint of the entire process. The recovered water can become an ingredient for new food products and, at the same time, valuable compounds, such as polyphenols, carotenoids, and nutrients, can be recovered and used in other industrial sectors, thus adding value to the food system.

Joint Research Centre (JRC) (2018) - Best Available Techniques (BAT) Reference Document for Waste Treatment. [https://eippcb.jrc.ec.europa.eu/sites/default/files/2019-11/JRC113018\\_WT\\_Bref.pdf](https://eippcb.jrc.ec.europa.eu/sites/default/files/2019-11/JRC113018_WT_Bref.pdf).

Mekonnen M.M. & Gerbens-Leenes W. (2020) - The Water Footprint of Global Food Production. *Water*, 12(10), 2696. <https://doi.org/10.3390/w12102696>.

Pervez M.N., Mishu M.R., Stylios G.K., Hasan S.W., Zhao Y., Cai Y., Zarra T., Belgiorno V. & Naddeo V. (2021) - Sustainable Treatment of Food Industry Wastewater Using Membrane Technology: A Short Review. *Water*, 13(23), 3450. <https://doi.org/10.3390/w13233450>.

Shrivastava V., Ali I., Marjub M.M, Rene E.R. & Soto A.M.F. (2022) - Wastewater in the food industry: Treatment technologies and reuse potential. *Chemosphere*, 293, 133553. <https://doi.org/10.1016/j.chemosphere.2022.133553>.

## Spatial and temporal patterns in the hydrogeochemistry of coastal aquifers in Campania Region (southern Italy)

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*Keywords:* groundwater quality, statistical analysis, trend analysis.

International regulations, such as those implemented by the European Union (i.e., Groundwater Directive 2006/118/EC), require the determination of groundwater quality status as well as its evolution. Groundwater quality in areas characterised by different geological formations (i.e., the presence of volcanic areas, carbonate rocks, alluvial-pyroclastic deposits), diversified ecosystems (i.e., wetlands), and located along the coastline may result in heterogeneous hydrochemical facies distribution and variable (e.g., non-linear) temporal evolution. Human activities (i.e., agricultural, industrial, residential and touristic activities) and rapid land use change can modify the amount and distribution of point and non-point sources of contamination affecting groundwater quality, while climate change may significantly impact water availability and quality (IPCC, 2012).

The area of interest is located in the northern part of Campania Region (Southern Italy) and it includes three Groundwater Bodies (DAM, 2021): the Volturno Plain, a coastal plain constituted of fluvial, pyroclastic and marine sediments, the Plain of Naples, an innermost plain of fluvial and pyroclastic sediments, and the Phlegrean Fields, an active volcanic area with a series of monogenic volcanic edifices. Hydrochemical data collected biannually by the Regional Environmental Agency at about 35 wells from 2002 to 2020 were considered for evaluating the spatial distribution and temporal variation (Mann-Kendall trend test) of the main physico-chemical parameters.

Groundwater chemistry reflects the geological characteristics of the study area, being influenced by volcanic edifices and related pyroclastic products and the closeness to carbonate rock formations. Calcium-bicarbonate facies is prevalent, with a gradual transition to alkaline type from the mountains towards the coast. In addition, ions concentration distributions highlighted the occurrence of seawater intrusion ( $\text{Na}^+$ ,  $\text{Cl}^-$ ) and anthropogenic contamination ( $\text{K}^+$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ) negatively affecting groundwater quality. Long-term trends show significant increases in ion concentrations in the innermost part of the plain and decreases in the coastal areas for most of the ions (exceptions are  $\text{Na}^+$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ ). The integration of land-use/land-cover information over the 2002-2020 period, together with the information regarding the decadal and seasonal variation of the population and the characteristics of the sewage systems and agricultural practices (i.e., water demand) allows detecting the singular and combined causes of the evolution of groundwater quality in the study area.

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IPCC (2012) - Managing the Risks of Extreme Events and Disasters to Advance Climate Change Adaptation.

DAM (2021) - Autorità di Bacino Distrettuale dell'Appennino Meridionale. Piano di gestione delle acque ciclo 2021-2027. <https://www.distrettoappenninomeridionale.it/index.php/piano-iii-fase-2021-2027-menu/piano-di-gestione-acque-iii-ciclo-2021-2027-menu?layout=edit&id=711>.

**S36.**

**Mineral deposits: understanding, exploring and exploiting,  
in a sustainable way**

*CONVENERS AND CHAIRPERSONS*

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## The case study of structural control on skarn ores in highly deformed domains in SW Sardinia and its application as a regional prospection guideline

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*Keywords:* skarn, structural control, CRMs.

Tectonic structures such as faults, joints, foliations and folds control the orebodies' genesis, geometries and mineralogical assemblage. Typically, minerogenic and tectonic events are related, so a coupled minerogenic and structural investigation and modelling are guidelines for prospecting in areas with similar features. Here, we present the application of this approach to the study on the skarns hosted in the Rosas Shear Zone (RSZ) and Fluminimaggiore in SW Sardinia.

The Rosas Shear Zone (RSZ) is a km-scale, NE-dipping, highly deformed domain set in the footwall of the Arburèse Thrust, the leading edge of the Variscan Nappe zone thrust over the External Zone (Cocco et al., 2022). The shear deformation testifies a crustal brittle-ductile transition, as confirmed by paleo-piezometry (Casini et al., 2010). A penetrative tectonic cleavage affects the lower Cambrian carbonates and the Upper Ordovician siliciclastic succession. A system of anastomosing low-angle thrusts bounds multiple tectonic slices mainly consisting of lower Cambrian limestone. The compressive deformation phase is post-dated by the intrusion of a mafic dike related to the onset of the late Carboniferous-Permian Variscan chain exhumation.

The carbonate tectonic slices host several skarn orebodies; mafic dykes are also locally metasomatised. The mineralisation consists of Zn-Cu-Pb sulphides with minor magnetite, cassiterite, pyrrhotite, and pyrite and rare Ag-sulphides, native Au and Ni-Co-arsenides and sulpharsenides.

The skarn orebodies in the RSZ are an example of passive structural control on metallogenic processes: the thrusts inherited from the Variscan compressive phase acted as a plumbing system, favouring a large-scale circulation of hydrothermal fluids from their Late Variscan granites source and mixing with meteoric water (Boni et al., 1990).

The Fluminimaggiore area shares many similarities with the RSZ. Several structurally controlled skarn orebodies occur along Cambrian and Devonian carbonate slices within an Upper Ordovician-Silurian siliciclastic succession in the footwall of the Arburèse thrust. The skarns host Zn-Cu-Pb-Fe-As sulphides, magnetite, and fluorite; their causative intrusion is the ilmenite-series granites of the Mt. Linas Pluton, genetically linked to several cassiterite mineralisation documented around Fluminimaggiore, Rosas and Mt. Tamara (Naitza et al., 2017). The same structural pattern was tapped by late (post-Variscan?) low-temperature fluids originating F-Ba-Pb-Zn-Ag veins both in the RSZ (Truba Niedda) and Fluminimaggiore (Mt. Argentu-S. Lucia).

The combined structural-mineralogical approach utilized for the RSZ skarn ores minerogenic modelling befits the Fluminimaggiore area, supporting its conceptual model and confirming it as a prospection guideline for highly deformed domains in the region. Hence, it will allow us to understand the structural control on Fluminimaggiore hydrothermal vein ores required for an economic potential evaluation.

Boni M., Rankin A.H. & Salvadori M. (1990) - Fluid inclusion evidence for the development of Zn-Pb-Cu-F skarn mineralization in SW Sardinia, Italy. *Mineralogical Magazine*, 54, 279-287.

Casini L., Funedda A. & Oggiano G. (2010) - A balanced foreland-hinterland deformation model for the Southern Variscan belt of Sardinia, Italy. *Geol. J.*, 45, 634-649. <https://doi.org/10.1002/gj.1208>.

Cocco F., Attardi A., Deidda M.L., Fancello D., Funedda A. & Naitza S. (2022) - Passive Structural Control on Skarn Mineralization Localization: A Case Study from the Variscan Rosas Shear Zone (SW Sardinia, Italy). *Minerals*, 12, 2. <https://doi.org/10.3390/min12020272>.

Naitza S., Conte A.M., Cuccuru S., Oggiano G., Secchi F. & Tecce F. (2017) - A Late Variscan tin province associated to the ilmenite-series granites of the Sardinian Batholith (Italy): The Sn and Mo mineralisation around the Monte Linas ferroan granite. *Ore Geol. Rev.*, 80, 1259-1278.

## Italian CRM's potential: the case of Sardinian F-Ba hydrothermal ore deposits

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Keywords: fluor spar, hydrothermal veins, CRMs.

Critical Raw Materials (CRMs) are strategic and essential for Europe's economy, leading the trend towards a "rediscovery" of its ore deposits. Sardinia has a long mining history and copious available mine data requiring updating. An ISPRA-UniCa project (Update of the regional mining and mineral resources database with priority on CRMs and SRMs for Decarbonization and Ecological Transition - Geoscience IR Project, WP 5.1) is devoted to the mapping of resources on a regional scale. Among them, F-Ba hydrothermal vein systems widespread within the Variscan basement of Sardinia, including the world-class deposit of Silius, hosting the only active fluor spar mine in Sardinia and representing a candidate for being a strategic mining project. Accordingly, three of the most relevant F-Ba vein systems showing geological and mineralogical similarities are currently under study: Silius (S Sardinia), Asuni (Central Sardinia) and Santa Lucia (SW Sardinia).

The Silius ore deposit is a pinch-and-swell system of veins extending NE-SW on 2-4 km and currently known unto 500 m of depth. The veins crosscut the kilometric SW-verging recumbent folds involving Ordovician to Silurian metasedimentary and metavolcanic sequences of the variscan External Nappe Zone. The ore minerals are predominant fluorite, subordinate galena and barite, and accessory Zn-Cu sulfides. The enrichment in sulfides and the recently discovered Ni-Co-Bi arsenides and sulfarsenides at depth results in a vertical zonation of the deposit, suggesting an evolution towards a polymetallic system (Scano et al., 2023). Banded and brecciated textures of the vein indicate an alternation of tectonically-controlled steady-state and more dynamic pulses of mineralization. The certified reserves exceed 2.1 Mt at 32% CaF<sub>2</sub> and 3% Pb; total REE reach contents of 1000 ppm (Mondillo et al., 2016).

The Asuni mineralization strikes NE-SW in the footwall of a thrust fault. This "Silius-like" ore is smaller and scarcely explored (Bakos et al., 1972a).

The Santa Lucia vein system is hosted in NW-SE and E-W high-angle faults in the footwall of the Arburès thrust, marking the variscan contact between the Nappe Zone and the External Zone. While the upper part of the deposit is exhausted, it remains poorly explored at depth (Bakos et al., 1972b).

The three deposits show geological and structural analogies, but it is clear that Asuni and S. Lucia require new mineralogical and structural investigations. A thorough structural study is necessary even in the best investigated Silius for geological modelling, crucial to evaluate the economic potential of these deposits and rarely applied to them until now. For instance, in all the studied cases, vertical and horizontal displacements and pinch-and-swell attitudes determined zones of impoverishment in ore minerals that in the past discouraged further exploitations; thus, the reconstruction of the host faults kinematics is essential for exploration targeting to find new mineralized zones.

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## Transmission-based muography for ore body prospection: results and next challenges

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Keywords: muography, ore body, mining prospection.

Transmission-based muography (TM) is an imaging technique based on the measurement and analysis of the cosmic ray muon flux attenuation within the investigated object. Muons are low-interacting particles that, owing to their high energy and mass, may travel through hundreds of meters of rock before stopping, which is why they are used in radiography investigations. These particles have a typical lifetime of 2.2  $\mu$ s and a mass that is approximately 200 times that of an electron. Muons are continuously formed in the upper atmospheric layers of the Earth (15–17 km), mostly by the decay of pions and kaons, which are particles produced by the collision of primary cosmic rays with nuclei of oxygen and nitrogen. This method allows for the imaging of changes in internal body density and has been utilized successfully in a wide range of research fields, including geology, archaeology, engineering geology, and civil engineering (Bonechi et al., 2020).

There are two types of muography: transmission-based muography (TM), also known as transmission muography, and scattering-based muography (SM). The former is generally used to study large and extended targets, such as mountains, volcanoes, or mine sites, while the latter is typically utilized to photograph smaller-sized targets, such as nuclear waste casks or truck containers (Bonechi et al., 2020).

The presented study validates and verifies the reliability of TM using the MIMA detector (Muon Imaging for Mining and Archaeology) for mining exploration and preliminary ore body prospection in Cu–Fe–Pb–Zn(–Ag) skarn ore deposits. This study highlights how muographic surveys can be utilized as a supplement to traditional geophysical techniques such as gravimetric, seismic and magnetic surveys.

Measurements were conducted at the Temperino mine (Baccani et al., 2019) in San Silvestro Archaeological and Mining Park (Campiglia Marittima, Italy). Here, several magmatic and metasomatic geological unit outcrops. Using muon imaging data collected with the MIMA tracker, the existence of a high-density vein inside the skarn body within the rock volume above the muon detector was recognized, located, and interpreted (Beni et al., 2023). By applying a back-projection method to the resulting 2D transmission map, it was feasible to estimate and visualize the detected high-density body and its relative distance from the detector in 2D and/or 3D environments (Borselli et al., 2022). In light of the potential reconsideration and re-evaluation of domestic mineral resources, including those of historical mining districts, the results of this study demonstrate the usefulness of TM as a complementary tool to other well-established geophysical techniques for mining/mineral exploration.

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## **Ensuring informed decision-making over mineral resources with the United Nations Framework Classification for Resources (UNFC)**

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*Keywords:* sustainable resource management, United Nations Framework Classification for Resources, sustainable mining.

The European Union's quest for reducing dependency and ensuring sustainable supply chains of mineral resources has been amplified by the need to safeguard availability of mineral resources. However, part of achieving this requires a thorough re-evaluation of domestic mineral resources including historical mining deposits. With this in mind, comprehensive, transparent, and coherent information becomes a critical factor for progress. Stakeholders require reliable and transparent information for proper decision-making. This signifies the need for different approaches that will enhance current knowledge of mineral deposits and technical efficiency, while placing greater emphasis on sustainable implications with regards to economic growth, environmental protection, and social development.

The United Nations Framework Classification for Resources (UNFC) provides a classification tool that is anchored on three fundamental pillars of sustainable development and can be effectively applied at any stage of the value chain. One of the major advantages of this classification tool is that it provides stakeholders with accurate and comprehensive information that is pivotal to informed decision-making for sustainable resource management, particularly in promoting best practices in line with social, environmental, and economic sustainability.

The UNFC can also be adapted to the public domain since it can furnish even non-experts with easily digestible information that permits the comparison of national resources and their potential impacts on sustainable development. This paper gives an outlook on the necessity of UNFC and how it can leverage communication with the various stakeholders. This is corroborated in this paper through a UNFC case study applied on the Piampaludo Titanium exploration project in Liguria, Italy. The paper shows how UNFC aligns with the public domain. Additionally, publicly available information is utilized to provide a valuable insight into the resource in question, thereby increasing the available data for decision-making purposes. Altogether, the paper tackles key points on how UNFC provides a comprehensive mechanism for enhancing transparency and the dissemination of accurate information, which is critical to ensure sustainable decision-making over mineral resources.

## **Critical raw materials in the EU and international agendas**

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*Keywords:* critical raw materials, circular economy, twin transition.

Building on the EU's experience in performing periodic criticality assessments and updating the EU list of Critical Raw Materials every three years, the contribution will provide a brief overview of what critical materials are, why they are so important in the context of the European Green Deal and more generally for the energy and digital transitions, who is assessing criticality in the international framework, how and for what purposes. The discussion will touch on possible causes of critical materials supply crises and possible mitigation countermeasures, including the role of circular economy strategies.

## Tectonically deformed SedEx and Irish-type deposits in the Cambrian of SW Sardinia

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Keywords: SW Sardinia, SedEx, Irish-type.

Pre-Variscan stratabound Zn-Pb-Ba orebodies are hosted in the Lower Cambrian carbonate rocks of SW Sardinia (Italy) (Boni et al., 1996). Two groups of genetically distinct ore types are known: (1) syngenetic(?)–early diagenetic massive sulphides consisting of pyrite>>sphalerite>>galena and barite layers in tidal dolomites, interpreted so far as SedEx-type ores; (2) late-diagenetic replacement and breccia-hosted ore bodies in shallow water limestones with a sphalerite>galena>>pyrite association, which have been classically interpreted as MVT ores, but could easily fall within the Irish-type deposits class (Wilkinson & Hitzman, 2014). At the regional scale, both types of deposits are primarily located along long-living synsedimentary faults (Boni & Bechstädt, 1994). The most characteristic among the economically significant Irish-type ores are the “Yellow Sphalerite *Blendosi*”, which occur as broad horizons of diffused impregnations of pale-yellow sphalerite replacing a peloidal mudstone carbonate facies. However, the most typical Irish-type ore concentrations in the western areas of the Iglesias mining district occur in the cement and matrix of multigeneration breccias.

The effects of deformation and low metamorphism on the pre-Variscan ores in SW Sardinia include changes in: (a) the geometry and thickness of sulphide orebodies, and (b) the mineralogy and textures of the ore and gangue minerals. Variscan tectonics produced a pervasive ductile deformation of the limestone breccia-hosted ores, resulting in the development of a strong foliation and redistribution of both the sulphides and the breccia clasts along the cleavage. The SedEx ores, being richer in pyrite, developed preferentially a brittle deformation, where sphalerite and galena show a significantly more ductile behaviour relative to pyrite (*boudinage*).

Major and trace element contents of ore and gangue minerals were also locally modified. New mineralogical and geochemical data on the sulphide ores show a marked difference in major and trace elements between the SedEx- and Irish-type ores, due to the possible effects of deformation and shearing on the redistribution of the metals. The recent investigations also allowed detecting abundant Ba-bearing muscovite in several mineralized intervals, generally far from the stratabound barite bodies.

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## **New insight on the Pb-Zn mineralization of Ruà Mine (Bagni di Vinadio, Cuneo, Piemonte)**

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*Keywords:* ore, mines, mineralizations.

The Ruà Mine is a historical extractive site in the Bagni di Vinadio Valley (Cuneo, Piemonte). The area was exploited during the Savoia Kingdom for Ag, Pb and Zn (Cevales, 1961). The Mine consisted of several production galleries following a NW-SE-verging hydrothermal veins system crosscutting the South and the North slopes of the valley. The mineralization consists of sphalerite and Ag-bearing galena with calcite and fluorite gangue (Cevales, 1961) hosted within Hercynian mylonitized orthogneiss of the Argentera Massif. According to literature (Omenetto & Brigo, 1974), the mineralization is related to fluids circulation during Hercynian tectonic events, with a likely re-mobilization of the metals during Alpine orogeny. This work presents a preliminary study aimed at a better understanding of the hydrothermal vein system in terms of i) structural setting, and ii) mineralogy, chemistry and petrology. The field activities focused on a geological survey and sample collection of host rock and mineralized material on site. Due to the inaccessibility of the old galleries, the mineralised material was collected from the extraction dumps still visible on the valley slopes. Mineral-petrological, micro-structural, and chemical characterization were carried out on selected samples by OM, XRD, SEM-EDS/CL, EPMA, and ICP-MS/AES analyses. At least three different microstructural settings were observed for the mineralization: I) in mylonitic orthogneiss, where the mineralization lays along the foliation planes and is ductile deformed along folds. Fluorite is present as porphyroclast and along the mylonitic foliation; II) cavity filling and breccia cement of highly brecciated cataclastic host rock, and III) mineralized veins crosscutting the host rock, and the former mineralization. The CL observations show different fluorite generations: a first one (fl-I), strongly brecciated and cemented by a second fluorite (fl-II). Moreover, fl-II, galena, and sphalerite locally fill strain shadows of quartz or fl-I porphyroclasts. SEM-EDS analyses improved our knowledge of mineralization. In detail, chalcopyrite in sphalerite and cobaltite in galena locally occur. Arsenopyrite may be the main ore in some samples. Fluorite hosts few REEs minerals (e.g., xenotime and synchsite) similar to other European Hercynian Zn-Pb hydrothermal deposits (Schwin & Markl, 2005; Mondillo et al., 2016). Chemical analyses confirmed the occurrence of REEs up to max. of ~403 ppm. Secondary phases (e.g., anglesite) occur in cavities and along fractures. The above-described frame reflects a complex genetic picture where different mineralization events occurred, likely linked to different tectonic settings from pre-Hercynian, syn-to-late-Hercynian and syn-to-post-Alpine. More detailed studies on Ages and paragenesis in the different mineralization types may help understanding the remobilization path of strategic metals (i.e. Co, REEs, etc.) hence vectoring new possible exploration targets.

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## The Platinum Group Elements enrichments and mineralogy of chromitites from the Serbo-Macedonian Massif, Chalkidiki, Northern Greece

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*Keywords:* platinum group elements, critical raw materials, chromitites.

Platinum Group Elements, namely Pt, Pd, Rh, Ru, Os, Ir are six noble, precious transition metals. They are important for several industrial applications, among which electronics and as catalysts in the automotive industry. These elements are classified as Critical Raw Materials for the EU, as they are currently produced mostly in South Africa (Bushveld complex) and in Russia.

Platinum Group Elements are also enriched to some degree in ophiolite chromitites where they form Platinum Group Minerals (PGM). Ophiolite chromitites mainly host Os-Ru-Ir PGM as accessory phases. They are usually primary sulfides, but secondary alloys, due to the remobilization of PGE through interaction with circulating fluids, are also widespread (Grieco et al., 2020).

Greece hosts numerous ophiolite-hosted chromitite deposits, several of which were exploited in the past. One of the largest chromite mining districts in EU, the Vourinos Complex, hosts several abandoned deposits with relatively low PGE contents (generally below 200 ppb of PGE total content). Higher PGE amounts are reported in the Veria deposits of Northern Greece, with up to 25 ppm of PGE total content.

Recent studies report the occurrence of PGE-rich chromitites from the Chalkidiki Peninsula in Northern Greece. Ophiolite bodies in this area are hosted within the Serbo-Macedonian Massif, and are not related to the nearby Vardar Zone ophiolites (Jurassic), but they were probably formed in the Early Triassic before the opening of the Vardar Ocean. The studied bodies are St. George, Limonadika and Tripes, all occurring near the Gomati village, and collectively known as “Gomati Ophiolite”.

The chromitites exhibit widespread alteration in ferrian-chromite, leaving only few preserved cores. This mineralization varies in terms of chromite mineral chemistry (Cr# 0.77 – 0.96, Mg# 0.36 – 0.51 at Limonadika, Cr# 0.66 – 0.75, Mg# 0.56 – 0.63, Mg# 0.22 – 0.55 at St. George, Cr# 0.57 – 0.61, Mg# 0.37 – 0.56 at Tripes), and in PGM suite and PGE distribution and total enrichments.

Limonadika hosts PGE-poor massive chromitite bodies with 175 ppb of PGE total content, and no PGM was detected in the samples. At St. George, chromitites have schlieren to densely disseminated textures, and the PGE total content is higher (380 ppb on average). Several euhedral laurite crystals were detected enclosed within unaltered chromite cores. Tripes hosts massive chromitites with a high PGE content (3516 ppb). PGM detected at Tripes are laurite, erlichmanite, but also PGE-rich sulfides. Unlike typical ophiolite PGE patterns, Tripes chromitites show a positive Rh anomaly.

The high PGE content at Tripes, as well as its spinel mineral chemistry, could be explained by a different mechanism of PGE enrichment in a magma chamber above the Moho, while St. George and Limonadika display typical features of mantle chromitites.

Grieco G., Bussolesi M., Eslami A., Gentile A., Cavallo A., Lian D., Yang J. & Ghaseminejad F. (2020) - Differential platinum group elements (PGE) re-mobilization at low  $fS_2$  in Abdasht and Soghan mafic-ultramafic complexes (Southern Iran). *Lithos*, 366, 105523. <https://doi.org/10.1016/j.lithos.2020.105523>.

## Resource corridors: a geological and strategic analysis within the EU Critical Raw Materials Act

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*Keywords:* resource corridors, critical raw materials, strategic supply chains.

The supply of critical raw materials has become increasingly important to meet the global ambitions of carbon neutrality by 2050. In the case of the European economy, the heavy dependence on critical raw material imports is pushing towards new sources of supply, both domestically and from partner countries. This study builds on previous work on EU-Africa strategic corridors (Baranzelli et al., 2022a, b) and contributes to the discussion on how geological aspects interact with future access to critical raw materials deposits.

The research is based on a review of existing scientific literature and the analysis of geological and geographical data of selected areas in the African continent.

The results confirm that the knowledge-base on a vast range of geological resources is still to be improved, including for rare metals, phosphates, cobalt, and other materials critical to decarbonisation and strategic sectors worldwide.

For example, the Central African Copperbelt rock, made mainly by metasedimentary rocks of Neoproterozoic age, is one of the world's main sources of copper, uranium and cobalt. In particular, the Katanga Formation in Congo contains 50% of the world's cobalt reserves (USGS, 2022), a critical material for the batteries used in electric vehicles, and 800 Mt @ 2.5% Cu.

Similarly, the Paleoproterozoic Bushveld Igneous Complex, the largest layered igneous intrusion within the Earth's crust located in the Limpopo province of South Africa, contains about 90% of the world's platinum reserves.

The study further investigates how some strategic corridors can offer prospective efficient access to these resources, despite the geological and logistical challenges that must be faced. Additionally, the analysis was conducted in relation to the 'Critical Raw Materials Act' published by the EU in 2023 and in the context of the project GeoSciencesIR (PNRR Infrastrutture di Ricerca).

The study also discusses some of the challenges that may arise in the complex and multi-stakeholder process of minerals exploration, from early stages to mine feasibility, including environmental concerns and socio-economic factors. Europe should build mutually beneficial partnerships with African countries to implement sustainable practices throughout the raw materials lifecycle, including fostering innovation in substitution or circular economy practices.

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## **Mineralizations of the Sila Massif (Calabria, southern Italy): The case study of the Zn-Pb ore deposit of Longobucco**

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*Keywords:* Mineral deposits, Longobucco, Zn-Pb deposit.

Although the mineral deposits of the Longobucco area in the Sila Massif (Calabria, southern Italy) are historically known as metal exploitation sites since ancient times, scientific interest in their study has only recently been renewed (Fregola et al., 2023a). In particular, a detailed mineralogical characterization using modern methodologies and framed in an updated geological context, would help to decipher their genesis. We have collected samples of the mineralized bodies outcropping along a fault zone crosscutting monzodiorites at the “Torrente La Manna” site in the Longobucco area, where Vighi (1953) first observed a sphalerite-galena-pyrite-quartz-calcite mineral association. We have characterized such minerals using optical microscopy, scanning electron microscopy (SEM), electron probe microanalyses (EPMA), and micro-Raman spectroscopy. Sphalerite is the dominant polymetallic mineral, showing color and chemical zoning, and can be used as fingerprint to differentiate the evolution stages of the mineralized deposit; noteworthy its mineralogical characterization is presented in a separate contribution to this congress (Fregola et al., 2023b; session P.40). Our reconstructed paragenetic sequence comprises almost five growth stages. Early minerals include a light-colored Fe-poor sphalerite-I, followed by a darker Fe-richer sphalerite-II formed in association to euhedral quartz-I crystals. The latter show color and chemical zoning of Al, Na, K, Ca. Moreover, we have observed a Mn-rich ( $1.19\pm 0.03$  to  $0.49\pm 0.02$  wt%) and Mg-poor (up to  $0.08\pm 0.01$  wt%) calcite, partly hosting REE-fluorcarbonates. The latter minerals are reported here for the first time in the Longobucco area, and consist of synchysite, with 20 to 60  $\mu\text{m}$  grain size, and total REE (Ce, La, Y, Nd, Sm, Pr, Gd, Dy) concentrations ranging between 42.64 and 2.40 wt%. Late stages minerals comprise sphalerite-III, quartz-II, pyrite, and Ag-free galena with low Sb-content (up to  $0.09\pm 0.03$  wt%).

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## The Allumiere-Tolfa mining district (Central Italy): new data on the mineralizations and hydrothermal alteration zones

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*Keywords:* Tolfa-Allumiere district, hydrothermal alteration, epithermal deposits.

The Tolfa-Allumiere mining district is located approximately 60 kilometers northwest of Rome (Italy) and has been characterized by a long-lasting history of exploitation for base metals (Pb, Fe), alunite and kaolinite mineralizations (Field & Lombardi, 1972). These deposits are genetically linked to the emplacement of a Plio-Pleistocene volcanic dome in arc setting consisting of latites and rhyolites, which intruded sedimentary carbonate and siliciclastic country rocks (Della Ventura & Patanè, 2020). The intrusive event first produced contact metasomatism of the limestones, and lately triggered hydrothermal activity, which caused a widespread epithermal alteration of the volcanic rocks (Masi et al., 1980).

This study presents the preliminary results of mineralogical and geochemical investigations aimed at better understanding the evolution of hydrothermal activity and the genesis of mineralization in the Tolfa-Allumiere area. The analysis performed on the altered volcanic rocks collected in old pits and outcrops, allowed identifying three main alteration facies: (1) residual silica, (2) advanced argillic, and (3) argillic facies. The residual silica facies is commonly sulfide-bearing, containing pyrite, As-pyrite, cinnabar, with traces of sphalerite, galena and chalcopyrite. In the advanced argillic facies, alunite occurs as aggregates of planar crystals in veins and cavities, is commonly zoned to natroalunite and is intimately associated with svanbergite. Smectite marks the zones interested by argillic alteration. Regarding the metasomatized host rock, the carbonates show recrystallization with presence of sulfides (pyrite and cinnabar), Sr-sulfates, thorutite, thorianite and fluorite. Either the epithermal assemblage in the volcanics and the metasomatized sedimentary rocks are affected by supergene alteration and gossan formation, which overprint the hydrothermal assemblage.

In conclusion, the preliminary results are in agreement with the occurrence of a magmatic-related hydrothermal system in the Tolfa-Allumiere area (Simmons et al., 2005). More detailed investigation is needed to determine if mineralized zones of greater economic importance occur in the surroundings of the investigated sites as proposed in typical genetical models of precious metals epithermal systems.

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## The Au-Bi-Te-W Tògoro vein system in the Monte Linas district: evidence of a Reduced Intrusion-Related Gold System in Southern Sardinia

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Keywords: ore deposit.

Reduced Intrusion-Related Gold systems (RIRGS: Hart, 2007) are a class of ore deposits related to reduced plutons (ilmenite-series granites and monzonites). These suites include metaluminous to peraluminous I-, S- and A- type granites, and are also commonly associated to W and Sn mineralization. Ore deposits in RIRGS districts (e.g., Tombstone belt, Alaska; Timbarra, E Australia; Salave, Salamòn and Jales, Iberia; Mokrsko, Bohemian Massif) usually include sheeted quartz vein systems hosted within the intrusions or the surrounding hornfels; skarn and greisen ores may also occur. The sheeted vein systems reflect hydrofracturing of the outer cupola and typically host Au-Bi-Te-W mineralization. Scheelite and wolframite are common; Au is mostly low-grade (< 1 g/t of Au) and associated to complex intergrowths of Bi-Te-Sb phases; sulfides are scarce. Fluid inclusions studies show that RIRGS usually form under ipo- (380°-300°C) to mesothermal conditions (280°-250°C) and from unmiscible fluids (Hart, 2007).

In SW Sardinia, several mineralisations are linked to a late Variscan granitoid suite emplaced at 289 Ma along a first-order tectonic structure (Arburèse thrust) which separates the Nappe Zone from the External Zone of the Variscan chain. The suite includes the F-bearing ilmenite-series granites of the Monte Linas pluton, which are the source of W, Sn, Mo and base metals (Pb-Zn-Cu) ore deposits (Naitza et al., 2017). However, old mine reports also mentioned traces of Au in association with Mo-, As- and W-rich orebodies in the surroundings of the pluton.

The Tògoro mineralization includes a km-scale system of NNE-SSW-directed, sub-vertical and sub-parallel quartz-wolframite veins. Veins vary in spacing (from dm-sized to metric), thickness (from 10-15 cm to about 1 m) and grade (higher in larger veins). Their gangue consists of quartz with white mica selvages. The ore includes large (mm- to cm-sized) ferberite platy crystals and very fine grains of native Bi, Au and droplets of Bi-Te-Au phases; sulfides are very rare (chalcopyrite, pyrite, arsenopyrite). Bismuth tellurides, including hedleyite (Bi<sub>7</sub>Te<sub>3</sub>) and Bi<sub>2</sub>Te, and maldonite (Au<sub>2</sub>Bi) were recognized by SEM-EDS; russellite (Bi<sub>2</sub>WO<sub>6</sub>) is a common secondary mineral. Preliminary assays on bulk samples revealed Au contents up to 0.7 g/t. Microthermometry of fluid inclusions entrapped in quartz indicate a formation under a temperature range of 400° to 250°C. In addition, abundant vapour-rich inclusions in quartz are consistent with fluid immiscibility. In conclusion, all features of the Tògoro quartz-wolframite veins point towards the very first report of Reduced Intrusion Related Gold Systems in the territory of Italy. This case study highlights that W-bearing mineralization linked to late Variscan reduced granites (e.g. Sardinia and Calabria) represent interesting perspectives for potential Au-Bi-Te-W mineral exploration.

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## **Mineralogical and Geochemical Characterization of the Punta Corna Fe-Co-Ni Mineralization in Piedmont, Italy: Implications for Late-Alpine Hydrothermal Ore Deposition and Metallogenesis**

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*Keywords:* five-element, cobalt, arsenides.

The Punta Corna Mining District is located in the Lanzo Valleys, Piedmont (Italy). It consists of Fe-Co-Ni mineralization exploited for Fe and Co until the 19<sup>th</sup> century and then abandoned. However, the global concern for strategic raw material supply, such as Co, has raised a renewed interest in old mining sites where economic potential was not fully investigated. Since 2018 the Junior Exploration Company AltaMin ltd. owns the exploration license of the Punta Corna area for assessing the economic viability of the ore.

The mineralization at Punta Corna consists of a complex vein system interpreted as the product of late Alpine (post metamorphic) hydrothermal events (Castelli et al., 2011). The host rocks are represented by the volcanic products (metabasalts) and the metasedimentary cover (calcschists and minor micaschists) of the Internal Piedmont Zone (IPZ) ophiolites (Dal Piaz et al., 2003).

The ore minerals detected so far are represented by dominant Co-Ni di- and tri-arsenides and base metal sulfides chalcopyrite, pyrite and rare sphalerite and galena, accompanied by tetrahedrite, Bi—Sb-rich phases, native Bi and argentite. The utilization of SEM imaging and EPMA analyses facilitated the evaluation of the relationships between the different Co-Ni arsenides as well as the precise identification and distribution of tetrahedrite and accessory Bi-Sb phases. The latter are represented by terms of the Cu-bearing emplectite-chalcostibite series and of stibnite – bismuthinite series (horobetsuite). Gangue minerals include calcite, dolomite, siderite, ankerite and quartz. Chlorite and white mica are common hydrothermal alteration products in the wallrocks. The ore precipitation sequence starts with Co-Ni arsenides, characterized by tri-arsenides often overgrown by concretionary Ni-Co di-arsenides. The last precipitation stage is represented by base metal sulfides, tetrahedrite intergrown with the Bi-rich phases and native Bi, plus late argentite. Mineralization is characterized by different textures suggesting various stages of brecciation, overgrowth and replacement, with polyphase deposition of carbonate-quartz gangue.

Mineral assemblage and deposition below 200°C from metal-rich brines (from preliminary fluid inclusion analyses; Moroni et al., 2019) suggest analogies with five element-vein deposits, while the occurrence of Bi-Sb phases at Usseglio may represent a link with the nearby Gran Paradiso Massif which hosts mineralization belonging to the regional Au- vein system of the Western Alps.

Further investigations will be addressed towards including new fluid inclusion analyses, detailed ore characterization during the upcoming drilling campaign, identification of possible sources for metals (especially Co) from metamorphosed volcanogenic ores in the local ophiolites; C-O isotope analyses of gangue carbonates and U-Pb dating of the Co-rich vein swarm within the framework of the late-alpine hydrothermal activity along the western Alpine sector.

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## Alluvial ethical gold: a pilot project of Tabor Srl in Bétaré-Oya (Cameroon)

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*Keywords:* alluvial gold, sustainable mining, Cameroon.

The concept of total sustainability of mining projects has greatly changed the vision and management of mining. Up until 20 years ago, statistically, out of every 1000 exploration mining targets, 3 could become mines and this was closely linked to economic feasibility relative to the deposit's cut-off grade and market prices. Today, it can be said that 1 project in 1000 can become a mine because sustainability requires a more accurate study and application of the feasibility concept to the social and environmental part as well.

The Bétaré-Oya district is geologically characterized by Neoproterozoic metavolcanic-metasedimentary rocks of the Lom Belt in eastern Cameroon. The district is known for its alluvial gold mining activities. The mining complex of the "Boyo I" concession gold deposit in the alluvial area of the Lom River basin was studied to characterize the composition and origin of the gold ore. Using the scanning electron microscopy (SEM) technique, a morphological and chemical characterization study was conducted on gold crystals from the concession, which was followed by a quantitative study on the geometric shape of the individual crystals for the geomorphological characterization of the individual gold grains by analysing a total of No. 1.124 samples from the mining concession. This investigation was performed with the use of the Java plugin encoded for the open-source programme "ImageJ", which through the digital processing of the samples in 2D formed the basis for a preliminary model describing the evolution of the shape of the gold grains during alluvial transport. An environmental sustainability project is ready to be developed at this mine by the Italian group Tabor Srl. Tabor's current partners have already developed the know-how for sustainable mining projects as they are also partners of the Goldlake Group, the first mining company in the world to receive the Responsible Jewellery Council (RJC) "Chain of Custody" certification for the production of "Ethical Sustainable Gold".

At the deposit, technologies based solely on gravimetric separation and free of chemicals will be used to extract gold from the placer. The project not only focuses on the environmental sustainability (to protect the environment and biodiversity) of the Boyo I deposit and the Lom River area, but also strongly believes in the development of self-financed social projects from its own mining production such as the organization of a formal artisanal miners' cooperative, an education programme for all employees, a health clinic to provide first aid in community emergencies, the development of basic infrastructure and training workshops for miners to raise awareness of the risks of using chemicals (such as mercury and cyanide) during gold mining.

## Characterization of granite scraps for REEs recovery

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*Keywords:* rare earth elements, circular economy, mineral processing.

The work aims to investigate the feasibility of Rare Earth Elements (REEs) recovery from scraps of the industrial processing of feldspar to optimise the Industrial chain, hence favoring a likely valorization and sustainable management of the processing scraps for Critical Raw Material in the frame of the Circular Economy (European Commission, 2020a, b). The material used for this work derives from the Montorfano quarry disposal site, located in the Verbano-Cusio-Ossola area (Piedmont, Italy), where granite bodies were quarried for ornamental purposes producing a huge volume of waste material, presently exploited to recover feldspar for ceramic and glass industries. The Montorfano pluton is a medium-grain white granite. The mineralogy consists of plagioclase, quartz, K-feldspar, and biotite, including typical accessory minerals such as apatite, zircon, and allanite (Boriani et al., 1988). The occurrence of allanite-(Ce), together with other REEs-bearing minerals (e.g., Y-Sc-REEs-silicates, Y-REEs phosphates, and Nb-Ta-Y-REEs oxides), has already been described in previous studies on the niobium-yttrium-fluorine (NYF) granitic pegmatite at Baveno (Guastoni et al., 2017). However, none of the previous studies investigated on the REEs- recovery for production.

The current work presents chemical and mineral-petrographic characterization performed by ICP-MS, XRPD, and Automated Mineralogy Systems. Granite waste rock samples were collected from the Montorfano quarry, subsequently crushed and ground to achieve a grain size between 1.2 and 0.1 mm and then subjected to two different steps of magnetic separation. The ICP-MS analyses on the 1.2 to 0.1 mm magnetic fraction, discarded after the separation of granitic material for feldspar production, highlight an enrichment in REEs, mainly Ce, La, Nd, and Y. The XRPD and SEM-EDS analyses indicate that monazite, allanite, and xenotime are the main REE-bearing minerals, commonly locked within phyllosilicates. SEM-EDS-based Automated analyses (AZtecFeature Suite and Mineralogic Systems) used for automatic identification of REEs-bearing minerals and particles/grain size revealed liberation issues preventing the effectiveness of the magnetic separation process; the average grain size of target minerals is extremely small compared to the associated gangue phases. Further grinding on the unprocessed material is required to enhance particle liberation; comminution to a particle size smaller than 0.1 mm, will likely lead to a more effective concentration of REEs minerals during magnetic separation and the possible consequent extraction of REEs metals through specific techniques. Additional lab tests (i.e., hydrometallurgy tests on improved concentrated material) will confirm the viability of the recovery.

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## New data on the Pb(Zn) Olovo deposit (Bosnia and Herzegovina)

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*Keywords:* Cerussite, vein deposits, faults.

The Olovo deposit (northeast of Sarajevo, Bosnia and Herzegovina) is characterized by several mineralized veins hosted by Triassic carbonate rocks, which contain several generations of high-grade cerussite and other Pb and Zn phases in calcite gangue. The most recent resource estimates for the Očekalj vein comprehend 1,996 Mt of ore at an average grade of 5.1% Pb, with an inferred resource of 1,626 Mt ore, at an average of 5.2% Pb.

The Olovo mineralization is characterized by several ore facies defined as: the High Clay domain, the Disseminated domain, the Cataclastic domain, and the Hard domain, with the latter representing the highest grade ore type. For this study, mineralogical, petrographic, geochemical and isotopic analyses were performed on several samples from the Vein 2. The ores belonging to the Cataclastic domain and the Hard domain have a fairly simple mineralogy consisting of galena, cerussite and calcite, which occur as cement of tectonic breccias. Early cerussite replaces galena, whereas late cerussite occurs as newly formed concretions, crystals or veins. Zn minerals were not detected in these facies. The High Clay domain comprehends material filling pseudo-karst cavities. Analysis of the clay fraction revealed that, besides barren clay species as mica, beidellite and kaolinite, fraipontite (a trioctahedral Zn-bearing phyllosilicate of the kaolinite-serpentine group) is the sole metal carrier.

Stable isotope analyses have been conducted on calcite and cerussite. It resulted that most of the calcite associated with the ore has positive  $\delta^{13}\text{C}$  ratios. Cerussites, although characterized by negative  $\delta^{13}\text{C}$  values, have  $\delta^{18}\text{O}$  compositions lower than those typically formed at ambient temperature. This anomalous O-isotopic composition could suggest that both the Pb-carbonates and their gangue formed either from a low-T hydrothermal or a  $^{18}\text{O}$ -depleted fluid. The Pb-isotope compositions of cerussites fit with a Paleozoic crustal reservoir (e.g. the pre-Triassic basement). However, these point out that in addition to the crustal reservoir, Pb was also derived from a so far unknown magmatic component.

In conclusion, the texture and the geochemical features of the ores suggest that the mineralization was emplaced along several fault zones, which had possibly driven the Pb-rich fluids deriving from the basement. The mineralization had an initial stage characterized by galena deposition, which was followed by a cerussite formation stage associated with either hydrothermal or supergene O-rich fluids. Interestingly, the Olovo mineralization seems to be relatively Zn-poor, in respect to other carbonate-hosted base metal deposits.

## Structural setting of late Alpine vein systems at Buca della Vena mine (northern Apennines): preliminary results

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*Keywords:* vein systems, polyphasic deformation, ore body.

Syn- to late-tectonic veins are widespread in deformed rocks that have undergone various degrees of metamorphism during orogenic events. Their occurrence is indicative of fluid flow coupled with local remobilization and/or external supply of different elements into the suitable dilation sites (e.g., Bons et al., 2012).

The Alpi Apuane (northern Apennines) hosts small pyrite ± baryte ± Fe-oxides orebodies associated to Paleozoic phyllites. The proto-ore was produced by Permian hydrothermal activity and later involved in Apenninic orogenesis causing recrystallization and local remobilization (e.g., Vezzoni et al., 2020).

Buca della Vena mine exploited one of the main Alpi Apuane pyrite ± baryte ± Fe-oxides orebody. A comprehensive structural investigation on ores and host rocks was recently performed in this area. Several papers have focused on the mineralogy of late Alpine vein systems characterized by exceptional assemblages including rare Ti- and V-bearing oxides and sulfosalts (e.g., Orlandi & Dini, 2004).

In this work, we propose a detailed geological-structural investigation linking the attitude of the vein systems with mineralogy and host-rock types. The results argue that the mineralogical assemblages of the veins are not controlled by their attitude but, on the contrary, by the host-rock types with i) carbonate+quartz±hematite±baryte in Triassic metadolostone; ii) quartz±hematite±baryte in tourmalinized phyllitic quartzite; iii) hematite±quartz in Fe-oxides+baryte ore. The veins are generally oriented in a narrow range compatible with a vertical shortening related to the early D2 event.

In conclusion, this work indicates how the exceptional mineralogy of the Buca della Vena veins, is controlled by local remobilization related to the switch in the deformation style from crustal-scale contraction to extensional settings.

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## A deeper insight into possible mineralogical barriers and extractable global resources

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Keywords: ultimate resources, metal, exploration.

The IEA report (2021) demonstrates, if proof were needed, the colossal needs in metals required by the energy transition. Of course, there are questions about our ability to meet this demand in the short term given the geopolitical tensions and growing societal opposition to any form of mining project, but there are also many who point to the imminence of peak production for several base metals (Henckens et al., 2016; Sverdrup et al., 2019). Wellmer and Scholz (2017) have clearly demonstrated the unfoundedness of such theories based on past production figures and highly theoretical modelling of deposit distribution in the crust, but the question of global extractable resources remains.

Surprisingly, while geologists have a very good knowledge of the geochemistry of the earth's crust and we also have comprehensive databases for most of the identified deposits, there remains a large grey area between economic grades and geochemical background grades. There is certainly a thermodynamic boundary that Skinner (1976, 2001) has termed a "mineralogical barrier", but this notion remains uncertain and has not really been systematically studied. However, Skinner's intuition that the limit of extractable resources represents 0.01% to 0.001% of the ultimate resources (total tonnage contained in the earth's crust) was used as a basis for the UNEP (2011) report on the long-run availability of resources and recently inspired Henckens (2021) to make alarmist considerations about the depletion of zinc or molybdenum resources before the end of the century.

Starting from an approach based on the exploration coverage of most of the world's regions and considering that it is technically realistic to exploit resources to a depth of more than 5,000 metres, we will show that there is no reason to think that we will not have resources for several more centuries. However, these considerations, which are valid for ubiquitous metals such as zinc, need to be qualified when we are talking about mineralogical resources (clay, high-purity silica, etc.) whose exceptional quality is clearly linked to superficial and exceptional alteration processes.

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## The Jadar (Serbia) Li(B) deposit: insights into borosilicate-type Li volcano-sedimentary systems

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Keywords: lithium, Jadar, volcano-sedimentary systems (VSS).

Volcano-sedimentary systems (VSS) have the potential for hosting significant resources of critical metals including lithium (Bradley et al., 2017; Benson et al., 2017). Lithium VSS are hosted by extrusive volcanics deposited in endoreic lacustrine basins developed nearby felsic volcanic and/or magmatic provinces displaying a pronounced crustal affinity (S- to A-type series). Conventional VSS belong to the clay-type (e.g., McDermitt Caldera, USA), with lithium being mostly enriched in hectorite-like Mg-smectites formed through closed-hydrologic system diagenesis (CHSD) of volcanic glass-rich volcanics (Castor & Henry, 2020). Several lithium VSS also display significant borates volumes (e.g., Turkey, Western Balkan Metallogenic Zone and Western US), however, these systems record a geochemical disconnect between Li and B that results in spatially and mineralogically decoupled Li and B resources. In this context, the Jadar Li(B) deposit (Serbia) represents an exception of this model as the main ore mineral is the unique Li-borosilicate jadarite  $\text{LiNaSiB}_3\text{O}_7(\text{OH})$ . The Jadar deposit, beside representing a mineralogical unicum of Li-mineralized VSS, is also one of the largest Li developments in Europe and a true greenfield discovery, holding a JORC Indicated and Inferred Resources of 143.5 Mt Li at 0.838% Li. In this contribution we present the first geological account of the Jadar deposit with the aim to shed light on the diagenetic history of the basin and ultimately on the ore-forming processes accounting for the formation of the unique “jadarite-type” Li-VSS. During early diagenesis, the jadarite-forming event effecting lacustrine-deposited volcanics occurred jointly with a suite of processes (i.e., zeolitization, K-autometasomatism and clay alteration), which mirror the CHSD observed in Li clay-type VSS. However, the presence of an extensive carbonate alteration (primary dolomite), the lack of primary quartz and the joint Li-fixation and zeolitization, indicate that as opposed to clay-type VSS, the early diagenetic stage at Jadar was aided by higher pH fluids. Under hyperalkaline conditions, silica along with Li(B) were stripped from volcanic rocks deposited in the basin to form a gel-like phase, which acted as a media for the formation of the jadarite–zeolite assemblage. The conditions of hyper-alkalinity needed for the jadarite formation were achieved through the presence of a poorly reactive host-rock (two mica tephra), which restricted fluid-rock interaction, thus allowing  $\text{Na}^+$  and  $\text{Li}^+$  to be fractionated in pore fluids to form a gel-like phase. Late diagenetic processes were triggered by the basin subsidence and coeval attainment of the oil-generation window. These processes led to the decay of organics, and subsequent release of acids. The late pH buffering towards acidity led to a localized redistribution and geochemical decoupling of Li and B ending with the formation of late diagenetic Li-phosphates and secondary borates.

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## Lithium micas as indicators of the magmatic-hydrothermal history of the Cornubian Batholith (SW England)

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*Keywords:* lithium, mica, Cornubian Batholith.

Mica-group minerals are major Li repositories in rare metals granites (RMGs) and associated lithologies. Due to their complex crystal structure, micas can host a large suite of trace elements, therefore, while in contact with evolving melts and/or fluids, micas easily re-equilibrate thus acting as a reliable archive of the geochemical and mineralizing history of magmatic-hydrothermal ores (Monnier et al., 2022). The Variscan Cornubian Batholith (CB) is an archetypal RMG with a long history of mining of its hosted ores. The recent rise in the Li demand has revived the mining interest in SW England, with ongoing exploration surveys targeting Li resources in brines and in hard-rock (mica-type) ores associated with the CB. In this contribution we present a combined petrographic, geochemical and statistical study of  $\pm$ Li-bearing micas from the granite series (G1 to G5; Simons et al., 2016), as well as from the associated greisen, pegmatite and elvan units. Our goal is to use the trace-elements of micas to assess the role of magmatic vs subsolidus processes and of fluxing elements (F and B) on the endowment and leaching of Li during the evolution of the CB. Micas in the CB are grouped as: (1) late-magmatic species, which include  $\pm$ Li-bearing trioctahedral micas (i.e., biotite–zinnwaldite I series) and dioctahedral micas (i.e., muscovite I and phengite I). (2) secondary Li-micas, including pneumatolytic and replacive species of the zinnwaldite II–lepidolite series. This mica type mostly occurs in the most evolved granite types (i.e., G5 topaz granite) and in the associated pegmatite; (3) secondary Li-free micas, which include dioctahedral micas (i.e., phengite II and muscovite II). The formation of secondary dioctahedral species (hereafter “muscovitization”) is aided by the breakdown of magmatic to metasomatic Li-micas and is the main process accounting the Li leaching from the batholith. Although muscovitization is a regional scale process, a close relationship between pervasive muscovitization and metasomatic tourmaline has been observed. The paragenetic study, coupled with EMPA and LA-ICP-MS geochemistry and multivariate statistics, indicate that: (1) (auto)metasomatic processes are the main triggers to the Li supercharging in secondary micas – a process that occurs jointly with a gain of Rb, F, B, W, Tl, Cs, Mn, W and Tl due to fractionation and with an increase of the Rb/K, Ta/Nb and W/Sn ratios. This footprint indicates an increasing contribution of a fluid component saturated in fluxing elements (B and F); (2) late muscovitization triggers a Li(F) vs B geochemical decoupling and the formation of Li-free dioctahedral micas enriched in B-Sn-Sr-Ba. Paragenetic and trace elements evidence suggest that muscovitization is likely a process occurring at surface, during and/or after the exhumation of the batholith and is triggered by low temperature hydrothermal fluids resulting from late tourmalinization mixed with a low Eh meteoric component.

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## Multiple sources of ores and late-Variscan post-collisional tectonic setting in the Arburèse district (SW Sardinia, Italy)

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**Keywords:** Arburèse district, sources of ores, Pb isotopes data.

The Arburèse region (SW Sardinia, Italy), hosts a wide spectrum of ore deposits, which may represent a potential source for critical raw materials such as Ni, Co, Bi and REE. It is located in the external zone of the low-grade Variscan basement, which was intruded at shallow crustal levels, during the post-collisional extension, by two different small EW trending ilmenite-series plutons: the Arbus granodiorite-leucogranite (304 Ma) and the Monte Linas monzogranite-leucogranite pluton (289 Ma), respectively. In the area occur: (1) granite-related and (2) epithermal to mesothermal polymetallic vein deposits. The first are related to the Monte Linas pluton and include hypothermal to mesothermal Sn-W-As-Bi veins, Mo greisens and Pb-Zn-Cu-Sn-W-Bi skarns (Naitza et al., 2017). Polymetallic veins roughly follow the margins of the Arbus pluton and can be subdivided into two main types which can be considered as different parts of the same system, the first representing the shallower portion, the second the deepest, respectively: (a) base-metal sulphide veins hosted in Cambrian to Ordovician metasandstones belonging to the Arburèse allochthonous unit and dominated by galena, sphalerite and minor chalcopyrite in quartz-carbonate (prevailing ankerite-siderite) gangue; (b) five-element (Ni-Co-As-Ag-Bi) veins, hosted in late-Ordovician siliciclastic metasediments and Silurian black shales of the para-autochthonous Iglesias Unit, and characterized by native Bi, Ni-Co-Fe arsenides/sulpharsenides and Pb-Zn-Cu-Sb sulphides in quartz-carbonate (ankerite-siderite) gangue. Fluid inclusions data on the HT ( $T_h$  range: 410-120°C and moderately saline fluids; Naitza et al., 2017) and LT polymetallic ores ( $T_h$  range: 90 - 130°C and highly saline fluids; Moroni et al., 2019), as well as multiple intersections between the two systems and textural features suggesting a different depth of emplacement, indicate a substantial age discrepancy between the two hydrothermal events (Deidda et al., 2022). Metal sources for LT polymetallic systems can be constrained by Pb isotopes data from literature: Galenas from the Arburèse district display roughly linear trends, approximately overlapping the lead isotope compositions of Cambrian clastic levels from SW Sardinia and pointing to the more radiogenic field of Silurian limestones metasomatized by Variscan granites. Consequently, lead in the studied systems could have been derived by different sources. A mixture in various proportions of Pb from an ancient Proterozoic basement and overlying metasediments belonging to the Arburese nappe is supported by a positive correlation of  $^{232}\text{Th}/^{238}\text{U}$  ( $k$ ) and (2 stage) Pb model age values. The observed discrepancy in Pb model age values between galenas from polymetallic ores and K-feldspars from Late-Variscan intrusives may be evidence of interactions with fluid circulation in Paleozoic sediments surrounding individual plutons in which are documented hydrothermal leaching effects.

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## **Sb-bearing and Sb-free Ni-Co arsenide assemblages from the Southern Arburèse hydrothermal district (SW Sardinia, Italy)**

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*Keywords:* Southern Arburèse hydrothermal district, five-element type veins, Sb-bearing mineral assemblages.

The Arburèse district (SW Sardinia, Italy), is considered as a potential source of critical raw materials (CRM), as Ni, Co, Bi and REE are found in hydrothermal veins cutting the Variscan low-grade metamorphic basement which was intruded by the Arbus (304 Ma) and Mt. Linas (289 Ma) plutons. The vein system surrounds the Arbus pluton: in the north, it is Pb-Zn mineralized; conversely, in the south it is represented by five-element type veins, showing a pinch and swell structure, breccia/cockades textures with alternating ore shoots and low-mineralized zones. New reflected light microscopy and SEM-EDS studies performed on historic samples show that ore deposition occurred in three main stages: 1) early native Bi + Sb-poor Ni-Co-Fe arsenide-sulfarsenides in quartz; 2) native Bi + Sb-rich Ni-Co arsenides-sulfarsenides, closely followed by base-metal sulfides and sulfosalts in siderite, and 3) abundant quartz, followed by pyrite and calcite sealing fractures. Stage 1 is characterized by Sb-poor arsenides such as pure nickeline (NiAs) sometimes very rich in native Bi and bismuthinite (Bi<sub>2</sub>S<sub>3</sub>) inclusions that are overgrown by gersdorffite (NiAsS). The latter also occurs in complex intergrowths with alternating layers of löllingite-safflorite (Fe-Co)As<sub>2</sub> and arsenopyrite-cobaltite (possibly glaucodot (Fe<sub>0.5</sub>Co<sub>0.5</sub>)AsS or alloclasite Co<sub>1-x</sub>Fe<sub>x</sub>AsS) solid solutions. Quartz sometimes contains euhedral LREE carbonates and phosphates. Fragments of stage 1 are often cemented or cut by minerals of the following stage 2: native Bi occurs in most samples and is overgrown by Sb-rich fibrous nickeline intergrown with breithauptite, mostly in the outer layers of the aggregates. Nickeline is rimmed by complex associations of Ni-Co arsenides/sulfarsenides-sulfantimonides such as rammelsbergite (NiAs<sub>2</sub>), gersdorffite and ullmannite (NiSbS): the outer layers of cockades are often surrounded by tetrahedrite, which also occurs separately intergrown with chalcopyrite and Fe-poor sphalerite, followed by galena in siderite. Stage 3 is represented by abundant bladed, late-stage quartz, which substitutes siderite encapsulating both former generations of arsenides and base metal sulfides. The sequence is followed by pyrite and calcite veinlets which crosscut all main stages. Textural and compositional evidence suggest that an Sb-rich fluid of stage 2 remobilized Ni and Co from stage 1 ores. The primary source of ore-forming elements as well as the ore precipitation mechanisms and triggering geological events have yet to be constrained.

## Mining dumps in Sardinia: from waste to resource?

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Keywords: CRMs, Sardinia, REE.

Mining activities still produce hundreds of millions of cubic meters of tailings per year in Europe, which are dumped in mining landfills. Consequently, these materials are considered industrial waste by environmental laws such as the Italian L. D. 152/2006. But can these materials be considered just waste, or may they be considered a resource?

On the Sardinian territory lays around 70 million m<sup>3</sup> of waste materials linked to the mining activities of the past centuries. Up to now a large part of these historical mining waste deposits has been studied for their related environmental issues, focusing more on the elements considered pollution sources. From a modern circular economy perspective, however, it would be appropriate to deepen the studies on the economic potential of the wastes, including not only the base metals (Zn, Pb, Cu, etc.) once primary targets in the mined ores but also the critical and strategic raw materials (CRMs, SRMs: European Commission, 2023) now essential for the technological development of our societies. Few situations of this kind are well known and well characterized in Sardinia. The most relevant of them are those related to the metallurgical processing of non-sulfide ores (“calamine”). The “red muds” of the old Monteponi mine, coming from the electrolytic processing of calamine, not only constitute a large source of pollution but also must be considered like a mineral deposit with average contents of 8-10 % Zn and 1.2% Pb (Buosi et al., 1999). Similarly, the relatively small dumps of the antimony smelter of Villasalto (SE Sardinia) must be regarded as one relevant Sb resource (Contini et al., 2008).

As part of an ISPRA-UniCa project of new mapping of resources on a regional scale (Update of the regional mining and mineral resources database with priority on CRMs and SRMs for Decarbonization and Ecological Transition - Geoscience IR Project, WP 5.1) a new ongoing campaign of field and archive data collection is increasingly highlighting interesting CRMs’ potentials for the mining dumps in the Sardinian territory. The first results come from the Montevecchio-Ingurtosu district (SW Sardinia), up to 1990’s one of the largest mining areas in Italy for Pb and Zn extraction, over 15 million m<sup>3</sup> of mining dumps are present. In this area, recent characterization of tailings located next to the “Cantieri Sanna” old processing plant revealed metal contents up to 1.2% Pb, and 2.6% Zn, as well as REE+Y concentrations ranging from 237 mg/kg to 579 mg/kg (Sedda, 2021).

These data confirm the necessity to characterize the Sardinian mining landfills as potential CRMs deposits and to evaluate if they may be considered a resource for technology development and the ecological transition. The latter may be favored precisely by reprocessing these landfills, involving the removal of a source of environmental pollution, generating an environmental and economic benefit, and completing the transition from waste to resource.

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## Satellite hyperspectral mapping of hydrothermal and supergene alteration footprints in the Escondida district (northern Chile): a vectoring tool for high-grade orebodies in porphyry copper systems

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*Keywords:* Escondida porphyry copper district, satellite hyperspectral data, feature-based band ratios.

The hyperspectral reflectance spectroscopy represents a powerful tool for mineral exploration, providing rapid and cost-effective mineralogical and chemical information that can be used as vector to high-grade economic orebodies in porphyry copper systems. The aim of this study is to map the surface-exposed hydrothermal and supergene alteration facies in the Escondida district (Antofagasta Region, Northern Chile) by using hyperspectral imagery of the Italian Space Agency's PRISMA and DLR's EnMAP satellite missions. Both satellites acquire images in the Visible Near-Infrared (VNIR) and Shortwave Infrared (SWIR) range, between 400 and 2500 nm, at a spatial resolution of 30 m. PRISMA has a spectral resolution of 13 nm and a signal-to-noise ratio (SNR) from 200:1 (VNIR) to >100:1 (SWIR), while EnMap has a spectral resolution of 6.5 nm in VNIR and 10 nm in SWIR, and a SNR from >500 (VNIR) to >150 (SWIR) (Cogliati et al., 2021).

The Escondida district is located in the Middle Eocene–Early Oligocene porphyry copper belt within the Domeyko Cordillera, and hosts several ore deposits centred on multiphase monzonitic-granodioritic-porphyry stocks, structurally controlled by the Domeyko Fault System. The hydrothermal alteration is well-developed and typified by upward and outward zonation evolving from an early potassic alteration at depth, to a late alteration stage with chlorite-epidote-sericite and quartz-sericite zones at intermediate levels. The younger advanced argillic alteration event forms a shallow lithocap, dominated by quartz-alunite in the centre grading outward into quartz-alunite-kaolinite. The uplift and denudational processes, occurred during the late Oligocene–Early Miocene until 14 Ma ago, have exposed the study area to supergene oxidation, resulting in an upper hematitic leached capping, and a lower copper oxide and secondary sulfide enrichment zone (Hervé et al., 2012).

Most of hydrothermal and supergene alteration minerals, such as Fe oxy-hydroxides (hematite-goethite), di- and tri-octahedral phyllosilicates (micas-kaolinite-chlorite), hydroxyl-bearing sulphates (alunite) and epidote, are optically active in the VNIR-SWIR range, allowing for their identification through the diagnostic spectral signature. In this study, a multiple feature-guided band ratios approach is applied, considering the spectral regions around 900, 1480, 1780 and from 2100 to 2300 nm. This method allows to determine the relative abundance of the investigated mineralogical phases, in relation to absorption depth, and the compositional variations that result in a shift towards longer or shorter wavelength positions (Laukamp et al., 2021; Chirico et al., 2022). The preliminary results observable as PRISMA- and EnMAP-derived mineral maps, coupled with geological and mineralogical field data available in literature, constitute a valid support for mineral exploration, allowing a better comprehension of the distribution of the hydrothermal facies at the district scale.

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## The Allumiere quarry test site (Latium, Italy): new insights into the proximal hyperspectral characterisation of high sulfidation epithermal deposits

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**Keywords:** Proximal Hyperspectral Analysis, mineral exploration, high sulfidation epithermal deposits.

The Allumiere quarry is located northwest of Rome (Latium, Italy), within the Tolfa Volcanic district (Pliocene-Pleistocene age) and is known locally for the occurrence of an alunite+kaolinite mineralization that has been intensely exploited since the 15<sup>th</sup> century onward. This mineralization is hosted in a lava dome and is considered to be genetically related to a post-volcanic magmatic-related hydrothermal activity, which has produced a widespread structurally controlled alteration spanning from vuggy silica and advanced argillic to intermediate argillic. The main minerals characterizing the different zones are quartz, alunite- and kaolinite-group minerals, and smectite. The hypogene assemblage was lately affected by supergene alteration due to near-surface oxidation, with the formation of widespread Fe-oxy-hydroxides, jarosite and other accessory phases (Conte et al., 2022). All these minerals are optically active in the Visible-Near (VNIR) to Short-Wave Infrared (SWIR) range. In this study, we report the preliminary results of the hyperspectral analyses at proximal scale carried out on the distinct alteration facies using the Headwall Photonics Nano- and Micro-Hyperspectral cameras, which cover the spectral range between 400 and 2500 nm, with 270 (VNIR) to 166 (SWIR) spectral bands. The hyperspectral data have been processed by applying feature extraction indexes for determining the relative abundances of Fe-oxy-hydroxides (hematite and goethite), by using the 900 nm absorption feature, and Hydroxyl-bearing minerals (white mica, smectite, kaolin group minerals, sulphates) and their compositional variations (Laukamp et al., 2021; Chirico et al., 2022). The high-resolution hyperspectral data allowed to: (1) discriminate among kaolinite polytypes (kaolinite, dickite and halloysite) based on the position of the OH absorption feature in the region around 1380-1400 nm, (2) discriminate alunite from natroalunite due to the wavelength shift of the 1480 nm absorption feature, (3) detect smectite through the double absorption feature deeper at 1900 nm and at 2200 nm.

This relatively fast and cost-effective method represents a cutting-edge tool for the identification and characterization of potential exploration targets and can be used either in laboratory or in the field.

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## The carbonate replacement Sn-W deposit of Monte Valerio (Campiglia Marittima, Tuscany)

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Keywords: cassiterite, carbonate replacement deposits, Monte Valerio.

Understanding the ore-forming processes of Sn and W deposits, though small in size, plays a key role in exploration and mining activities, given the growing demand for these metals by the industry. In this context, the Sn-W deposit of Monte Valerio (southern Tuscany) represents a relevant case study, with cassiterite (SnO<sub>2</sub>) and scheelite (CaWO<sub>4</sub>) hosted in carbonate and silicate rocks as both diffuse mineralization and/or small localized masses (Venerandi-Pirri & Zuffardi, 1982; Dini & Senesi, 2013). Monte Valerio is located in the southern part of the Campiglia Marittima horst, an area characterized by Mio-Pliocene multiple felsic and mafic intrusions associated to skarn, base metal ores and iron sulfides and oxides.

The present study investigates the Sn-W mineralization of Monte Valerio by surface and underground geological surveys, integrated with a critical review of mining activity documentation, and mineralogical, petrographic, geochemical and C-O stable isotope analyses. The analyses were performed on representative samples from different lithological units and mineralizations investigated during the geological survey as well as from mineralogical collections (e.g., Natural History Museum of the University of Pisa).

The results allowed to reconstruct the geometries, as well as the petrographic and geochemical features of mineralized bodies. In detail, two levels with an attitude sub-parallel to the planar anisotropy of the host rocks have been identified close to the stratigraphic contact between *Calcarea Massiccio* and *Rosso Ammonitico Fms.* The bodies with low Sn grade are characterized by subvertical veins and sparse cassiterite in carbonate host-rock, associated with scheelite, sulfides (e.g., pyrite, arsenopyrite), tourmaline and fluorite. On the other hand, the bodies with high Sn grade (Sn > 10 wt%) form monomineralic primary cassiterite aggregates. The  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values for carbonates collected from mineralized veins and from the host rocks, suggest a significant contribution of magmatic fluids in the genesis of the Sn-W mineralizations.

In conclusion, the integration of multiple analytical methods provides a genetic framework of the cassiterite and scheelite ores of Monte Valerio, that indicate a linkage with the Campiglia Marittima intrusive system and allow to relate the Monte Valerio ore deposit to the typology of carbonate replacement deposits.

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## Trace element content in sphalerite from the Raibl Mine (NE Italy)

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Keywords: mines, Raibl, sphalerite.

Several carbonate-hosted mineralizations occur at different stratigraphic positions in the Eastern and Southern Alps such as the Middle Triassic deposits of Bleiberg (Austria) and Mežica (Slovenia) in the Austroalpine Drava Range and northern Karawanke, and the deposits of Salafossa and Raibl in the eastern Italian Southern Alps. The Zn-Pb Raibl mine is in Cave del Predil (Friuli Venezia Giulia, Italy), close to the borders with Slovenia and Austria. The Raibl Zn-Pb deposit is located within a thick (more than 1000 m) carbonate sequence (the Sciliar Formation, locally known as Dolomia Metallifera, of Middle-Upper Triassic age). The Dolomia Metallifera is divided in an upper and a lower part according to a peculiar intercalation consisting of well-stratified, dark bituminous limestones, green tuffaceous sandstones and tuffites. It is covered by the Carnian units (Raibl Group). The mineralization is considered to develop along both the upper and lower Dolomia Metallifera up to the contact with the Raibl beds. In general, Zn-Pb ores are spatially related to north-south trending Triassic extensional faults.

Sphalerites from two different open pit areas (about 150 m above the level 0), several veins at level 0 and some veins from level XIII (at a depth of about 240 m) of the underground mine have been sampled and more than 700 LA-ICP-MS analyses have been performed. Among the different trace elements, the most abundant are Cd (avg. 3448 ppm; up to about 23000 ppm), and Pb (avg. 2158 ppm; up to about 13700 ppm), followed by As (avg. 1045 ppm; up to about 7200 ppm), Fe (avg. 500 ppm; up to 18200 ppm), Tl (avg. 256 ppm; up to 1770 ppm) and Ge (avg. 199 ppm; up to about 1400 ppm).

Brigo & Cerrato (1994) analysed mineral separates by ICP and AAS and found out a zonal distribution suggesting that Ge, Cd, Ga are related to sphalerite, while Tl, As, Sb seemed to be related also to other sulphides. Similarly, we found a possible zonation, with almost all the analysed trace element (As, Tl, Fe, Pb, Ge, Mn, Bi) hinting at a decrease from the sphalerites of the open pit areas to those of level XIII passing by those at the level 0. Cadmium is the sole element with a reverse trend (decrease from level XIII to open pits). In addition, for certain elements (such as Hg and Ga) it is possible to recognise a different concentration between samples from the same area (e.g. open pits) but related to different faults. Application of the empirical geothermometer of Frenzel et al. (2016) to the obtained sphalerite trace elements compositions give sphalerites crystallization temperatures in the range 180-250°C, in which corresponds to the upper limit of temperatures for sediment-hosted Pb-Zn deposits.

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**S37.**

**Deciphering tectono-metamorphic processes in the continental  
crust from field to micro-scale**

*CONVENERS AND CHAIRPERSONS*

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## **Structural setting of the Pb-Zn vein system of Rua mine (Bagni di Vinadio Valley, Cuneo, Piemonte)**

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*Keywords:* veins, mines.

The Argentera Massif, together with Mont Blanc, Aiguilles Rouges, Belledonne, Pelvoux and Aar-Gottard, belongs to the Alpine External Crystalline Massifs (ECM) in the Western Alps that crop out west of the Penninic front and belong to the Helvetic-Dauphinois domain. The ECM represent fragments of the southeastern sector of the Variscan belt and are of Gondwanian affinity. The Argentera Massif is composed of the Gesso-Stura-Vesubie (GSV) and Tinee (TMC) metamorphic complexes (Malaroda et al., 1970) which are separated by the Ferriere-Mollieres Shear Zone (FMSZ), a NW–SE oriented shear zone that extends for about 20 km and has a thickness ranging in map view between 100 m and 2 km (Carosi et al., 2016; Simonetti et al., 2021). In the Vallone dei Bagni, one of the Val Stura's suspended valleys, located in the SE sector of the massif, there are several shear zones lying sub-parallel to the FMSZ, often associated with important hydrothermal veins, representative of the “Giacimento di Pb-Zn di Ruà”. In correspondence with these structures several entrances of ancient mines, active until the 90s of the last century, are located. A detailed mesostructural analyses has been performed in the key area and oriented samples have been collected in order to investigate the structural relations among shear zones and mineralization. A microstructural analysis was carried out by SEM/EDS and polarized light microscopy to better investigate these structural relationships. A complex deformation history has been highlighted pointing out several steps of mineralization related to both ductile and later ductile-brittle events.

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## The 4D geological characterization strategy for the Einstein Telescope site selection: the case of Sardinia (Italy)

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*Keywords:* Sardinia, crystalline rocks, faults.

The Einstein Telescope (ET) will be the European third-generation underground interferometric detector of gravitational waves, whose future location has to present very low seismicity and anthropogenic seismic noise. Among the three different candidate sites to host such a structure, which is currently projected as a triangle (10 km long sides), Italy and Germany have proposed two sites in two different crystalline basement settings, while Belgium and the Netherlands candidate a sedimentary setting around their joint border. The Sardinian site proposed by Italy, lays in geodynamic quietness and is far from regional faults. However it is crossed by minor brittle structures, that need to be spatially and temporally characterized. As time is essential in determining the risk of geological processes such as faulting, we aim at the 4D characterization of the relationships between faults and intrusions in an area that has been candidate for hosting ET in Sardinia.

Here, we illustrate our transition from 3D to 4D strategy, that encompasses and integrates lithostratigraphic and geophysical data, structural and microstructural geology, petrology, geochemistry, and geochronology.

The syn-orogenic deformation of the Paleozoic metamorphic rocks consists of distinguished fold and cleavage generations with at least two ductile phases ( $D_{2+3}$ ) almost completely transposing the original bedding and the oldest schistosity ( $S_{0+1}$ ), that is still visible in the south where the thermometamorphic grade is lower.

The later brittle fault network is segmented and it affects the metamorphic-plutonic ensemble with faults that mostly run parallel to the orientation of both dykes and plutonic contacts. Fault zones are generally NNW, and WSW-striking and are associated with either more altered bedrock and/or cataclastic bands that are locally affected by late hydrothermal circulation with thick quartz veins, thin chlorite fibers or pseudotachilites and gouge that can be as thick as a meter each. Beside the seismic reflection and geoelectric, and drilling campaigns at north and western vertices, low-temperature thermochronometry and fault gouge sampling was undertaken, covering the whole study area with the aim of detecting the thermal history and spotting the age of the most recent brittle events and exhumation history. If applied also to other candidate settings, this strategy can provide absolute age constraints to other 3D field-based and subsurface information.



## Mapping the Dora-Maira metamorphic basements: the example CARG project sheet n. 172 “Pinerolo” (Western Alps)

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*Keywords:* Western Alps, geological mapping, Dora-Maira.

The internal Western Alps is a complex tectonic-metamorphic wedge formed by the stack of continental and oceanic units during Late Cretaceous-Paleogene subduction of the Alpine Tethys and the final Europe-Adria collision (Michard et al., 2022 and references). Despite being separated from the Briançonnais s.s. units by the ocean derived Piemonte-Ligurian units, the Dora-Maira Massif is often thought to be derived from the pre-Triassic basement of the Briançonnais domain s.l.

From the geological mapping point of view, only the northern and southern portions of the Dora Maira Massif have been mapped in detail until now. The portion of Dora-Maira Massif between the Chisone and Po valleys has been relatively poorly studied to the extent that even tracing the tectonic contacts between the different units in this area is problematic. The only geological maps analyzing this area, besides the Geological Map of Italy at 1:100.000 scale, are by Vialon (1966) and, for a small part, by Borghi et al. (1984).

Recently, in the framework of the CARG sheet n. 172 – “Pinerolo” (1:50.000) an intensive geological mapping of this poorly-explored area has started. Mapping the Dora-Maira crystalline basement is not an easy task due to its polyphase deformation and metamorphic history as well as the outcrops exposure conditions.

Field mapping is carried out with new digital mapping tools (Gencarelli et al., 2022) and integrated with many other disciplines. The mapping is performed with digital instruments such as FieldMove Clino and Qfield apps. Photo interpretation of remote sensing data is used to improve the geological and structural data. Field oriented thin sections are studied in order to acquire preliminary information about microstructures, kinematics, flow regime and deformation temperatures associated with the various deformation phases. An integrative approach will contribute to shed light on issues that cannot be directly solved with fieldwork and will allow to improve the quality of the geological sheet.

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## **Tectonics and rheological evolution of the Gotthard nappe (Central Swiss Alps): constraints from integrated field and *in-situ* petrochronological analyses of the Rotondo granite**

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*Keywords:* shear zone, Alps, tectonics.

The tectonometamorphic and rheological evolution of crystalline basement units during continental collision directly control the large-scale geometry of orogens and strain localization processes. Their evolution can be tracked through detailed structural analysis and *in-situ* petrochronology, overcoming the entangling effects of prolonged tectonic and polymetamorphic histories. Here we integrate field structural analysis, pseudosection calculations and *in-situ* U-Pb and Rb-Sr geochronology to define the structural evolution of the Rotondo granite (Gotthard nappe, Central Swiss Alps). We identify a sequence of kinematically-consistent deformation structures developed at different times, P-T-fluid conditions, and rheological regimes.

The earliest set of deformation structures (D1) include brittle cataclases, shear fractures and breccias, hosting a quartz-biotite-garnet bearing fine grained matrix. Field evidence and *in-situ* U-Pb Grt dating constrain the development of the D1 structures prior to the thermal peak in the area, which occurred from 32 to 23 Ma, at 580°C and 0.9 GPa. D1 structures controlled the localization and formation of a second phase of deformation, D2 ductile mylonitic shear zones. These are interpreted to have developed at retrograde amphibolite facies conditions (550°C and 0.7 GPa), during the exhumation of the Gotthard nappe at around ~18 Ma, as revealed by *in-situ* Rb-Sr dating of syn-kinematic white mica. The subsequent structural evolution of the Rotondo granite was characterized by transpressional tectonics during the latest stages of Alpine continental collision. Ductile D2 shear zones were initially reactivated at greenschist facies conditions (400°C and 0.5 GPa) with a dominant dextral, strike-slip kinematics during the D3a deformation stage at 14 Ma, based on Rb-Sr ages of syn-kinematic micas. Conjugate brittle-ductile, transpressive D3b faults developed later coevally to normal-slip D4 discrete faults. The latest deformation stage D5 involves zeolite and gouge-bearing brittle faults that exploited and reactivated pre-existent structural and compositional discontinuities under a dominant strike-slip tectonic regime, active until recent times. The integration of field structural analyses with *in-situ* petrochronology allows to define the evolution of kinematics and rheology during collisional tectonics. In particular, the case study of the Rotondo granite offers insight into the effects of pre-collisional (Pre-Alpine) brittle faults on the mechanical and rheological evolution of crystalline basement units during Alpine collisional tectonics.

## **Influence of inherited multiphase deformation on thrust system structural style**

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*Keywords:* 3D modeling, shear strength, structural inheritance.

The structural style of a fold-and-thrust belt (FTB) strongly depends on the mechanical properties of the involved rocks, and on the role played by inherited tectonic structures (Lacombe et al., 2019). Most of the predictive models that define the evolution and geometry of thrusts assume that a FTB develops in a layer-cake stratigraphic succession, with the possible occurrence of previous normal faults related to inherited basins. In this research, we deal with a different and more complex structural setting, investigating the structural style of a FTB developed in a faulted and folded poly-deformed basement, focusing mainly on the influence of the 'no-layer cake' attitude of strata on the thrust geometry (Cocco & Funedda, 2021).

The study area is a sector of the Variscan external zone in SW Sardinia. Here, the FTB affects a lower Cambrian-lower Carboniferous stratigraphic succession previously involved in: 1) lower Cambrian normal faults; 2) Middle Ordovician E-trending folds with vertical limbs; 3) E-trending Variscan open folds; 4) N-trending Variscan inclined folds. The interference of perpendicular fold systems gave rise to a domes-and-basins pattern so that the thrusts cut across strata with a high variable attitude, with steepness ranging from horizontal to vertical and strike from parallel to perpendicular to the FTB shortening direction.

A peculiarity of the Variscan external zone in Sardinia is the extensive back-thrusting development. Our findings suggest that this is due to the domes that, acting as an inherited buttress, prevent fore-ward propagation of deformation. During the progressive shortening the back-thrust cut across the Middle-Ordovician folds with axis perpendicular to the back-thrust strike. The geometry of the back-thrust varies along strike according to the attitude of the involved strata in the footwall: it takes either a synformal shape when cut across a hinge of a synform dipping in the same dip direction of the thrust, or an antiformal shape when cut across a vertical limb perpendicular to the thrust strike. The displacement accumulated by the back-thrusts also varies depending on the attitude of the bedding in the footwall, decreasing moving from the hinge to the vertical limbs of the folds.

The structural analysis and sequential restoration show also that the back-thrusts with a steepness of about 70° arose from the inversion of the middle Cambrian normal faults. It is worth noting that, despite these faults were rotated during the Middle Ordovician folding event, their attitude remains suitable to be reactivated as a back-thrusts during the Variscan shortening phase.

The main conclusions are that the attitude of the strata involved in a FTB could influence, besides the structural style and the geometry, also the amount of shortening that the thrusts can accommodate. Moreover, this finding suggests that a variation in shear strength within a stratigraphic succession could be related to the structural inheritance.

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## Crystal plasticity and fluid availability govern the ability of titanite to record the age of deformation: the case of the Anzola shear zone (NE Italy)

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*Keywords:* microstructure, petrochronology, fluid-mineral interactions.

Dating the time of shear zone activity remains challenging. Here, we present a study of the relationships among titanite-hosting microdomain, intragrain chemical variation, microstructure and fluids with the aim of deciphering the reliability of titanite U–Pb dating to constrain the age of deformation in mylonitic rocks. We address this topic to a post-Variscan amphibolite-facies shear zone developed in the mid-low continental crust (Ivrea-Verbano Zone, Southern Alps, Italy). Quantitative orientation analyses along with textural imaging of titanite are combined with trace-element analyses and U–Pb age dating. Titanite is studied in mm- to cm-scale layered rocks showing compositional variation consisting of alternating ‘amphibole-rich’ (i.e., amphibolites) and ‘clinopyroxene/plagioclase-rich’ domains (i.e., calc-silicates). Titanite from amphibole-rich domains shows predominance of crystal–plastic deformation features, as abrupt or progressive core-to-rim increasing of lattice distortion and local dislocation density, associated with the development of abundant subgrains and rare new grains. Such microstructures document the interaction with small amounts of fluids circulating along the grain boundaries in controlling, locally but significantly, the chemistry of titanite. In the clinopyroxene/plagioclase-rich domains, titanite is mostly undeformed and rarely shows bending localized in discontinuous narrow rims/tips. In these domains, fluid-mediated replacement reactions are either rare or absent, as also indicated by weak chemical variations across and among grains. These observations suggest a different reactivities with respect to the same fluid of the two compositional domains, coexisting within the same sample at the thin section scale. U–Pb data show correlations with chemical and microstructural domains that differ as function of the composition of the microdomain. This correlation is more apparent within amphibole-rich domains where microstructures characterized by high lattice distortion/dislocations and/or subgrains show significant variations of REE, Zr, Y, Nb, U with respect to the low deformed portion of grains. These titanite domains define an isotopic population providing the youngest (Jurassic) lower intercept age. A less clear correlation between titanite chemistry and microstructures is observed in clinopyroxene/plagioclase-rich domains. Here, the rare titanites showing lattice distortion and minor Sr depletion define a population providing a similar Jurassic lower intercept age. Therefore, our results demonstrate that microstructurally and chemical calibrated U–Pb dating of titanite provide realistic ages of shear zone activity, only in case of predominance of crystal-plastic processes and of local interaction of titanite with small amounts of fluids focus along grain boundaries.

## Two stage of garnet growth in mylonitic micaschist from NE Sardinia: evidence from major and trace elements in garnet

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Keywords: garnet, major- and trace-element zoning, P-T path.

Mylonitic micaschists in the south-eastern sector of the Posada-Asinara Shear Zone in the Axial Zone of the Sardinia Variscan consist of garnet porphyroblasts associated with plagioclase, quartz, biotite, staurolite, white mica, and chloritoid. The garnet porphyroblasts, enveloped by the S2 schistosity, preserve an internal foliation identified by the alignment of quartz, sometimes arranged into a sigmoidal pattern suggesting rotation of the garnet during growth. Major element compositional variation follows a bell-shaped zoning profile with Ca and Mn contents progressively decreasing, and Fe and Mg increasing, from the core ( $\text{Alm}_{45}\text{Grs}_{25}\text{Prp}_1\text{Sps}_{29}$ ) to the outer rim domain ( $\text{Alm}_{86}\text{Grs}_3\text{Prp}_{11}\text{Sps}_1$ ; Cruciani et al., 2022). LA-ICPMS trace element mapping revealed that the boundary between core and rim is marked by a thin *annulus* enriched in Y and HREE. The garnet core consists of an inner and an outer zone where the maximum concentration of elements from Lu to Tb progressively moves outwards with decreasing atomic number. This trend continues in the rim outside the *annulus*, where a further distinction between a Sm-, Eu-, Gd-, Tb-rich inner rim and a REE-poor outer rim was observed (Franceschelli et al., 2023). The P-T path of the mylonitic micaschist, which was reconstructed from major element zoning in garnet, and from K-white mica composition and mineral assemblage preserved in garnet, is clockwise, subdivided into two different stages. The P-T trajectory was refined by the Compositional Zoning in Garnet and its Modification by diffusion software by Faryad and Ježek (2019). The garnet growth occurred into two stages, marked by partial resorption of the garnet core. The first stage of the P-T path is a prograde segment up to the peak pressure (T 430–490°C, P 1.3–1.4 GPa) whereas the second one reflects garnet rim growth and staurolite formation at peak metamorphism (560–630 °C/0.6–1.1 GPa) followed by exhumation.

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## Structural architecture of a subducted passive margin revealed through integrated geological mapping: a case study in the Briançonnais units (south Western Alps)

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*Keywords:* Western Alps, Briançonnais, paleofaults.

In the south Western Alps, several Briançonnais continental-derived units are stacked between Alpine Tethys-derived units (Gidon et al., 1994). Each Briançonnais units is variably detached and affected by polyphase structural evolution (Michard et al., 2004). In this contribution we demonstrate how through an integrated geological mapping approach it was possible to reconstruct part of the pre-Alpine deformation history of these units. A geological - structural map of the area was realized combining microtectonics and RSCM analysis (Lahfid et al., 2010).

The integrated geological mapping approach made it possible to recognize some evidence of a late extensional event that affected the Briançonnais paleomargin during the Upper Cretaceous - Paleocene (Michard et al., 2022). This evidence includes (i) deformed paleofaults and (ii) breccias and olistholites sequences frequently reported in the Briançonnais units.

Paleofaults, having undergone intense polyphase deformation, often mimicking tectonic contacts can be misinterpreted (Pantet et al., 2020). In our study area, we documented such a case of a Late Cretaceous - Paleocene paleofault simulating a tectonic contact. The data acquired through the microtectonic study and the RSCM spectroscopy were compatible with this hypothesis. According to our reconstruction this Late Cretaceous - Paleocene normal fault has been folded and overturned by the intense retrovergent D3 deformation phase that dominates the studied area architecture. Finally, we propose to treat two historical units, separated by this Upper Cretaceous - Palaeocene palaeofault, as two sub-units part of one larger Alpine tectonic unit.

This case study demonstrates how an integrated geological mapping approach, based on several disciplines, can facilitate the recognition of possible inherited structures that may be more common than expected and frequently misinterpreted.

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## Combined thermodynamic modelling and elastic barometry to unveiling the metamorphic evolution of the Zicavo Metamorphic Complex, central Corsica (France)

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Keywords: Variscan Corsica, elastic barometry, shearing.

The Zicavo Metamorphic Complex (ZMC) represents one of the few relicts of the Corsica Variscan basement. Here, three tectonic units are recognized, separated by strike-slip shear zones: the orthogneiss unit, the leptynophibolite unit, and the micaschist unit. The complex shows a polyphasic deformation history, with the main phase resulting in the regional axial plane  $S_2$  foliation with a strike-parallel  $L_2$  object lineation; development of ductile, strike-slip shear zones and top-to-the-SE shearing is coeval with this main  $D_2$  deformative phase.

In the Micaschist Unit, a garnet zone and a staurolite zone are described. The highest-grade rocks consist of Grt+St porphyroblasts and a Ms+Chl+Ilm+Qz±Pl matrix, with post-kinematic andalusites. Garnets show inclusions-rich cores and mantles, with included Cld+Ilm+Wmca+Ap+Mrg (ilmenite growing on rutile), and almost inclusion-free rims. Garnet are compositionally zoned, with a decrease in Mn and Ca and an increase in Fe and Mg towards the rim (core: Alm<sub>0.54</sub>Sps<sub>0.24</sub>Grs<sub>0.18</sub>Prp<sub>0.04</sub>, rim: Alm<sub>0.80</sub>Sps<sub>0.02</sub>Grs<sub>0.09</sub>Prp<sub>0.09</sub>). Peak P-T conditions have been estimated by using trace element thermometry and elastic barometry. Zr-in-rutile results in temperatures of 430-470 °C for garnet core formation. Peak pressures have been inferred using the apatite-in-garnet elastic barometer (Ashley et al., 2017); Raman shifts of entrapped apatite inclusions have been measured, and compared to those of exposed ones; entrapment pressures at temperatures of ~450 °C have been estimated to ca. 6-11 kbar. The P-T evolution has been refined through phase diagram modelling, using PerpleX package (Connolly, 2005) and Thermolab MATLAB code (Vrijmoed & Podladchikov, 2022). Compositional isopleths of garnet core, chloritoid and white mica indicate P-T conditions of 9-12 kbar and 440-490°C, in the stability field of Grt+Cld+Ms+Chl+Rt+Qz; equilibrium assemblages do not differ between the two code packages. Formation P-T conditions for garnet rim have been estimated, using compositional isopleths of garnet, white mica, staurolite and chlorite, to be 5-8 kbar and ~500 °C, after little consumption of garnet to form staurolite. Furthermore, phase diagrams calculated with Thermolab show small amounts of stable biotite, which is in agreement with relict biotite overgrown by chlorite observed in thin sections. Phase equilibrium modelling results are consistent with P-T conditions estimated with elastic barometry and rutile thermometry. Finally, plagioclase and chlorite characterize the onset of the retrograde path, preceding the last high-temperature event responsible for staurolite consumption to form post-kinematic andalusite. To summarize, the newly presented data reveal a Variscan evolution for the Micaschist Unit of the ZMC featured by a clockwise P-T path, with prograde metamorphism at relatively high pressures, and peak temperatures, after decompression and heating, in the amphibolite facies, during the main deformation and shearing.

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## **Shear zones in blueschist facies continental metasediments: a tool to disclose potential fossil deep episodic tremor and slow slip events**

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*Keywords:* shear zone, episodic tremor and slow slip events, veins.

Episodic tremor and slow slip events (ETS) have been proposed as a common feature of the geophysical signature of subduction zones. Their geological record, however, remains sparse.

We studied metamorphosed continental metasedimentary rocks of the Northern Apennines (Italy) as part of a metamorphic broken formation composed of boudinaged metaconglomerate enveloped by metapelite displaying a pervasive mylonitic foliation. Dilational hydroshear veins occur in both lithotypes but are more common and laterally continuous in the metapelite. The veins are generally parallel to the metamorphic foliation and are composed of iso-oriented stretched quartz and carpholite fibres. Thermodynamic modeling constrains the formation of the high-pressure veins and the mylonitic foliation to ~ 1 GPa and 350°C, corresponding to c. 30-40 km depth in the subduction channel.

Dilational hydroshear veins formed by incremental crack-sealing under supralithostatic pore pressure conditions. The veins experienced limited subsequent reworking, as shown by minor recrystallization of quartz by subgrain rotation recrystallization. Adjacent metapelite bands acted as decollement horizons, probably by slip on the basal plane of phyllosilicates. Blueschist facies mylonites formed mainly by a combination of dissolution-precipitation creep and slip along phyllosilicate bands.

Dilational hydroshear veins in subducted metasedimentary successions have been suggested to be potential records of ETS. We propose these microstructures and deformation mechanisms as geological evidence for deep ETS in subducted continental metasediments. Pore pressure cyclically reached supralithostatic values, triggering tremors and causing fracturing of all lithotypes involved. Likely, slow slip was accommodated preferentially by slip on phyllosilicate bands. Aseismic creep occurred mainly by dislocation creep with subgrain rotation recrystallization in vein quartz, slip on the basal plane of phyllosilicates, and dissolution and precipitation creep in the host rock.

<sup>39</sup>Ar–<sup>40</sup>Ar step-heating analyses constrain the growth of phengitic muscovite of the mylonitic foliation to ca. 16-18 Ma, consistent with age estimates for several high-pressure units of the Northern Apennines. In-situ  $\delta^{18}\text{O}$  SIMS measurements constrain values between 18.4 and 19.2 ‰ for the quartz fibres in the veins.  $\delta^{18}\text{O}$  bulk rock analyses by laser fluorination range between 12.3 and 15.7 ‰ for the host metasediments and ca. 14 ‰ for the adjacent metabasites. These data suggest that the different fluid batches were externally derived and not in equilibrium with the host rock.

In conclusion, our results suggest that the role of quartz-carpholite veins formed coevally with metamorphic foliation should be reconsidered as a possible record of deep ETS in similar geological settings of other convergent orogens.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 839779.

## New geochronological data from Valsugana and Agordo metaporphyrroids

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Keywords: metaporphyrroids, geochronology, Southalpine basement.

The metaporphyrroids are quite common in the Southalpine metamorphic basement (e.g., in Bressanone, Comelico, Valsugana and Agordo areas). They are the results of Ordovician widespread acidic magmatic events, later involved in the Variscan orogenic event in the lower Carboniferous (Meli, 2004).

The metaporphyrroids of Borgo Valsugana area are characterized by heterogeneous composition and texture because they reflect the different products of volcanic activity, from volcanoclastites to massive volcanites. The mineralogical association consists of abundant quartz, chlorite, sericite and feldspar. The main variable lithological features are the dimension of the feldspar eyes (from 1 mm up to 4-5 cm), the amount of quartz, the grain size and the proportion between chlorite and white mica. These rocks outcrops at different altitudes. NW of Novaledo, at the low altitude (400-500 m a.s.l.) a metaporphyrroid layer up to 600 m thick is stratigraphically below the qtz-phyllites. N of Samone, at high altitudes, 1300-1450 m a.s.l., more discontinuous bodies are interbedded within qtz-phyllites. The latters are very rich in biotite due to the overprint of contact metamorphism produced by the Permian intrusive bodies of Cima d'Asta.

The geochronological data on the Southalpine metaporphyrroids yielded concordant U/Pb ages of 479-485 Ma in Comelico area (Meli & Klötzli, 2001);  $471.6 \pm 3.5$  Ma on the Merano geological sheet, NE Mt. Catino (Bargossi et al., 2010);  $472.0 \pm 3.0$  Ma and  $451.5 \pm 6.1$  Ma from two different zircon population in Funes Valley (Arboit et al., 2019). As part of the Borgo Valsugana geological sheet (CARG project) it was chosen to date 4 metaporphyrroid samples, from different altitudes, with the purpose to understand if they are originated by different volcanic events and therefore to reconstruct the lithostratigraphy of the Valsugana basement. Furthermore, a metaporphyrroid sample from Agordo area is being dated to enrich the comparison of the pre-Variscan volcanic activity in the whole Southalpine basement.

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## **Mapping crystalline basements from map-scale down to microscale and backwards: an example from Central Himalaya**

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*Keywords:* crystalline basements, Himalaya, structural geology.

Crystalline basements are central elements for the reconstructions of mountain belts' formations, lithosphere dynamics, and the shaping of tectonic/geodynamic models.

Defining and mapping tectono-metamorphic units, deciphering their long-lasting tectono-metamorphic evolution, and unrevealing the often-complex history of their tectonic boundaries can be challenging for geologists working on crystalline basements, as demonstrated by different and pioneering studies on the Alps, the Scottish Highlands, and the Himalaya.

For several reasons, including outcrop conditions and exposure, quite often numerous solutions/possibilities can be considered. To reduce these uncertainties, the method of “multiple working hypotheses” (Chamberlin, 1890) must be followed, and a multidisciplinary and multiscale approach is required. Basic tools of geological mapping, such as lithostratigraphy and lithostratigraphic correlations are still valid but they must be accompanied (and supported) by detailed structural-geological mapping, meso- and microstructural investigations, petrofabric analysis, petrologic data, and geochronological/petrochronological constraints (Carosi et al., 2018).

In this contribution, the advantages of this integrated approach will be illustrated for the Manaslu Massif (Nepal) as study-case in the Central Himalaya. Despite being one of the most investigated areas in the Nepalese Himalaya (Colchen et al., 1986), geological mapping of the Manaslu Massif area still presents several debated aspects within the geological community (e.g., Searle & Godin, 2003; Parsons et al., 2016; Walters & Kohn, 2017).

The integrated approach of combining structural geology (at the different scales) with petrology and petrochronology, helped to: (i) identify the occurrence of a high-temperature shear zone within the Greater Himalayan Sequence (GHS), the largest crystalline unit in the Himalaya; (ii) improve the mapping of the boundaries of the GHS; (iii) define the shear zones kinematics in the area, and (iv) clarify their timing of shearing. These results provide general implications on the assembly and exhumation of the middle crust in syn-collisional settings as well as, locally, on the relationships between a main syn-collisional low-angle normal fault and the igneous bodies in this part of the belt.

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## **Monazite and titanite behaviour within amphibolite-facies mylonites: the Forno-Rosarolo shear zone (Ivrea-Verbano Zone; Italy)**

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*Keywords:* monazite, titanite, petrochronology.

Mylonites reflect zones of high-strain rate where dominantly ductile deformation at variable temperatures has been localized. Dating the time of shear zone activity has been described as one of the most difficult problems in geochronology. Here we present a study from a mid-crustal shear zone, the Forno-Rosarolo Shear Zone (FRSZ), exposed in the Ivrea-Verbano Zone (e.g. Rutter et al., 1993). Although the activity of this structure has been associated to the Mesozoic rifting (e.g., Beltrando et al. 2015) its age is still unconstrained. We attempt to date the amphibolite-facies deformation by integrating monazite and titanite U-(Th)-Pb data. The FRSZ is a sub-vertical structure with a thickness of about 500m (Siegesmund et al., 2008) located at the amphibolite/granulite-facies transition. Mylonites developed mainly at the expense of paragneisses, mafic rocks and minor calc-silicates. Paragneisses and calc-silicates were selected for *in-situ* U-(Th)-Pb monazite and titanite geochronology, respectively. Mylonitic paragneisses consist of garnet, sillimanite, feldspar and biotite with accessory zircon, monazite and rutile. Monazite occurs in different microstructural positions (included in porphyroclasts or along the mylonitic foliation) and commonly presents Th and Y complex chemical zoning allowing to identify three different generations. Preliminary data suggest a late Triassic-Jurassic recrystallization event induced by deformation. Mylonitic calc-silicates are made of calcite-rich and calcite-poor layers. The latter are richer of amphiboles, clinopyroxenes, feldspars and quartz ( $\pm$  garnet) and exhibit large titanite grains (up to 1mm). Two types of titanite were identified: i) strongly zoned grains with LREE depleted rims/tips and ii) homogeneous grains. Both types show evidence for intracrystalline deformation (e.g., deformation twins and systematic crystal lattice bending). U-Pb dating across titanite grains revealed a coupling between chemical domains and isotopic data. The rims/tips of zoned titanite provided an alignment of isotopic data with the youngest intercept age at the Triassic-Jurassic transition. The application of two independent geochronometers allowed us to shed light on the age, duration and evolution of deformation associated to the Triassic-Jurassic period. Our approach is particularly appropriate when dealing with large-scale shear zones involving different types of rocks.

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## **How to unravel the evolution of a regional scale shear zone: a plunge into the Vinschgau Shear Zone (Eastern Alps)**

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*Keywords:* Vinschgau Shear Zone, Ar/Ar geochronology, vorticity analysis.

The Vinschgau Shear Zone (VSZ) is one of the largest and most significant shear zones developed in ductile conditions within the Austroalpine domain. The VSZ juxtaposed the Ötztal and the Texel units to the Campo, Scharl and Sesvenna units during the building of the Eo-Alpine Orogen. The VSZ dominates the structural setting of a large portion of the central Austroalpine Late Cretaceous thrust stack. To assess the full evolution of the VSZ, a multi-faceted approach based on detailed multiscale structural and petrochronological analyses has been carried out across representative transects of the shear zone in the Vinschgau Valley, characterizing kinematics, P-T conditions and timing of motion of the VSZ.

Our fieldwork-based analyses suggest that the dip angle of mylonitic foliation increases from W to E with an E-W trending stretching lineation which dips alternatively to the W and to the E, due to later folding related to the Cenozoic crustal shortening. The dominant top to the W shear sense of the mylonites documented in the field and confirmed by microstructural analyses led to exhumation of the upper Austroalpine nappes in the hanging wall of the shear zone: the Texel unit with Late Cretaceous eclogites, the Schneeberg and Ötztal units both affected by Eo-Alpine amphibolite-facies metamorphism. Timing of deformation along the VSZ has been constrained for the first time through <sup>40</sup>Ar/<sup>39</sup>Ar dating of syn-shearing micas, which reveal a Late Cretaceous age of the VSZ mylonites with ages ranging between 80 and 97 Ma. A systematic younging age of deformation occurs towards the central part of the shear zone in the studied transects. Vorticity analysis shows a clear decrease in the simple shear component correlated to the younging of mica ages towards the core of the shear zone. This evolution is consistent with the growth of a shear zone where shear strain localizes into its central part during deformation. The constrained evolution of the VSZ sheds new light on how regional-scale thrust-sense shear zones act and how much exhumation they can accommodate in the frame of an evolving orogenic wedge.



## Unveiling the importance of $M_{H_2O}$ in the tectono-metamorphic evolution of shear zones: a case from the Dora-Maira Massif (Western Alps)

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Keywords: mylonites, phase equilibrium modelling, fluid content.

Metamorphic reactions are easily driven to completion within shear zones thanks to fluid circulation, making the re-equilibration of the mineral assemblage the dominant petrologic process. In fact, the relationship between deformation and metamorphism is related to the access of fluids and fluid/rock interactions. In forward thermodynamic modelling calculations,  $H_2O$ -(over)saturated conditions (i.e., the presence of a free fluid phase inducing fluid-present metamorphism; e.g., Fyfe et al., 1978; Thompson, 1983) are usually assumed. However, metamorphic rocks are thought to experience only fluid loss during increasing temperature (e.g., Thompson, 1983). We investigate the  $P$ - $T$ - $M_{H_2O}$  evolution of the Mt. Bracco Shear Zone (MBSZ, Avigad et al., 2003), an Alpine ductile tectonic contact which marks the boundary between two HP units, the polymetamorphic Ricordone Unit and the monometamorphic Sanfront-Pinerolo Unit, in the Dora-Maira Massif (Western Alps, Italy). The analysed mylonitic samples allowed us to reconstruct a polyphase  $P$ - $T$  history related to exhumation and a complex fluid regime evolution and its influence on the shear zone behaviour. After the eclogite-facies peak, the subsequent mylonitic event is constrained at amphibolite-facies conditions, continuing its evolution at decreasing pressure and temperature during rock exhumation.  $P/T$ - $M_{H_2O}$  thermodynamic modelling predicts the attainment of both  $H_2O$ -saturated and -undersaturated conditions. After reaching a maximum  $H_2O$  content at the transition from eclogite to amphibolite-facies conditions, a significant fluid gain is modelled just before the mylonitic event. Then, the MBSZ evolves toward  $H_2O$ -undersaturated conditions in a closed system. This work thus proposes the necessity of investigating the  $H_2O$  evolution within shear zones, as the  $H_2O$  content is susceptible to change through time, especially during metamorphism, due to dehydration reactions or fluid infiltration events. As a corollary, the difference in behaviour between the considered samples suggests that fluid evolution within shear zones could result from both externally and internally derived fluid flux. The MBSZ can be considered as a preferential pathway for fluid fluxes during exhumation but also determines a redistribution of the fluid.

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## **Microstructures of sheared metagranitoids of the Pollino Massif: possible relics of the Mesozoic rifting?**

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*Keywords:* Frido Unit, mylonites, shear bands.

The Pollino Massif is located in the border zone between the sedimentary cover of the Southern Apennines and the basement rocks typical of the Calabria terrane. In the area, fragments of continental crust and ophiolites derive from the Jurassic Alpine Tethys domain and testify rift processes that led to the formation of this ocean. This is evident in the Frido Unit, consisting of very low-grade metasediments with an *HP/LT* overprint, associated with metabasites, serpentinites, gneisses, amphibolites and metagranitoid rocks. This latter lithology is frequently affected by m-thick mylonitic bands, which are well exposed in the Serra del Prete Area, near the tectonic contact between the Frido Unit and the underlying North-Calabria Unit. The emplacement of the metagranitoids took place around  $292 \pm 11$  Ma, according to U-Pb ages on zircons (Laurita et al., 2014).

The purpose of this work is to reconstruct the deformation history and the thermal conditions under which the mylonitic process developed, framing the shearing event in the late-Variscan to Apennines geodynamics. To this end, we collected oriented samples along strain gradients, from undeformed to mylonitic metagranites, which were analyzed under the optical microscope and the SEM to determine their mineral association, microstructures and kinematics. Accordingly, we classified samples into: i) metagranites, consisting of a granoblastic aggregate of quartz, albite, white mica and chlorite; ii) protomylonitic metagranites, with an incipient foliation outlined by mm-thick bands of fine-grained quartz and albite; iii) mylonites, characterized by a banded fabric outlined by alternating, mm-thick levels consisting of quartz-chlorite aggregates and prevailing white mica. The analyzed microstructures document crystal plasticity of quartz and albite by bulging recrystallization and subgrain rotation processes. The development of S-C' type shear bands in mica-rich domains and later dislocation of quartz veins along foliation planes are also observed. Recrystallization processes indicate temperatures between 300°C and 400°C during the mylonitization. Shear sense indicators are mainly consistent with a top-to-the-SW tectonic transport.

SEM analyses allowed to determine the chemical compositions of minerals. Application of the chlorite thermometer by Bourdelle et al. (2013), indicates that chlorite equilibrated at temperatures of about 200°C to 250°C.

Microstructures of the mylonites, indicating relatively high temperatures during deformation, are possibly related to the Lower Jurassic rifting event at ~193 Ma (Shimabukuro and Battistella, 2022). This is compatible with the anomalous top-to-the-SW shear sense, which does not coincide with the Apennine deformation (top-to-the-E). Lower T estimates obtained from chlorites can be interpreted as due to cooling and re-equilibration of mylonites at the end of the shearing event.

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Laurita S., Prosser G., Rizzo G., Langone A., Tiepolo M. & Laurita A. (2014) - Geochronological study of zircons from continental crust rocks in the Frido Unit (southern Apennines). *Int. J. Earth Sci.*, 104, 179-203. <https://doi.org/10.1007/s00531-014-1077-7>.

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## How much can contour maps help? Flow kinematics map of the Posada-Asinara shear zone (NE Sardinia, Italy)

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*Keywords:* Variscan basement, shear zone, strain partitioning.

Although contour maps are widely used in Earth Sciences to show the variation of quantities over the surface (Groshong, 2006), relatively few attempts have been made to exploit the potential of these maps in flow kinematic analysis. Flow kinematics estimations are necessary to determine how the deformation is partitioned in shear zones at different scales (Xypolias, 2010). A graphical representation of the flow kinematic distribution at the map scale could be a helpful tool for investigating the Wk spatial variation of shear zones, identifying zones affected by different amounts of simple and pure shear. The Posada-Asinara shear zone (PASZ) in northern Sardinia (Italy) is a well-constrained crustal-scale km-thick transpressive shear zone, separating the High- from the Medium-Grade Metamorphic Complex (Carosi & Palmeri, 2002; Carosi et al., 2020). After microstructural analysis, the vorticity of the flow was estimated to investigate the southernmost boundary of the PASZ, highlighting a dominant pure shear component far from the core of the shear zone. These results have been integrated with existing data to derive a regional-scale flow kinematic map of the Baronia region. This work highlights the potentiality of automated geostatistical mapping to become a powerful complementary tool in the investigation of flow kinematics in collisional environments. Since vorticity analysis is a powerful tool and the kinematics of flow is a fundamental parameter for investigating the complex evolution of regional-scale shear zones, when an adequate amount of estimations is available, graphical-based data like contour and interpolated maps could improve the traditional data interpretation. In this way, it is possible to explore the Wk distribution, compare the different deformation regimes linked to high- and low-strain domains and unravel the distribution and partitioning of deformation throughout different crustal-scales shear zones.

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## **The crystalline basement of Asinara Island (NW Sardinia, Italy): a multidisciplinary approach in a CARG project**

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*Keywords:* geological mapping, structural analysis, CARG project.

Mapping crystalline basements is difficult due to their polyphased deformation and metamorphism. Furthermore, the emplacement of intrusive bodies can determine metamorphic processes in the hosting rocks overprinting previous ones.

The CARG project started with a traditional approach to geological mapping and subsequently was implemented with a digital database. However, up to now it was never regulated and coded how to deal with the issues linked to the mapping of crystalline rocks.

The Sheet n. 425 - “Isola Asinara” (Geological Map of Italy on a 1:50.000 scale) is the first attempt to integrate the CARG project normative with new digital mapping tools (Gencarelli et al., 2021), such as FieldMove Clino and Qfield apps, with traditional fieldwork (lithostratigraphic data). Such an integrative approach contributes to solving issues that cannot be directly resolved from the fieldwork. Furthermore, remote sensing, meso- and micro-structural analysis, and petrology data was powerful tool to improve the geological and structural data.

This multidisciplinary approach has been tested in Asinara Island which represents a segment of Sardinian Variscan basement. This new approach led us to recognize two tectono-metamorphic units (medium- to high-grade metamorphic complex) made of several lithologies that share a common tectonic and metamorphic evolution and two intrusive units that comprise magmatic rocks with probable different origins.

From a structural point of view, four ductile deformation phases are recognized (Carosi et al., 2004):

D1 is locally preserved and the S1 is visible in D2 hinges;

D2 is the most pervasive deformation phase and S2 is the main foliation that progressively becomes a mylonitic foliation approaching the Posada-Asinara shear zone (Iacopini et al., 2008);

D3 is weak and produced upright folds, mainly developed in the central and northern parts of the island;

D4 is associated with a sub-horizontal crenulation cleavage.

For each deformation phase the pre-, syn- and post-tectonic minerals as well as microstructures (observed in field-oriented thin sections) were recognized in order to have preliminary and qualitative information about the P-T conditions associated to the deformation. The termo-metamorphic aureoles associated to the magmatic intrusions were recognized thanks to the static growth of index minerals.

This integrated approach to geological mapping is currently the most effective way to adequately describe and represent crystalline rocks from a cartographic point of view.

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Iacopini D., Carosi R., Montomoli C. & Passchier C.W. (2008) - Strain analysis and vorticity of flow in the Northern Sardinian Variscan Belt Recognition of a partitioned oblique deformation event. *Tectonophysics*, 446(1-4), 77-96. <https://doi.org/10.1016/j.tecto.2007.10.002>.

## **Tectono-metamorphic evolution of a post-Variscan mid-crustal shear zone in relation to the Tethyan rifting (Ivrea-Verbano Zone, Southern Alps)**

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*Keywords:* Forno-Rosarolo shear zone, Ivrea-Verbano Zone, Tethyan rifting.

In the last decade, studies of rifted margins have benefited from an increasing quantity of high-quality data from several disciplines. However, the direct observation and investigation of rift-related structures at the mesoscale is not so common and often the structures related to such geodynamic process lack of a complete characterisation.

The Ivrea-Verbano Zone (IVZ), in the Italian Southern Alps, represents a complete section of middle to lower continental crust, which records both the Variscan and subsequent Alpine Tethys rift-related tectonics (Beltrando et al., 2015; Simonetti et al., 2021).

One of the most important structures is the Forno-Rosarolo shear zone (Siegesmund et al., 2008) that influenced the post-Variscan tectonic evolution of the IVZ. It is a NE-SW-oriented, subvertical shear zone made of metapelites, amphibolites, calc-silicates and granulites involved in anastomosed proto- to ultramylonite layers enveloping weakly deformed lenses. Mylonites formation postdate Variscan metamorphism and deformation and predate Jurassic brittle fracturing and faulting, locally associated with pseudotachylites.

In present day orientation, the kinematic indicators point to a sinistral sense of shear. Removing the Alpine tilt at high angle of the IVZ, this kinematic points to a former extensional shear zone. Investigations on the mylonitic flow kinematic reveal a non-coaxial deformation characterized by dominant pure shear (between 70% and 50%) and minor simple shear. Metamorphic conditions of the wall rocks vary from the upper amphibolite (SE, footwall) to the granulite facies (NW, hanging wall). Within the mylonites, PT estimate from mineral assemblage points to amphibolite facies conditions during deformation (~650°C and ~5.5 kbar).

Such kinematic data and metamorphic conditions allow to constrain the development of the Forno-Rosarolo shear zone mylonitic deformation, together with other similar structures of the IVZ, during the intermediate phase of the Tethyan rift (Beltrando et al., 2015; Simonetti et al., 2021) known as “thinning mode” (Manatschal et al., 2007). This stage was characterized by general shear conditions (pure shear between 70% and 50%) suggesting a phase of transition from a symmetric to an asymmetric configuration of rift.

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Manatschal G., Müntener O., Lavie L.L., Minshull T.A. & Péron-Pinvidic G. (2007) - Observations from the Alpine Tethys and Iberia–Newfoundland margins pertinent to the interpretation of continental breakup. *Geol. Soc. Spec. Publ.*, 282, 291-324. <https://doi.org/10.1144/SP282.14>.

Siegesmund S., Layer P., Dunkl I., Vollbrecht A., Steenken A., Wemmer K. & Ahrendt H. (2008) - Exhumation and deformation history of the lower crustal section of the Valstrona di Omegna in the Ivrea Zone, southern Alps. *Geol. Soc. Spec. Publ.*, 298, 45-68. <https://doi.org/10.1144/SP298.3>.

Simonetti M., Langone A., Corvò S. & Bonazzi M. (2021) - Triassic-Jurassic Rift-Related Deformation and Temperature-Time Evolution of the Fossil Adriatic Margin: a review from Ossola and Strona di Omegna Valleys (Ivrea-Verbano Zone). *Ofioliti*, 46. <https://doi.org/10.4454/ofioliti.v46i2.544>.

## Mapping crystalline basements integrating field geology and analytical data: criteria, methods and standards

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Keywords: geological mapping, crystalline basement, field geology.

Crystalline basements are made of metamorphic and/or intrusive rocks. They are usually affected by a long-lasting metamorphism and deformation history, thereby the principle of stratigraphic superposition is rarely respected. This makes the working in such terranes very challenging. Over the years several approaches have been proposed for mapping crystalline basements (e.g., Spalla et al., 2005). Some approaches have been formalized in stratigraphic codes, such as lithostratigraphic units (Salvador, 1994) following the suggestions by the International Subcommittee on Stratigraphic Classification (ISSC), or lithodemic units (Leslie et al., 2012) according to the North American Stratigraphic Commission (NASC). Despite the efforts undertaken to understand the best way to represent the crystalline basements from a cartographic point of view, the approaches proposed by the various stratigraphy codes are limited and/or extremely reductive. In fact, in their application, there is the risk of mapping together, in an unique lithological unit, rocks showing nowadays similar lithological/petrographical features but with contrasting geological evolutions. In a modern effort of geological mapping, it is, therefore, necessary to integrate lithostratigraphic data, with structural geology, petrology, geochemistry, and geochronology (e.g., Carosi et al., 2022). Field observations and mesoscale structural data are therefore integrated by further multidisciplinary analyses in order to recognize tectonic units, and their boundaries, which are not easily or univocally recognizable only by field observations. Such units, group rocks with a homogeneous tectono-metamorphic evolution.

This multidisciplinary method was applied to a segment of Variscan basement in NW of Sardinia to realize Sheet N. 425 Isola Asinara (Geological Map of Italy on a 1:50,000 scale) which represents a good example of the effectiveness of this working procedure and representation technique.

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## Tectonic overpressure and thermal dissipation within a cold lower crust: Markers for the seismic cycle

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*Keywords:* seismic microstructures, quartz dauphine twinning, amorphous gel inhibiting frictional slip.

We have investigated garnet-kyanite-staurolite mylonitic micaschists and garnet-kyanite/sillimanite mylonitic paragneisses from the Serra dei Meriani–Passo Fosso del Lupo Shear Zone in Calabria (Festa et al., 2022), within and at the margin of the shear zone, respectively. The parent rock of these mylonites are Variscan garnet-sillimanite restites, cooled below 300°C at ~88 Ma (Festa et al., 2022; Schenk, 1989). Unexpectedly, these rocks show unequivocal seismic microstructures that suggest a so far hidden weakening and power dissipation mechanisms, that might be a precursor to mylonites. Through FEG-SEM ultra-high-resolution imaging and SEM-EDS-WDS microanalysis we have observed kyanite-staurolite pseudomorphic intergrowth partially substituting sillimanite and garnet deformed by cataclastic flow. Garnet clasts are surrounded by a goethite/ferrihydrate cryptocrystalline aggregate, as revealed by micro-Raman spectroscopy. High-resolution EBSD analysis shows that the cryptocrystalline material in some sites appears to be amorphous since indexing is not possible except for a few ferrihydrate dendritic crystals. Additionally, SEM-EBSD analysis of quartz highlights activation of dauphine twinning, suggesting that these rocks were subjected to differential stresses varying from 145 to 460 MPa. Dauphine twinning is overprinted in the highest strain domains by dislocation creep. EBSD analysis shows that dislocations are also activated within the fractured garnet. The presence of goethite/ferrihydrate cryptocrystalline material surrounding garnet, along with mica-rich domains outside cataclastic garnet aggregates and kyanite-staurolite intergrowth partially substituting sillimanite and garnet, indicate fluid access due to dilatancy following garnet fracturing. Thermodynamic modelling of the garnet+fluid system using the software THERMOCALC (Holland & Powell, 1998) with the updated version of the Holland & Powell (2011) thermodynamic dataset (file tc-ds633, created on 23.06.2017), indicates that kyanite, staurolite, hematite, and chlorite are products of garnet dissolution at about 0.8–1.6 GPa and 600–700°C, which represent the thermal peak conditions assuming local equilibrium. These peak conditions are below the frictional melting point of the rock, which was not reached since (i) the presence of amorphous-cryptocrystalline gel between garnet grains lowered friction, and (ii) the precipitation of garnet dissolution products further inhibited temperature increase, favouring cooling. Hence, these mylonites are the product of seismic events affecting a cold lower crust.

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## New geochronological data confirm Late Cretaceous thrusting in the Italian central Southern Alps

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*Keywords:* structural geology radiometric dating, Southern Alps.

In the frame of the FAST 2020 PRIN Project, we have planned an extensive radiometric dating campaign on fault rocks related to thrusting across the central Southern Alps (cSA). We applied different geochronological techniques according to the heterogeneous rock types of the analyzed thrust sheets, which include metamorphic rocks, carbonates and terrigenous units.

Starting from the north, new Ar-Ar ages on pseudotachylite confirm the Late Cretaceous ages (80-68 Ma) previously established for the Orobic Thrust by Zanchetta et al. (2011, 2015). Analytically identical ages have been obtained by K-Ar illite geochronology on kinematically-related fault gouges from both the hanging wall (Variscan metamorphic rocks) and the footwall (Permian-Triassic cover successions) of the Orobic thrust plane. Several new calcite U-Pb radiometric dates from carbonate fault rocks, including calc-mylonites and veins were also obtained for the main thrusts in the central part of the belt, which consists of a thick pile of thrust sheets affecting the Lower to Middle Triassic succession of the Lombardian Basin. These data are the first direct evidence for a Late Cretaceous phase of deformation affecting a large part of the cSA, which, until now, had only been postulated on the base of indirect evidence (Schönborn et al., 1992; D'Adda et al., 2011; Zanchetta et al., 2015).

Late Cretaceous ages were also obtained from within Norian "Dolomia Principale" thrust sheets within the southern portion of the cSA, where the Dolomia Principale overrides the Rhaetian Argillite di Riva di Solto immediately to the north of the frontal portion of the cSA belt, which resulted in younger ages.

When the new geochronological data are integrated with paleothermal indicators derived from the clay-size fraction of sediments, a clearer picture of the early stages of development of the cSA belt emerges.

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**Architecture and deformation partitioning across a brittle-ductile detachment zone:  
geological and structural constraints from the Mykonos Detachment  
(Aegean Rift System, Mykonos Island, Greece)**

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*Keywords:* Mykonos Detachment, Cyclades, Aegean rift.

Detachment zones were, and are, commonly active during and after the onset of crustal extensions and thinning, which generally follow the formation of subduction-obduction orogeny and fold-and-thrust belts along several active contractional margins and allow the exhumation of even deep subducted slices of continental and oceanic crust. Triggered by multiple mechanisms (e.g., slab retreat), regional scale ductile (deeper) and brittle (shallower) detachment zones accommodate several kilometres of vertical and horizontal displacement during crustal extension, and allow the opening of wide back-arc basins through millions of years of evolution. This long evolution is invariably reflected in a high architectural complexity of fault zones, which thus represent the summation of multiple deformation phases. The understanding of this architectural complexity is thus pivotal toward the exact reconstruction of their evolutions and toward the analysis of the deformation localisation during progressive extension.

In this perspective, with the aim to provide new insights into the processes that steered the evolution of the still active Aegean rift system, we analysed the architecture of the Mykonos Detachment (Cyclades, Aegean Sea), which accommodated tens of km of horizontal and vertical displacement since the Middle Miocene. The EW-striking and NE-dipping Mykonos Detachment is described as top-to-the NE low-angle detachment and consists in two branches that evolved in brittle-ductile (Livada branch) and brittle (Mykonos branch) fashion during the opening of the Aegean Sea. These two branches bring in contact the Miocene syn- to post-tectonics siliciclastics onto the (?) Jurassic metabasites, which are in turn put in tectonic contact with the Mykonos granite, intruded during the Miocene. By integrating geological mapping and a detailed structural analysis on key exposures, through the characterisation of the Brittle Structural Facies (BSFs), we show that deformation localises in different manners along and across the Mykonos Detachment. Where metabasites are tectonically elided, deformation is extremely localised along a main, single, and sharp slip surface, with only small lenses of fault gouge, whereas deformation is extremely partitioned where metabasites are preserved. There, the Mykonos Detachment was probably formed through the superposition of multiple faulting phases, highlighted by multiple generations of both massive and foliated fault gouges.

The localisation of deformation might be related to (i) the lithology of the Miocene siliciclastics in the hanging wall and (ii) the role of metabasites that, if preserved, allow the deformation partitioning. In conclusion, we provide new evidence on the evolution of the Mykonos Detachment in relation to the opening of the Aegean Sea, and we propose a new BSFs-based conceptual model for the formation of the Mykonos Detachment and for the related deformation localisation.

**S38.**

**Deformation and faults: from deep to shallow crust and from  
long term to seismic hazard**

*CONVENERS AND CHAIRPERSONS*

*Riccardo Lanari (Università degli Studi di Firenze)*

*Silvia Crosetto (GFZ)*

*Stefano Gori (Istituto Nazionale di Geofisica e Vulcanologia)*

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## How to reconcile active structures with the complexity of seismogenic sources in tectonically polyphasic areas? Insights from the Northern Apennines

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*Keywords:* seismic hazard, intermontane basins, active tectonics.

Increasing our understanding and evaluation of seismic hazard in tectonically active regions requires multidisciplinary approaches for the characterization of the seismogenic source that integrate geophysical observations (mainly seismology) and geological constraints. However, in tectonically complex areas, the indications from earthquake focal mechanisms and structural geological observations at the surface might be controversial and lead to incorrect evaluation of the seismic hazard. This is particularly true when dealing with active and capable faults whose evolution might result from different tectonic regimes through time. As a matter of fact, the complex surface expressions of fault systems that experienced a change in their kinematics in recent times might make it difficult to perform a correct evaluation of their potential in generating surface deformation during earthquakes.

In the Northern Apennines, the main drainage divide is considered as a major boundary between the internal part of the orogen (to the SW), which is already experiencing late- to post-orogenic extension, and the external part (to the NE), which is still under contraction. Accordingly, major active tectonic structures and intermontane basins straddling this boundary show ambiguous relationships between the registered seismicity and the surface expression of the potentially seismogenic faults. Key examples are the Mugello intermontane basin and a WNW-ESE-trending narrow valley to the south of the Castiglione dei Pepoli ridge (Brasimone Lake area). There, earthquake focal mechanisms show clear evidence for an extensional regime, while the field expression of the associated structures is more ambiguous and often interpreted as related to the previous compressional regime. Preliminary field observations suggest that the tectonic evolution of the structures bounding the main morphotectonic features is rather complex, and the polyphasic reactivation/overprinting of these structures reveals the summation of multiphase deformation.

We apply an integrated approach to unravel the complexity of seismogenic sources combining field observations, structural analyses, geochemical studies and geochronology. At this preliminary stage of the work, detailed field observations allow for the high-resolution characterization of active and capable faults and represent fundamental pinpoints for geochemical and geochronological investigations that we will carry out. Such a comprehensive workflow will eventually allow the reconstruction of fault evolution through-time, and to explore the feedbacks between fluid flow in fault zones and their earthquake potential. This deterministic approach will likely represent a solid base to build probabilistic models for the seismic response of fault zones and to integrate geological constraints in seismic hazard assessment protocols.

## The contribution of SAR interferometry to the long-term structural assessment of Mt. Etna

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Keywords: Etna, SAR, volcano dynamics.

From the first applications (e.g., Massonet et al., 1995), the Synthetic Aperture Radar (SAR) interferometry is largely proved to measure ground deformations at the scale of the volcanoes with space and time resolution suitable to monitor the dynamic induced by the volcanic activity and to assess dynamics and geometry of their active tectonic features. Particularly fruitful for the structural studies are the techniques based on the interferometric analysis of time series of SAR passes for two main reasons: first, because the time series analysis allows reducing or removing the most common atmospheric or geometric artefacts in the SAR interferometric images and second, because long lasting subtle deformations along faults are optimally defined (Ferretti et al., 2001; Lanari et al., 2007). Mt. Etna was one of the first volcanoes in which SAR was used for structural studies (Bonforte et al., 2011 and reference herein). In this presentation, the results of twenty-five years of interferometric SAR analysis is presented and discussed to update the earlier studies with the twofold aims: to confirm, detail or modify the structural assessment of the active features of the volcano and to evaluate the possible effects of the volcanic activity on the dynamic of the structural features. To this aim, we will use the information from the velocity fields measured at different time windows.

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## **Active and capable faults and railway lines planning: assessing seismic hazard through a multidisciplinary and multiscale workflow**

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*Keywords:* active and capable faults, seismic hazard, railways.

An Active and Capable Fault (ACF) is a fault capable of producing deformation/displacement of the ground surface in response to macro-earthquakes generated by a seismogenic source at depth, within a period of the order of tens of thousands of years (e.g., Upper Pleistocene–Holocene, i.e., the present, following the IAEA safety standards for nuclear installation).

The Central Apennines represent the most studied orogenic segment of Italy in terms of ACFs parametrization, especially after the dramatic earthquake events occurred during the last twenty years. Tectonic deformation in this sector of the belt is accommodated by faults, oriented either subparallel or sub-perpendicular to the strike of the orogen, defining a complex structural pattern of dominant master faults and subordinate structures causing heterogeneous stratigraphic offsets during the Quaternary. The key parameters of these ACFs (e.g., slip rate, displacement, recurrence time) are only in part reported by ITHACA, the national reference database for ACFs in Italy. This lack of information has forced the scientific community to systematically investigate the pattern of coseismic ruptures of each new seismic event with the ultimate goal to progressively increase our knowledge on ACFs and to support studies specifically devoted to the assessment of seismic hazard.

Planning infrastructures in active tectonic areas is an engineering operativity that requires the evaluation of the potentially negative impact due to the occurrence and attitude of ACFs. This is particularly challenging for railway lines, which may run for hundreds of kilometers across the orogen and intersect various ACFs with different crosscutting relationships.

We developed a multidisciplinary workflow aiming at improving and standardizing the parametrization of ACFs and defining systematic geological criteria that are useful for assessing scenarios of seismic hazard along railway lines. We have applied the workflow to a number of selected ACFs in the Central Apennines for which the key parameters are only partly defined by ITHACA, and we sorted into classes of varying hazard, each requiring different approaches and study levels. According to different geological and geomorphological settings, the workflow suggests the most suitable methods and investigation approaches for the best possible characterization of the ACFs parameters. It also includes the detection of site effects due to stratigraphic and topographic amplifications, which might contribute to increasing the seismic hazard of the area in which a railway line will pass in the future. Our approach is based on logical paths that integrate methods at regional, sub-regional, and local scale, making it possible for a complete fault parametrization to be used as direct input for probabilistic seismic hazard analyses.

## **A new 3D geological model of the Northern Apennines between Parma and Bologna: a further step toward the parametrization of Active Faults and Seismogenic Sources and a refined local seismic hazard map**

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*Keywords:* Northern Apennines, seismic hazard, 3D seismotectonic model.

Constraining how the surface brittle deformation pattern of a seismic area relates to its seismogenic source(s) is crucial for seismic hazard assessment protocols and should rely on deterministic geological inputs. Linking surface faulting with deep geometries and kinematic patterns is, however, challenging, especially in areas with blind seismogenic faults. Aiming at a better picture of the subsurface along the Pedepenninic Front of the Northern Apennines, we built a new 3D geological model of the area between Parma and Bologna, based on new geological surface constraints and deep geophysical data, with the final goal of locating and characterizing possible active and capable faults. The investigated area extends from mountain environments in the southern internal sector of the Apennines to the flat Po Plain in the north. Its geology is controlled by the Adria-related Tuscan Units in the chain sector, overthrust by allochthonous Ligurian and Epiligurian Units. Pliocene and younger units crop out along the Pedepenninic Front. A compressive tectonic regime is currently dominant, as expressed by the regional NE-verging thrust system that shapes the first-order architecture of the Pedepenninic Front and the Po Plain blind thrusts. This thrust system is dissected by transverse normal and transpressive/transtensive faults. Eight new geological cross-sections have been produced across the Pedepenninic Front and they have been combined with existing ones and with data from deep seismic profiles, borehole data, and seismicity databases to gather an unprecedented overview of the local 3D architecture. The model is organized in fault blocks, the geology of which has been subdivided according to the regional chronostratigraphy. Currently, 50 faults have been mapped and sorted according to criteria such as level of uncertainty, type of structure (active or seismogenic fault), kinematics and crosscutting relationships. In addition to a versatile and powerful visual impact, the model offers a 3D database with well-constrained geometric parameters for each of the constituent elements. It implements realistic fault shapes, as well as other fundamental parameters among which, for example, the along-strike fault displacement. Our new 3D geological model thus represents a net improvement of our current knowledge of active faulting and seismogenic sources in the study area, allowing us to better understand the link between deep and shallow crustal structures. Our results feed an on-going effort to generate an earthquake source model that will be implemented into a probabilistic seismic hazard assessment analysis (PSHA). The latter, by also relying on an accurate surface acceleration model computed considering site effects from the local stratigraphic amplification factors, will finally allow merging deterministic geological inputs with geophysical and stochastic parameters.

## **Closed vs. Open fluid-rock-fault systems tracked by structural, geochemical, geochronological, and thermal constraints**

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*Keywords:* fluid-rock system, tectonic mineralization, seismic cycle.

Structural and geochemical studies on tectonic mineralizations have highlighted different patterns of fluid ingress, circulation and fluid-rock interaction in thrust and normal fault zones during the seismic cycle. Understanding fluid-rock relationships in exhumed faults, from different tectonic settings, is useful for forecasting the role of fluids in still ongoing seismic cycles. We present data on the chemical-physical characteristics of tectonic mineralizations formed by fluids that assisted fault-related deformation in the Apennines (Italy). We combine multiscale structural analysis, stable C, O, and carbonate clumped isotope analysis, U-Pb and K-Ar geochronology, and burial-thermal modeling to constrain the thermal and isotopic features of the fluid-rock systems at the time of tectonic carbonate precipitation. Our data indicate that thrust-related (orogenic) deformation mainly occurred in a closed fluid-rock system, in which pore fluids are in chemical-physical equilibrium with the host rocks. Post-compressive normal faulting instead occurred in an open fluid-rock system, in which pore fluids mixed with meteoric and/or deep fluids in chemical-physical disequilibrium with the host rocks. Evident disequilibria have been identified for paleoearthquakes. This observation is supported by hydrogeochemical and geophysical data attesting to the occurrence of deep fluid batches pressurized within the orogenic wedge and forced upward during recent and seismogenic extensional tectonics.

## Interseismic creep of carbonate-hosted seismogenic normal faults (central Italy)

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*Keywords:* fault rocks, fault slip behavior, seismic cycle.

It is crucial to comprehend the fault slip behavior in carbonate formations as they are potential sites of earthquake initiation. We studied three carbonate-hosted seismogenic normal faults in the northern Apennines by using (micro)structural and geochemical analyses of fault rocks combined with new seismic coupling estimates. The (upper bound) seismic coupling is  $\approx 0.75$ , meaning that at least 25% of the study-area long-term deformation is released aseismically in the upper crust. Microscopy and electron-backscatter diffraction analysis reveal that whereas the localized principal slip zone records seismic slip (as ultracataclastic material, calcite crystallographic preferred orientation - CPO, truncated clasts, and possibly mirror-slip surfaces), the bulk fault rock below behaves differently. Cataclasites in massive limestones deform by cataclastic flow, intergranular pressure solution, and crystal plasticity, with CPO development. Foliated tectonites in micritic limestones deform by pressure solution and frictional sliding, with CPO development. We suggest these mechanisms accommodate on-fault interseismic creep. This is consistent with experimental results reporting velocity-strengthening behavior at low slip rates.

Models of fault slip behavior usually assume that (i) seismic vs. aseismic slip take place in separate fault patches, (ii) creep is limited to lithology-controlled weak domains, and (iii) rate-weakening patches are interseismically locked. We herein bring multi-scale clues of co-existing seismic and aseismic sliding along the same fault in limestones at different times during the seismic cycle. Our results imply that on-fault aseismic motion must be added to seismic slip to pair the long-term deformation rates and that creep is not exclusive of phyllosilicate-bearing units. Our work provides new insights into the fault slip behavior in carbonate rocks and may profoundly impact the comprehension of the seismic cycle and fault seismogenic potential.

## Quaternary Geology to uncover seismogenic faults reveals the modernity of an Italian way to Neotectonics decades after its definition

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Keywords: seismogenic faults, neotectonics, Carlo Bosi.

Active faults are the “product” and manifestation of the stress regime presently acting in a given region. Despite a few known cases of creeping faults, or faults along which the so called “slow earthquakes” occur, or the still tricky phenomenon of sympathetic fault slip, movement of active faults results in the sudden release of stress accumulated by the rock masses, with the consequent generation of elastic waves, that is, earthquakes.

If a seismogenic fault is large enough and, consequently, if an earthquake generated by the fault is big enough, seismic rupture propagates at speed of km per second along the fault shear zone and it can reach the topographic surface, displacing and deforming it permanently. These faults are generally referred to as active and “capable”, meaning that they are able of displacing the ground. The sense of displacement reflects the kinematics of the causative fault and, in turn, is related to the active stress regime to which the fault is genetically connected. The repetition of surface faulting events along the earthquake fault (commonly referred to as primary effect of earthquakes, i.e., displacement occurring along the main fault directly connected to the propagation of the earthquake rupture to the surface; e.g. IAEA, 2015) determines the generation of the fault trace, which is the intersection of the fault shear zone with the topographic surface.

Therefore, studying a primary active fault gives direct information on the related seismogenic source, allowing to achieve fundamental data to assess the hazards connected ground shaking and surface displacement/deformation.

The foregoing raises main issues concerning active and seismogenic faults: under which conditions a given fault can be considered as active and the expression of a deep seismogenic source? What are the characteristics that a fault must have to be considered as active? When a fault can be considered as active?

Since the seventies of the past century the definition of a fault as active has been linked to the tectonic regime affecting a given region. Therefore, to assess fault activity it is fundamental to ascertain the tectonic regime affecting a given region.

Neotectonics, as defined by Bosi (1992), represents the procedure that allows to answer to these fundamental questions. Indeed, the author defined Neotectonics as “*an integrated set of researches with the aim to define the Plio-Quaternary tectonic evolution defined through a temporal scan of hundreds of thousands of years. The noteworthy aspects of this definition are represented by the evolutive perspective and by the chronological framework on which the investigations should be based. This aspect may give an own individuality to Neotectonics and define its nature greatly interdisciplinary*”.

Neotectonics is a fundamental and irreplaceable “procedure” to assess the tectonic regime affecting a given territory and thus to make inferences on fault activity in a seismotectonic perspective.

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## **Bias and validation criteria for calcite U-Pb dating: Insights from the Olevano-Antrodoco thrust fault (Italy)**

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*Keywords:* U-Pb, open system, oxygen.

The application of U-Pb dating method performed on syn-kinematic calcite has exponentially increased over the last years, since it may provide a specific timing of faults movement. The potential gain of this approach is evident but the robustness of the U-Pb method performed on calcites has been not yet systematically tested. We tested the applicability of the U-Pb dating on calcite slickenfibers from the Olevano-Antrodoco thrust fault (Italy), a regional tectonic structure, whose multiphase tectonic activity is well constrained by stratigraphic data between Late Miocene and Lower Pliocene. We demonstrate that mineral/fluid interaction may indeed affect the regression of the  $^{238}\text{U}/^{206}\text{Pb}$  and  $^{207}\text{Pb}/^{206}\text{Pb}$  data-points, thus yielding calculated ages that do not represent crystallization times and are thus unsuitable for geological reconstructions. In this study we propose a new strategy to identify and reject analytically robust isochrons based on the combination of U-Pb dating and stable isotopes.

We combined U-Pb dating performed with different methods with carbon and oxygen stable isotopes compositions measured on the same fibers of calcite. The high precision  $^{207}\text{Pb}/^{206}\text{Pb}$  measured by Thermal Ionization Mass Spectrometry revealed that every sample experienced a certain degree of U-Pb re-organization, potentially due to fluid interaction. However, samples with clustered  $\delta^{18}\text{O}$  yield consistent ages measured with the different methods, whilst a large spread in  $\delta^{18}\text{O}$  results in scattered data-points on U/Pb and significantly divergent ages between different methods. Our results show that only 5 out of 27 samples provided ages that can be interpreted as representative of the calcite slickenfiber crystallization, indicating that Olevano Antrodoco thrust fault was active at least during the Messinian, in agreement with geological constrains. We conclude that  $\delta^{18}\text{O}$  can be used as a proxy to discriminate samples that can provide robust U-Pb dating that could then be interpreted as crystallization times.



## The structural knot of the Valsugana area (TN, Italy)

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Keywords: Southalpine, Valsugana, faults.

In the Valsugana area (Southern Italian Alps) a NE-SW trending pre-Permian Southalpine phyllitic basement is intruded by an Early to Middle Permian magmatic complex (Cima d'Asta), and locally overlapped by volcanites of the Athesian Volcanic Group (AVG) of the same age, and covered by Upper Permian to Miocene sedimentary sequences. A complex system of faults juxtaposes these different geological domains. In particular, old tectonic structures have been repeatedly reactivated during Mesozoic and Tertiary. The phyllitic basement, which suffered Variscan deformation and metamorphic events, was locally dismembered by NE-SW and NW-SE tectono-magmatic faults associated with the opening of Permian calderas related to the AVG. The main tectonic system of the Valsugana area is the ENE-WSW oriented Valsugana fault system (Gianolla et al., 2022) of Middle-Late Miocene age (Heberer et al., 2017). The master fault separates the metamorphic basement from the sedimentary sequences (e.g., M. Armentera, M. Civerone and M. Lefre); at the footwall of the master fault, other faults deformed in a compressive to transpressive regime the sedimentary sequences. Some of these are extensional faults reactivated at least three times from Triassic to Lower Jurassic. The Valsugana fault system ends against the Permian to Mesozoic Calisio fault to the SW, and it is continuing to the NE towards Brocon and Cereda Passes. In order of relevance, the Val di Sella fault, oriented c.a. E-W, has to be considered. This fault was activated during Late Miocene (Barbieri & Grandesso, 2007). It deformed the northern walls of the Asiago Plateau transporting slices of metamorphic basement and Permo-Mesozoic sequences to the north, over the Middle Miocene sandstones and marls, which filled the Adriatic paleoforeland. The most recent tectonic system consists of a set of NNW-SSE to N-S faults which cut across the ENE-WSW Valsugana and E-W Val di Sella fault systems. The N-S Grigno-Tolvà fault cuts across the Cima d'Asta magmatic complex from Val Vanoi to the north to Asiago Plateau to the south. This fault separates the Belluno fault, another E-W to NE-SW thrust fault, from the Val di Sella fault at the footwall of the Valsugana fault system.

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## **Origin of non-cohesive fault rocks in carbonate fault zones: insights from the Roccapreturo Fault (central Apennines, Italy)**

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*Keywords:* inherited structures, carbonate-hosted faults, fault structure.

The origin and distribution of non-cohesive fault rocks within carbonate-hosted faults are still not fully understood. These rocks are often attributed to the dynamic propagation of seismic ruptures, but there are uncertainties regarding their interpretation and distribution along faults. We studied the footwall damage zone of one of the main segments of the NW-SE-striking Roccapreturo Fault (Middle Aterno valley, Central Apennines), which is characterized by non-cohesive fault rock domains elongated in a NE-SW direction for about 200 m from the main slip surfaces of the Roccapreturo Fault. To better understand the origin of these fault rocks, and the parameters controlling their anomalous distribution, we assessed the geometry and throw distribution along the main fault segments by performing several fault-perpendicular geological cross sections. The distribution of non-cohesive rocks and secondary faults was mapped using field and photogrammetric analyses (using a Mavic Mini 2 drone to gain more than 500 photos) of a key exposure located in a quarry area.

The Roccapreturo Fault displaces Cretaceous rocks deposited in various depositional environments from internal or restricted carbonate platform-to-margin environments and to proximal slope environment from NW to SE. The non-cohesive fault rocks crop out between the margin and the proximal slope, where the Roccapreturo Fault is characterized by the greatest vertical displacement (about 600m). There, this fault intersects a NE-SW-striking fault located at the transition between margin rocks and proximal slope carbonate rocks and is therefore interpreted as Mesozoic in age. At the intersection zone, secondary faults have two preferred orientations, parallel and perpendicular to the Roccapreturo fault, with the latter showing both dip-slip and strike-slip kinematics.

These results suggest that inherited Mesozoic faults controlled the distribution of the different depositional environments and the distribution of the displacements of the Plio-Quaternary Roccapreturo Fault. The distribution of non-cohesive fault rocks is consistent with the reactivation of inherited Mesozoic faults during the Plio-Quaternary extensional phase of the central Apennines. A more detailed on-site analysis is planned, combined with microscopic observations of the non-cohesive fault rocks to better understand their possible coseismic origin. This study shows the role of pre-existing faults in controlling the distribution of non-cohesive fault rocks adjacent to carbonate faults, with implications for seismic hazard assessment in regions where such faults occur.

## Why do faults weaken with strain, fault maturity and size? Insights from the rock record

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Keywords: faults, carbonates, evolution.

Despite the importance of how fault strength changes over the evolution through time for our understanding of earthquake behaviour and associated risk, the underlying physical reasons for fault behaviour changes through time remain elusive. Data comparing intracontinental and plate boundary faults suggest that fault strength decreases with increasing strain, fault size, and fault maturity.

Here, we take advantage of an unique set of active faults in the central Apennines, Italy. These faults developed within carbonates and exhibit a range of fault lengths and cumulative displacement i.e. strain. The faults also demonstrate a range of Holocene fault slip rates, from ~0.2 to 1 mm/yr, based on <sup>36</sup>Cl cosmogenic isotope analyses, though these rates vary with time. Microstructural features change systematically from short to long faults, a proxy for fault maturity. With increasing fault length and average slip rate, the average grain size and grain size distribution width decreases, while the grain size D value, and grain circularity increase. Filled fractures change from within clasts to along clasts with increasing fault length. Our data suggests that with increasing fault length and strain the fracture mechanisms change from in-clast to grain boundary fracturing. For mature, long, and faster slip rate faults this then results in smooth, low asperity faults at all scales. Our observations of fault evolution are consistent with recent observations that earthquake stress drop decreases with fault displacement as increased smoothness will result in a decrease in the bulk friction or fault strength.

Furthermore, quantitative crystallographic orientation data show at the same time that brittle fracturing is accompanied by significant crystal plasticity and dynamic recrystallization which contributes to grain size reduction and initiates in the immature and adolescent faults a crystallographic preferred orientation. In mature faults, though, this signature is largely lost.

We suggests that a combined effect of changes in fracture mechanism, grain size and relative significance of brittle versus ductile processes have a major impact on the behaviour of faults throughout the earthquake cycle.

## Scar left by a fossil earthquake: coseismic deformation affecting high-porosity sandstone under shallow burial conditions (Croton Basin, Italy)

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*Keywords:* shallow faulting, coseismic slip, dark gouge.

Most earthquakes occurring in nature nucleate in a depth interval between 5 and 35 km, within the crustal portion defined as the seismogenic zone. However, earthquake hypocenters may be located at depth shallower than 5 km under different kinematics (extensional, contractional and strike-slip) and in different tectonic-geodynamic settings. Moreover, the shallow seismicity could represent a serious threat in areas with high seismic risk and should be implemented in seismic hazard assessment studies.

We hereafter present the results of a study dealing with shallow faulting affecting the Plio-Pleistocene siliciclastic stratigraphic succession of the Croton Basin, South Italy. The fault zone has a total displacement not exceeding 50 m. Due to the high porosity of deformed media, deformation along the fault zone is mainly achieved through deformation banding. Clusters of deformation bands and subsidiary faults locally occur in the footwall damage zone. The ~1 m-thick fault core is composed of an indurated (calcite cemented) cataclastic volume with a wealth of closely spaced deformation bands and slip zones. On the hanging wall side, the fault core domain is decorated with a continuous 2-3 cm-thick layer of dark gouge. Petrographic and microstructural analysis conducted on the dark gouge allowed to document the presence of a fine-grained cataclastic matrix with interspersed survivor coarse-grained clasts. The gouge displays an asymmetric structure with localization of deformation on the footwall side and a fading deformation gradient (increasing grain size) toward the hanging wall side. XRD analysis performed on several key samples (undeformed host sandstone, deformation bands, deformation band clusters and subsidiary faults) showed no significant changes in mineral assemblages. Temperature estimated from Illite-Smectite mixed layers (grain size fraction < 2 μm) is in the 50-60°C range, which is compatible with a maximum burial of < 1 km. Conversely, the dark gouge is characterized by a higher percentage of Illite in short-ordered Illite-Smectite mixed layers, suggesting deformation temperatures in the 100-120°C range, hardly ascribable to burial-related temperature, assuming a standard geothermic gradient.

Considering the strong grain size reduction, the strain localization, and the estimated temperature of deformation, we interpret the dark gouge to be formed under transient coseismic deformation. Regardless of the high porosity shown by deformed sandstone, the coseismic rupture was able to propagate through sediments up to surficial conditions. This latter aspect could help in better understanding the process of coseismic surface rupture and its propagation up to the surface. Applying this systematic study to several faults displaying the same peculiar dark gouges could help in evaluating and revising the earthquake risk in seismically active regions.

## **Uplift vs extension related normal faults: insights from the Northern and Central Apennines, Italy**

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*Keywords:* normal faults, Apennines, surface processes.

Normal faults develop worldwide, and multiple parameters are expected to control the evolution of the displacement (D) to length (L) ratio through time, such as geodynamic context (e.g., uplift or extension), amount and rates of surface exhumation and uplift, sedimentation, fluid interaction or lithological competence. Long-term D/L are expected to range from 10<sup>-2</sup> to 10<sup>-1</sup>, while coseismic typical ratios between maximum slip on a single rupture and the surface rupture length of the faults are usually in the range 10<sup>-5</sup> to 10<sup>-4</sup>. In this work, we explore the role of the geodynamic setting in controlling the geometry, the characteristics, and the evolution of normal faults. We select the Italian Apennines as a study area since the geodynamic setting is proposed to evolve from subduction in the Northern Apennines (NA), to slab break-off in the Central Apennines (CA). Moreover, in the CA the normal faults exhibit extremely high D with respect to their L. We address the questions: (i) what is the role of the CA normal faults predominating inland? (ii) Are such normal faults similar or different from the NA faults? (iii) How does the geodynamic setting control the long-term normal fault evolution? To answer these open issues, we provide a new set of geological sections across the CA, by which we assess new fault D and L estimates that we extensively compare with the vast number of published measurements. We also measure the amount of extension across the CA over Quaternary times by schematically restoring geological cross-sections. Our findings show that the normal fault network in the CA involves a wide region with fewer faults that are remarkably shorter with respect to the NA faults, suggesting a more diffused and/or delocalized extension. In agreement with previous estimates, the CA normal faults return D/L ratios in the order of 0.4-0.1, much higher than the NA, where D/L ratios never exceed 0.1. In addition, the long-term amount of extension calculated over the last 3 My indicates that the CA only extended ~6 km (~5%) compared to the NA that extended, over the same time span, ~11 km (~24%).

Finally, we compare the D/L variation with the along-strike total amount of horizontal extension, the cumulative vertical fault displacement, the topography elevation, and the short-term uplift rates (vertical GPS), concluding that along the Apennine the normal faults are likely generated by different processes. We then speculate that the possible presence of slab break-off beneath the CA, that developed a large wavelength uplift, may have triggered diffused normal faulting primarily accommodating vertical motion rather than horizontal extension.

## Sedimentary evolution of Valsugana area in the geologic record of “Borgo Valsugana”, sheet 61

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*Keywords:* geological mapping, Borgo Valsugana, palaeogeography.

The geological mapping of sheet 61 “Borgo Valsugana” allowed new constrains to the stratigraphic aspects and insights for a better palaeoenvironmental and palaeogeographic reconstructions and tectonic-sedimentary evolution of this area of the Southern Alps.

At least four phases of extensional tectonics have been identified (Lower Permian, Illyrian, upper Anisian, Middle Triassic), Carnian and Sinemurian-Pliensbachian (Lower Jurassic), before the compressive orogenic phases whose evidence in this area can be found from the Miocene.

The various extensional tectonic phases have produced different palaeoenvironmental domains such as platforms, slopes, and nearby basins, whose rock evidence today appears, having been subjected to intense deformations, very often as single scattered outcrops. The extensive geodynamic event of the lower Permian, witnessed by the Volcanic Atesian Group (GA) in this area is represented by the southernmost part of this large volcanic system. Two other events are related to the Triassic. The first is represented by the coexistence of carbonate platform deposits (Contrin Formation) and basinal, sometimes brecciated, deposits of the Margon Dark Limestone Formation, the second indicatively can be associated to the clast breccia deposits outcropping at the base of the Dolomia Principale, Carnian in age. The important and well-known event in the Lower-Middle Jurassic, linked to the formation of the Ligure-Piemontese Ocean, which caused the drowning of the structural unit called “Trento Platform” with the general pelagization of the area through the deposition of Upper Jurassic red ammonitic limestone and subsequently of Cretaceous chalk-like limestones.

A reestablishment of shallow sea conditions occurred during the Paleogene (Upper Eocene to Oligocene) with the coexistence of siliciclastic and bioclastic sediments with corals, echinoids, bivalves, and red algae. Terrigenous deposits of the Miocene are the result of the orogenic compressive phase along the Valsugana line, which produced uplift and erosion. These siliciclastic deposits are rich in coastal to shallow marine fossils and define the timing of proximal deposition in the Adriatic foreland.

Since the end of the Miocene to the Pleistocene, Alpine compression reactivated Jurassic extensional faults, which were unevenly shifted, segmented, underwent rotations and uplifted up to constituting the structural arrangement that the spread of Pleistocene glaciers and erosional processes have modeled in its current landscape: a wide truncated valley, with sedimentary filling up to 300 m thick and steep slopes.



**The November 2022 Mw 5.5 offshore Pesaro earthquake (Adriatic Sea, Italy):  
matching seismicity and seismogenic structures based on the interpretation  
of seismic reflection profiles and well data**

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*Keywords:* earthquake, thrust faults, Adriatic coast.

On the 9th of November 2022, an Mw 5.5 earthquake occurred at about 5 km depth on the Adriatic coast between Ancona and Pesaro (Italy), as part of a complex seismic sequence, including 6  $M > 4$  events, with thrust fault focal mechanisms. The event was followed by another earthquake of  $M_w = 5.2$  about a minute apart.

In this study, we use unpublished seismic reflection profiles and well data to reconstruct the geological setting at depth and identify the active earthquake-causing faults within the area. We identify two main thrust faults with gentle slopes that correlate with the depth and location of the main earthquake shocks and can be mapped in four NW-SE trending seismic reflection profiles.

We identify five horizons (Top Pleistocene unconformity, Base of Pliocene -Pleistocene unconformity, Top of Middle Pliocene, Top of Messinian, and Top of Oligocene) throughout well to seismic tie correlation and interpretation of the main reflections. Upon defining a velocity model, we convert the twt-interpreted subsurface structures into depth. The depth-converted structures are used to match the seismicity (primarily the mainshocks earthquake hypocenters) associated with the major compressional structures identified as thrust faults. The result of the study identifies the location, geometry, and kinematics of the main potentially active faults in the study area, aiding seismic hazard assessment of this sector belonging to the central Adriatic Sea.

## Structural architecture and maturity of the seismically active and hydrocarbons productive Val d'Agri basin (Southern Italy)

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*Keywords:* shallow to deep fault architecture, rock seal as partly-decoupling horizon, U-Pb dating.

Structural analyses of exposed faults provide information as fault lengths, downdip rupture length, bottomset depth, and structural maturity, which is relevant for seismic hazard evaluations (e.g., Wells & Coppersmith, 1994). Motivated by these topics, we study the Val d'Agri area, which consists of an intermontane basin within the southern Apennine fold-and-thrust belt (Italy) hosting a giant oilfield.

The basin is bounded by two extensional fault systems respectively labelled as the East Agri Fault System (EAFS), along the eastern side of the valley, where productive hydrocarbon wells are located, and the Monti della Maddalena Fault System (MMFS) along the western side of the valley. The seismic activity of these fault systems is marked by paleoseismological evidence, strong historical earthquakes ( $M_w \leq 7.1$ ), and both natural and induced instrumental seismicity.

At present, geometry, kinematics, and location of main seismogenic structures within the Val d'Agri basin are still debated. In this work, we characterize the shallow-to-deep fault architecture and structural maturity of the fault systems bordering the Val d'Agri Basin through a multi-scale structural analysis.

Results show that the fault attitude and kinematics of the MMFS are consistent with the current NE-SW extensional stress regime (Mariucci & Montone, 2020). Differently, those of the EAFS are non-systematic. Contrary to previously geomorphological studies (Zembo et al., 2009), the fault length analysis evidenced a higher structural maturity of the MMFS than the EAFS.

Such differences are interpreted as due to the 3D geometry of the seal rocks topping the hydrocarbon reservoir at depth. The seal rocks include low permeability overpressured deepwater mudstone-siltstones, forming a ductile package. This package is thick below the EAFS, where it acts as an efficient decoupling horizon, while it thins below the MMFS (Catalano et al., 2004), where it is unable to kinematically decouple the sub- and supra-seal layers.

Furthermore, U-Pb dating on syn-tectonic calcite slickenfibers show the slip longevity of the MMFS, characterized by a pre- to post- orogenic extensional activity.

In conclusion, our results suggest that the MMFS could be interpreted as the main seismogenic source for the Val d'Agri Basin, in accordance with previous seismological studies (e.g., DISS, 2021). Moreover, we shed new light on the structural configuration of the depth carbonates hosting the hydrocarbon and of the allochthonous terranes topping the seal rocks. Since the fault architecture influences the integrity of deep reservoir and fluid migration, these outcomes of the work can have an important implication for environmental studies and hydrocarbon exploration.

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## Investigating the Influence of Coulomb Stress Transfer in the Activity of the Central Apennine Fault System (CAFS) Over the Last Millennium

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*Keywords:* coulomb stress transfer, Central Apennine Fault System, seismic sequences.

The Central Apennine Fault System (CAFS) is a highly active tectonic region in central Italy which experienced numerous destructive earthquakes over the past few centuries. Several studies demonstrated the influence of Coulomb Stress Transfer (CST) in the occurrence of some of the largest earthquakes in the world, however, nowadays a very limited bibliography regarding the CST within the CAFS exists. In this study, the effects of Coulomb stress transfer for the most significant historical and instrumental earthquakes related to the CAFS in the last thousand years were computed and investigated. The main objective of the presented study is to better understand the likelihood that consecutive ruptures on nearby faults can be triggered by CST, emphasizing the related spatio-temporal limitations.

The CPTI15 catalog lists 15 earthquakes in the CAFS region with a magnitude higher than Mw 6.0 from 1279 to present. We selected 9 of these earthquakes for computing the CST, based on proximity to subsequently activated faults, both spatially and temporally. We employ a new approach for modelling three-dimensional faults to improve the reliability in CST computations. This method is developed around the basic idea that an ellipse is the most accurate approximation of the 2D fault geometry. The displacement variation, which is maximum at the fault center and equal to zero at the elliptical tip-line loop is the core of this idea. Furthermore, faults are typically represented as planar geometries in Coulomb computations, however, CST is particularly sensitive to the strike-variable geometries of the receiver faults. We used a new strike-variable and ellipse-shaped three-dimensional model as the input file for the CST simulations since a realistic CAFS base model is crucial for lowering computation inaccuracies.

The results show how CST is clearly contributing to the activation of faults within the CAFS in the last thousand years. In most study cases, it is evident how the faults that have been subjected to more transferred stress have subsequently reactivated in relatively short periods. On the other hand in some cases this correlation is missing, indicating that other factors are determining in triggering a rupture (e.g., fluid circulation, elastic strain energy accumulation and dynamic stress transfer).

Understanding the role of CST in the occurrence of historical earthquakes may contribute to the ambitious goal of foreseeing the eventual evolution of future seismic sequences and is crucial for earthquake hazard assessment and mitigation strategies. By studying the interactions between the faults in this complex system, researchers can better predict the likelihood of future earthquakes and develop strategies to reduce their impact on local communities.

**S39.**

**Field analogue studies of fractured reservoirs and discrete  
fracture networks**

*CONVENERS AND CHAIRPERSONS*

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## DFN modelling of multiscale geo-cellular volumes after field and digital structural analyses

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*Keywords:* multiscale DFN modelling, fractured carbonates reservoirs, Mesozoic platform carbonates.

Diffuse, strata bound and non-strata bound fractures in platform carbonates mainly control the rock storage properties, while localized, fault-related fractures have a profound effect on fluid transport (Panza et al., 2018). However, both porosity and permeability computed after DFN modelling may differ at varying scales (Giuffrida et al., 2020). To define the scale-factor, we compute the values of porosity and equivalent permeability for geocellular volumes representative of outcrop-to-reservoir scales of observation conducted at specific sites at Viggiano Mt., southern Italy. The fault and fracture properties are inputted to compute the horizontal permeability anisotropies at all scale of observation. Eventually, the final result will be key to decipher the porosity and permeability upscaling factor from the outcrop to reservoir scale.

The study area of the Viggiano Mt. lies along the axial zone of the southern Apennines fold-and-thrust belt (ftb), Italy, and exposes Mesozoic platform carbonates crosscut by the high-angle faults of the East Agri Fault System (EAFS). The first studied outcrop is the Il Monte - Cretaceous carbonates (ILM), made up of carbonate rudstones and grainstones deposited close to the paleoslope of the carbonate platform. The second outcrop is the Piana del buon cuore – upper Jurassic Carbonates (PBC), exposing middle-upper Jurassic oolitic and oncolithic limestones, deposited in a high-energy platform margin environment. The third outcrop is the Scarrone La Macchia I - Oolitic lower Jurassic Carbonates (SLM I), originally deposited in a ramp rimmed by oolitic sand shoals. The fourth one is the Scarrone La Macchia II - well layered lower Jurassic carbonates (SLM II), originally deposited in a low-energy open lagoon environment and constituted by carbonate wackestone-packstones to grainstones arranged in well-layered, discrete bed packages bounded clay-rich interfaces.

The methodology involves integrated field (linear and circular scanlines) and digital data collection (drone acquisition and 3D digital photogrammetry model) to assess geometry, distribution, kinematics of the high-angle faults, and the multiscale properties of both diffuse and fault-related fracture. The data are then used as inputs to build outcrop-to-reservoir scale multiple DFN models. In detail, results from outcrop scale DFN models (50 m-side) are used as matrix input for a medium size model (500 m-side), that is populated with the faults documented by digital outcrop analysis. The reservoir scale model (5 km-side) incorporates the latter petrophysical results as matrix input, whereas structural discontinuities are those reported in the 1:10,000 scale geological map of the study area.

Results obtained from these models will capture the orientation and connectivity of fractures over a range of scales and provide a powerful tool for predicting the behaviour of fluid flow and storage in Mesozoic platform carbonate reservoirs.

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Giuffrida A., Agosta F., Rustichelli A., Panza E., La Bruna V., Eriksson M., Torrieri S. & Giorgioni M. (2019) - Fracture stratigraphy and DFN modelling of tight carbonates, the case study of the Lower Cretaceous carbonates exposed at the Monte Alpi (Basilicata, Italy). *Marine and Petroleum Geology*, 112, 104045. <https://doi.org/10.1016/j.marpetgeo.2019.104045>.

## **P-wave velocity anisotropy and the spatial distribution of fractures in carbonate rocks, Monte Alpi (Southern Apennines, Italy)**

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*Keywords:* carbonates, fractures, P-wave velocity.

Carbonate rocks are characterized by a high heterogeneity of their properties at the outcrop scale that shows complex interactions during fracturing processes. One method for investigating the impact of fractures on rock properties is to establish a connection between the spacing or characteristics of fractures and the anisotropy of mechanical wave velocity or amplitude changes with offset or azimuth. This occurrence is produced by the preferred orientation of open fractures at seismic frequencies, as explained by Queen & Rizer (1990); Rüger & Tsvankin (1997). The present study uses a multidisciplinary approach to investigate the impact of fractures/joints that affects carbonate units. This study focuses on the outcrop-to-micro scales structural, stratigraphic, petrographic characterization and P-wave velocity measurements of Lower Cretaceous, shallow-water, tight limestones of the Inner Apulian Platform exposed along the axial sector of the southern Apennines fold-and-thrust belt, Italy. The study sites are located in two sub-vertical outcrops, Solarino and Teduro sites (Teduro A and Teduro B sites), trending ca. N-S and NW-SE, respectively.

The fracture sets, already documented by (La Bruna et al., 2020) are: (i) bed-perpendicular, stratabound and non stratabound joints/veins. Four joint/vein sets and two stylolites sets were documented.

In all the analyzed outcrops, porosity range from 1.3 to 2.7% and permeability is concentrated from 0 to 0.1 mD intervals.

P-wave velocities measured on the Solarino outcrop range from 0 to 4155.12 m/s with an average of 1887.20 m/s. P-wave velocities measured on Teduro A range from 0 to 5555.56 m/s with an average of 2514.20 m/s.

With respect to the in-situ field analysis, higher values of P-wave velocity were documented for the collected sample plugs of the Solarino and Teduro sites (Teduro A and Teduro B) and subsequently analyzed in the laboratory. The average of P-wave velocity on the plugs from Solarino outcrop is 5933.26 m/s, ranging from 3235.71 to 6606.06 m/s. Porosities are very low and homogeneous, corresponding to 1.33% and 1.35%. These two plugs show permeabilities of 0.05 mD and 0.06 mD. In Teduro A, the average value is 6503.90 m/s comprised between 6268.38 m/s and 7113.73 m/s. In Teduro B, the average of plug P-wave velocities is 6322.20 m/s, ranging from 4921.88 to 6632.79 m/s.

The presented results illustrate the discrepancy between the P-wave velocities measured in outcrop and laboratory highlighting how structural elements control the P-wave velocity distribution in intensely cemented carbonate rocks.

La Bruna V., Lamarche J., Agosta F., Rustichelli A., Giuffrida A., Salardon R. & Marié L. (2020) - Structural diagenesis of shallow platform carbonates: Role of early embrittlement on fracture setting and distribution, case study of Monte Alpi (Southern Apennines, Italy). *Journal of Structural Geology*, 131. <https://doi.org/10.1016/j.jsg.2019.103940>.

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Rüger A. & Tsvankin I. (1997) - Using AVO for fracture detection: Analytic basis and practical solutions. *The Leading Edge*, 16, 1429-1434. <https://doi.org/10.1190/1.1437466>.



## Methods for merging fragmented facets obtained from point cloud segmentation algorithms

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Keywords: DOM, DFN, python.

With the new point cloud visualization and data analysis module for the open source 3D geomodelling software PZero (Bistacchi et al., 2021), it is now possible to import and analyse digital Outcrop Models (DOMs). Furthermore, the users are now enabled to carry out geological, and in particular structural, analysis on DOMs and replicate a working segmentation workflow, already tested in CloudCompare, to extrapolate fracture facets (i.e. the morphological expression of planar discontinuities on an outcrop face, Dewez et al., 2016). Our pipeline can be used to analyse fracture networks on outcrops with arbitrary orientation, but unfortunately, as an inevitable by-product of the segmentation procedure, continuous fracture facets are usually fragmented in multiple adjacent smaller polygons. This effect ultimately leads to skewing towards smaller values the estimation of statistical distributions of many important fracture network parameters, such as spacing, length, and height. Moreover, the results of topological analysis of fracture connectivity are completely distorted by this kind of problem.

We propose new techniques and approaches to overcome these obstacles. The introduction of new geometrical and topological constraints, in addition to classical orientation parameters, can be used to identify which facet can be merged. We also implement new topological and spacing distribution analysis modules to extrapolate significant fracture set and network information, needed as input parameters for the creation of stochastic Discrete Fracture Networks models.

By including these methods, new possible applications arise such as filtering and cleaning the model from “improper” facets, training more sophisticated algorithms to automate the merging process and calibrating fracture network parameters (such as P32). The open nature of PZero and the readability of its Python code, offers a clear advantage over other closed alternatives in terms of ease of editing and writing new functions. By embracing the open science philosophy, external revisions and contributions are encouraged, thus leading to a faster development cycle and quicker results. By including the DOM workflow in a geomodelling package, geologists can approach the modelling problem with new valid tools and techniques, seamlessly including in the final model quantitative and statistically robust properties (Bistacchi et al., 2015).

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Bistacchi A., Arienti G., Pecorella E. & Soldo L. (2021) - Zero: A New Open-Source Python Geomodelling Platform. 2021 RING Meeting, Abstract book, 14.

Dewez T.J.B., Girardeau-Montaut D., Allanic C. & Rohmer J. (2016) - Facets: a cloudcompare plugin to extract geological planes from unstructured 3d point clouds. *Int. Arch. Photogramm. Remote Sens. Spatial Inf. Sci.*, 41, 799-804. <https://doi.org/10.5194/isprs-archives-XLI-B5-799-2016>.

## **Reconstruction of 3D fracture pattern, attributes and topology in the Cristal Cave, Brazil, integrating field data with photogrammetric models: implications for karstified carbonate reservoirs**

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*Keywords:* karstified, carbonate, reservoirs.

This study aims to provide knowledge about fractured and karstified carbonate reservoirs through the reconstruction of 3D patterns, attributes and fracture topological characteristics of the Cristal cave, São Francisco Craton, Brazil. The hypogenic cave maze developed along a regional fold system in a hydrothermally silicified Mesoproterozoic carbonate sequence (Souza et al., 2021). The Cristal cave is 6.7 km long, has a maximum vertical extension of about 20 m and is composed of a network of linear conduits and large chambers, which follow three main preferential directions: NNE-SSW (fold hinges), NW-SE and ENE-WSW (conjugate fracture system) (La Bruna et al., 2021).

Structural data collected in the cave have been integrated with a 3D digital outcrop model using Mosis XP, an in-house developed software for fracture pattern analysis, in order to (1) determine the type, orientation and attributes (length and topology) of fractures, and (2) relate fracture attributes and connectivity with the amount of dissolution in the cave maze.

Fractures measured in the field have been hierarchically divided and classified into three main types: (1) clusters of throughgoing fractures, mainly developed along NNE-SSW fold hinges, (2) throughgoing individual fractures, and (3) strata-bound fractures distributed in the layered carbonates. The analysis of the digital outcrop model allowed us to better constrain the fracture attitude in the cave conduits, and to quantify the dissolved rock volumes along major cave conduits/chambers. The reconstruction of the fracture network allowed us to quantify the trace length distribution and fracture topology (nodes and branches) for the entire cave maze. The comparison between structural data and cave pattern in different domains shows that (1) the fracture clusters are oriented NNE-SSW and controlled the distribution and length of major cave conduits, and (2) the intersection of NW-SE and ENE-WSW fracture sets, together with the presence of linkage zones, enhanced hypogenic dissolution of rocks, resulting in greater cave chambers.

Results obtained in this work can provide useful templates to predict karst dissolution features in folded and faulted subsurface carbonate reservoirs.

La Bruna V., Bezerra F.H.R., Souza V.H.P., Maia R.P., Auler A.S., Araujo R.E.B., Cazarin C.L., Rodrigues M.A.F., Vieira L.C. & Sousa M.O.L. (2021) - High-permeability zones in folded and faulted silicified carbonate rocks – Implications for karstified carbonate reservoirs. *Mar. Petrol. Geol.*, 128, 105046. <https://doi.org/10.1016/j.marpetgeo.2021.105046>.  
Souza V.H.P., Bezerra F.H.R., Vieira L.C., Cazarin C.L. & Brod J.A. (2021) - Hydrothermal silicification confined to stratigraphic layers: implications for carbonate reservoirs. *Mar. Petrol. Geol.*, 124, 104818. <https://doi.org/10.1016/j.marpetgeo.2020.104818>.

## **Semi-automatic workflow for quantitative structural interpretation of fracture networks in outcrop analogues: Case study in fractured carbonate rocks (Puglia, Italy)**

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*Keywords:* digital outcrop model, outcrop analogue, fracture networks.

The study and characterization of fracture networks find applications in a wide range of fields including, with the ongoing climate crisis and energy transition, CCS (Carbon Capture and Storage), hydrogen geological storage, characterization and management of deep fractured aquifers and exploration/exploitation of medium/high enthalpy geothermal fields.

Fracture networks cannot be characterized at the mesoscale (meters to tens of meters) in the subsurface, due to limitations of well log and geophysical datasets, however large quantitative structural dataset can be collected from digital outcrop models (DOMs), using a combination of field and remote sensing technique. These data can then be used to constrain models of subsurface fracture networks in the so-called outcrop analogue approach.

The interpretation of sub-vertical outcrops in association to horizontal “pavement” outcrops leads to a complete 3D characterization of fracture network properties, based on a large number of parameters. Individual fracture sets are identified by genetic features (e.g. joint vs. stylolite), relative chronology, spatial distribution, surface density ( $P20$ ) and intensity ( $P21$ ), and by statistical distributions of spacing, orientation, length (measured on horizontal outcrops) and height (measured on vertical cliffs). Topology and connectivity are also core parameters of the analysis, since fracture density or intensity alone are not sufficient to control percolation properties of the fracture network.

A key condition to achieve an effective and objective interpretation of vertical outcrops is automatic extraction of planar surface elements, providing a large number of facets (morphological expression of discontinuities on the outcrop) from which all the parameters cited above can be measured. Unfortunately, the existing methods tend to extract small and fragmented facets, resulting in biased spatial, spacing and height distribution. Here we present our workflow for structural interpretation of digital outcrop models based on new methodologies for the extraction of planar features.

We will analyze the fracture network parameters within the context of the dismissed Pontrelli quarry site in the Murge Plateau, in the forebulge of the outer Apulian Platform in the southern Apennines (Panza et al., 2019). The quarry provides 18.000 m<sup>2</sup> of horizontal pavement, where the fractures are beautifully exposed, thanks to the continuous maintenance of the dinosaurs' footprints discovered for the first time by Nicosia et al., 1999, and more than half of kilometer in length and tens of meters in height of vertical outcrops.

Nicosia U., Marino M., Mariotti N., Muraro C., Panigutti S., Petti F.M. & Sacchi E. (1999) - The Late Cretaceous dinosaur tracksite near Altamura (Bari, southern Italy). *Geologica Romana*, 35, 231-236.

Panza E., Agosta F., Rustichelli A., Vinciguerra S.C., Ougier-Simonin A., Dobbs M. & Prosser G. (2019) - Meso-to-microscale fracture porosity in tight limestones, results of an integrated field and laboratory study. *Marine and Petroleum Geology*, 103, 581-595.

## **Integrated approaches for the characterization of mesoscale permeability of faulted and altered granitoid units**

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*Keywords:* fault, permeability, granite.

Granitoid rocks and crystalline basement units in general are increasingly gaining attention as potential geofluids (H<sub>2</sub>O, H<sub>2</sub>, heat) reservoirs, as well as disposal sites for (CO<sub>2</sub>, nuclear) waste. The productivity, storage capacity and operative timeframe of such unconventional reservoirs mainly depend on the (brittle) deformation of the rocks and past and present fluid-rock interaction processes, which might have variable and contrasting effects on permeability evolution through time and space. Thus, a detailed characterization and quantification of the mesoscale spatial distribution and temporal evolution of faults and fluid-rock interaction zones is fundamental to quantify reservoir permeability, understand how it developed and might evolve through time.

Here we present the results of integrated multi-disciplinary and multi-scale investigations on the mesoscale permeability of the faulted and altered granitoid basement of the Island of Bømlo (Norway), which represents the accessible onshore analogue of altered and faulted offshore basement highs in the Norwegian North Sea. The crystalline basement is characterized by a pervasive, multi-scale network of brittle fracture and fault zones, and overlain by a thick saprolitic layer resulting from past sub-aerial weathering of the granite.

In-situ air minipermeametry allowed us to constrain the progressive evolution of permeability as resulting from alteration and fluid-rock interaction at sub-aerial conditions during saprolitization, revealing how permeability first increases and then decreases with progressive saprolite maturation. By integrating field analyses, virtual outcrop models, and Discrete Fracture Network modelling we were able to constrain the evolution of mesoscale permeability related to fracture occurrence, fault zone maturity and fault rock development. Mesoscale fault-related fracturing significantly enhances structural permeability, the increment of which is, however, counteracted by the development of phyllosilicate-rich fault rocks. Remote sensing analysis allowed us to quantify the spatial distribution of different types of fractures and fault rocks, and thus to gain a semi-quantitative understanding of the regional-scale spatial distribution of permeability in the altered and faulted granitoid reservoir.

The integration of field structural and petrophysical analyses, virtual outcrop model and Discrete Fracture Network modelling is a viable approach for the definition of semi-quantitative conceptual models of permeability distribution in unconventional reservoirs. However, care must be taken when comparing and integrating permeability quantification from different analytical methods and scales of observation. Rigorous approaches in the analysis of multi-scale remote sensing datasets might also improve our capability of understanding mesoscale permeability distribution related to fracture networks.

## **A new workflow to calibrate fracture parameters for Discrete Fracture Networks (DFN) models based on outcrop data: applications to fractured carbonates in Malta**

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Keywords: DFN, DOM, UAV.

Stochastic Discrete Fracture Network (DFN) methods are commonly employed to model fracture networks in the subsurface. These models are of outmost importance for studies on hydraulic and mechanical properties of discontinuous rock masses, and allow upscaling and homogenization of these properties with applications in carbon-dioxide sequestration, groundwater and geothermal exploitation, oil and gas reservoir production mechanics of earthquakes, etc..

A variety of commercial and open source codes for DFN modeling are currently available, differing from each other for the level of complexity allowed and for the input information required. In general, all these methods use a stochastic approach to model fracture networks based on statistically derived parameters from observations on outcrops or wells. The a-priori information that is typically required by these codes includes, for each fracture set, distributions of orientation, length, height, aspect-ratio, density/intensity. Also, aperture is required to model porosity and permeability, but this is a very critical parameter to be measured in the field. On the other hand, spatial distribution is not an input parameter since all codes use a random distribution that can be obtained with a Poissonian process.

In this contribution, with the aim of improving the reliability and geological “realism” of stochastic DFN solutions, we present a new strategy that allows for an adaptive calibration for the main fracture parameters. This strategy is implemented in the open source PZero 3D modelling package (<https://github.com/andrea-bistacchi/PZero>) and allows calibrating stochastic fracture networks produced with the most popular commercial and open-source software (e.g. MOVE, Petrel and dfnWorks).

Our workflow is based on the extraction of two- and one-dimensional fracture network information from stochastic DFNs, by means of intersection with arbitrary surfaces or lines, resulting in datasets with the same format as that of data collected on outcrops. Statistical distributions of the aforementioned parameters can be, therefore, derived from the DFN and directly compared with those obtained from outcrop observations. A quantitative evaluation of the goodness of the fit can be performed by “manually” adjusting the input distributions or with inverse methods, and this misfit analysis permits an iterative process of DFN model improvement in order to match the outcrop observations. This calibration approach is tested on real datasets from carbonates of the Malta Islands.

## Deformation bands characterization in porous carbonates: a case study from the Matera High (Southern Italy)

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*Keywords:* porous carbonates, deformation bands, Matera.

The petrophysical properties of carbonate rocks control their ability to accommodate deformation as brittle fractures or as deformation bands, with strong implications on their fluid transport properties. Here, we describe the preliminary results of a structural study carried out in the Matera's High, Southern Italy, located at the boundary between the Apulian foreland and the foredeep of the southern Apennines thrust belt. There, the Cretaceous tight carbonates of the Apulian platform (Calcare di Altamura) are unconformably overlain by Plio-Pleistocene shallow-marine porous calcarenites (Calcarenite di Gravina). This setting allowed us to compare the deformation style of tight and porous carbonates which shared a similar geological evolution from the Pliocene onward. In this study, we integrated geological and structural mapping, quantitative measurements of deformation structures on scanlines and scan-areas in the field and on digital outcrop models, petrophysical logging (uniaxial strength, in situ air permeability, gamma ray), microstructural and optical cathodoluminescence analysis and He-density and Hg-intrusion porosimetry.

The Calcare di Altamura is moderately tilted and is crosscut by NW-SE striking normal faults with throw variable from centimetres to tens of meters and NW-SE striking joints, whose intensity increases approaching faults. The Calcarenite di Gravina is crosscut by few brittle faults, while deformation bands are widespread. Deformation bands dip at high angle and strike mostly between N-S and NE-SW, with NW-SE striking deformation bands are locally present. Most subvertical deformation bands do not produce an appreciable shear offset, while deformation bands dipping at intermediate angle, localized in proximity of a NS-striking fault, produce a component of normal shear. Discontinuous subvertical joints having the same orientation as deformation bands are locally observed at the top of the Calcare di Altamura. Deformation bands are laterally and vertically persistent for meters to tens of meters, and show uniform spacing ranging from about 5 to 20 cm. Where more than one set of deformation bands are present, they are arranged in a polygonal pattern. Calcarenites have high porosity (20 – 48%) and in situ air permeability, both showing an up to fivefold reduction in deformation bands. Grains in deformation are more closely packed than in the wall rock and show a limited reduction in size, while the intergranular porosity is filled by calcite cement.

Our preliminary results suggest that deformation bands in the Calcarenite di Gravina calcarenites have a dilatant component, while normal faulting is only locally observed. Moreover, deformation bands are pervasive features, significantly affecting the porosity of calcarenites at the hectometric scale. Further investigations will be addressed to unravel the interplay between deformation and calcite precipitation in porous clastic carbonates, process which did not affect the underlying tight limestones of the Calcare di Altamura.



## **Unravelling complex crystalline basement-hosted 3D fracture and fault arrays through time: A proposed integrated field and modelling-based approach**

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*Keywords:* fractures, 3D, modelling.

Convolute fracture and fault arrays in crystalline basement on Smøla Island, located in central Norway and belonging to the Mid-Norwegian Passive Margin, provide an opportunity for characterising and resolving complex polyphase brittle deformation histories of basement volumes. Smøla forms an onshore analogue for basement structural highs offshore Norway. Unconventional hydrocarbon reservoirs within these offshore features are typically poorly constrained in terms of structural and petrophysical characteristics, such that any findings from Smøla may have implications on de-risking possible offshore basement-related exploration targets and basement-hosted greenhouse gas repositories elsewhere. In this ongoing study, we propose an integrated ‘toolbox’ approach developed in collaboration with the Geological Survey of Norway (NGU), whereby we combine various multiscalar field, drilling, geophysical, and geochronology datasets with different modelling approaches to constrain the 3D brittle evolution of Smøla through both time and space. Lineament patterns derived from analysis of both potential field geophysical data and DTM data, integrated with field mapping, centimetric structural logging of four diamond drill holes, and subsequent microstructural analyses indicate at least five deformation episodes affected Smøla through time. They are characterised by different mineral assemblages and geometric trends: E-W striking epidote-prehnite features (D1), NE-SW and NW-SE striking sericite-chlorite-quartz features (D2), NE-SW, NNE-SSW striking hematite-chlorite-carbonate features (D3), NW-SE, NE-SW striking zeolite-hematite-carbonate features (D4), and NW-SE striking quartz-carbonate features (D5). K-Ar geochronology, undertaken at the NGU laboratories, of fault gouge material formed during some of these deformation episodes suggests fault activity from the Late Carboniferous/Early Permian (D1) to the Late Triassic-Early Jurassic (D2), Late Carboniferous/Early Permian to the Mid-Cretaceous (D3). These deformation episodes responded to paleo-stress conditions that broadly correlate with reactivation of the Møre-Trøndelag Fault Complex (MTFC), known rifting and opening of the North Sea, and later hyper-extension of the Mid-Norwegian margin. On-going explicit and implicit 3D modelling of the available fault and fracture trends demonstrate how variations in the stress regime through time led to the development of complex deformation patterns with numerous cross-cutting or reactivation relationships, and the eventual saturation of the considered basement volumes with fractures and faults. Stochastic modelling utilising structural trends derived from the 3D models and field-measured fracture properties, provide preliminary indications on secondary permeability anisotropy, connectivity, and petrophysical characteristics for the Smøla basement volume, which can be potentially applied to the offshore domain.

## **Fault architecture and fault permeability structure within heterolithic siliciclastic rocks, Macigno Fm., Italy**

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*Keywords:* heterolithic siliciclastic rocks, fault architecture, permeability structures.

The understanding of the permeability behavior of sub-seismic faults in heterolithic siliciclastic rocks is crucial for a geofluid reservoir assessment due to their potential impact on the distribution of the storage capacity, fluid migration, and compartmentalization. Their control on the reservoir properties depends on the presence and distribution of areas with very low permeability values acting as barriers; and, the areas with high permeability acting in a conduit manner.

We investigated sub-seismic scale fault zones in the siliciclastic Oligocene-Miocene Macigno Formation (Tuscany) in order to analyze their permeability structure arrangement. The layering of sandstones-claystones not only impacts the distribution of the primary porosity but contributes to the differentiation of fracture distribution and development of corresponding fault core. Inspected faults with vertical displacement <5m show that the damage zone width is not only dependent on the scaling relationship (fault length, displacement) but on the lithologies of present siliciclastic layers. We present examples of faults that display a variation in fracture linear intensity (P10), fracture areal density (P20), fracture areal intensity (P21), and fracture connectivity, that are influenced by bed thickness and lithotypes, as well as the presence of fault-related many non-stratabound fractures. The studied fault cores presented a significant variability in terms of thickness and texture highly controlled by the juxtaposition of host-rock lithology in hanging wall and footwall, fault segments interaction, and the thickness of shale beds.

## Effect of lithology on deformation patterns and fluid flow in a faulted siliciclastic-carbonate sequence

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*Keywords:* faults, mechanical stratigraphy, fluid flow.

This study investigates faults in a mixed siliciclastic-carbonate sequence. We utilize structural fieldwork, in-situ measurements of rock permeability and hardness, as well as microstructural studies to better understand the effect of lithology on deformation pattern and fault rock properties. Furthermore, we analyze the effect of this mixed sequence on the fluid flow behavior of faults using USGS-Modflow. Our studied outcrops involve normal faults located in the Logudoro basin, northern Sardinia, Italy.

The Logudoro Basin is a Burdigalian half-graben that includes mainly subhorizontal continental to marine deposits. Stratigraphic units involved in faulting are i) Langhian marlstones, ii) Burdigalian limestones, sandstones and weak to non-cemented sands and iii) Aquitanian pyroclastic flow deposits, considered as the basin's basement. The study describes and compares the outcropping N-S striking extensional Torralba-fault and Lachesos-fault affecting the same mixed lithological sequence mentioned above.

The mechanically and lithologically contrasting units were analyzed using the following parameters: orientation, distribution and frequency of deformation structures, permeability, porosity, mineral composition, grain size, uniaxial compressive strength, and layer thickness. These parameters were then used to compare the two fault zones and to model the conceptual fluid-flow pathways through the Torralba fault-zone with USGS-Modflow.

The Lachesos fault is a ca. 3.5 km long, east-dipping normal fault with a maximum displacement of 50-70 m. Deformation in the weak carbonate-cemented high porosity sands in the footwall damage zone (FDZ), is accommodated by fault parallel calcite veins and by small shear fractures in proximity to the fault core (FC). Low-permeability marlstones in the hanging-wall are characterized by open fractures (aperture ca. 0.05 mm) in the FDZ and by smearing of a marly gouge in the FC. The FC includes a 50 cm thick low-permeability calcite cemented gouge with sharp boundaries.

The Torralba fault is a 4 km-long, west-dipping normal fault with a maximum displacement of 10-15 m. The FDZ is characterized by cataclastic deformation bands (DB) in arkosic, weak- to non-cemented high-porosity sands that change to fractures in the overlying layers, namely: 1) open fractures (aperture ca. 1 mm) in the high-porosity carbonate-cemented sandstones, 2) open fractures affected by karstic carbonate dissolution (aperture ca. 50 mm) in the low-porosity limestones, and 3) open fractures (aperture ca. 0,05 mm) in the uppermost marlstones. The fault core (FC) is formed by juxtaposing units and characterized by a lower permeability than the surrounding rocks of the FDZ.

The hydrogeological fluid-flow model in the Torralba fault reveals that DBs reduce the effective hydraulic conductivity, while fault-parallel open fractures favor drainage throughout the overlying layers.

## Controls of karst formation in silicified reservoirs: the example of Crystal Cave, Brazil

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Keywords: karst, hydrothermal silicification, Cristal Cave.

The Crystal Cave is a large karst system of 4500 m long cave conduits, located in the northeast of Brazil. The evolution of this karst system is associated with an interplay between stratigraphic and structural characteristics (Souza et al., 2021; La Bruna et al., 2021). The exposed deformed, silicified and dissolved carbonate rocks, represent an analog for the Pre-salt Brazilian reservoirs. Therefore, understanding how the karst processes operated in the Crystal Cave karst system could contribute to understanding the main factors that control the migration of geofluids reservoirs.

A stratigraphic reconstruction and a systematic sample collection along the 54 m of a rock sequence have been performed. A total of 120 thin sections were analyzed for petrographic characterization by means of optical microscope, scanning electron microscopy, and Cathodoluminescence. A mineralogical and compositional description was performed with Qemscan, X-ray diffraction and X-ray fluorescence analyses. Furthermore, petrophysical analysis were performed to define the porosity characteristics of the studied rocks. We observed that the main lithofacies identified are oolitic grainstones, intraclastical rudstones, stromatolites, intraformacional breccia and, marls. All these aforementioned facies are essentially composed by dolomite, quartz, and microcline. This rock sequence also underwent a strong dolomitization and hydrothermal silicification processes, leaving, among others minerals, barite and pyrite as accessories. The porosity is essentially moldic, fenestral and, associated to fractures. In the most porous layers, the pore volume reaches approximately 30% of the rock. In the most karstified region, total grain density varies between 2.1 and 2.7 g/cm<sup>3</sup>. The main dissolution features and the principal cave conduits are localized and limited under a thick marly layer, which represents the top of the cave (Souza et al., 2021). This layer and is characterized by higher content of phyllosilicates such as muscovite, kaolinite and vermiculite, with respect to the other layers. The presence of these minerals gives this layer a more plastic and less brittle behavior than the others.

Preliminary results suggested that the dolomitization of primary calcite crystals were the main responsible for the formation of carbonic acid, which strongly controls the silica dissolution and the karst formation. In the same way, the differentiated composition and mechanical behavior of the thick marly layer prevent the development of karst above this sealing interval.

Preliminary conclusions hint at a multifactorial origin of the Cristal Cave Karst System, where stratigraphic, lithological, geochemical and structural characteristics played a fundamental role. This study could allow to better understand the super-k conduit development and their distribution in fractured-karstified reservoirs.

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## The role of solution surfaces in the pore space properties of tight platform carbonates

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*Keywords:* carbonates, porosity, pressure solution.

Diagenetic and tectonic processes taking place in platform carbonates produce significant textural and mineralogical modifications through time, influencing the pore space properties (Lucia, 2007). Focusing on pressure solution processes, this study is conducted on Lower Jurassic, mud- and grain-supported carbonates, and on Cretaceous, grain-supported and bioclastic carbonates currently exposed at the Viggiano Mt. of the southern Apennines (Manniello et al., 2022). The primary porosity of these rocks was occluded by pervasive blocky cements, which precipitated during burial diagenesis of the carbonates. The pressure solution processes were active since early diagenesis, as documented within the grain-supported limestones, and lasted during the whole sedimentary burial with formation of well-developed, bed-parallel, wavy-type stylolites. The pressure solution processes took also place during Pliocene thrusting tectonics, and caused formation of low-angle to bedding, seismogram-type stylolites, bed-oblique slickolites, and rare high-angle to bedding microstylolites. By integrating field and laboratory analyses, we aim at assessing the role exerted by the bed-parallel and low-angle to bedding solution surfaces on the pore space geometry and localization within selected rock plugs representative of the study carbonate beds.

We combine the results of microstructural observations with those after petrographic and petrophysical analyses, including N porosimetry (f) and permeametry (K), Nuclear Magnetic Resonance (NMR), and X-ray Microtomography ( $\mu$ CT) conducted on bed-perpendicular plugs. All plugs show an amount of effective f lower than 5%, with mean values of ca. 3%, and K values spanning between 0.3 mD and 0.001 mD. Excluding microfractures, results of petrographic analysis show that the secondary pores mainly localize along the solution-enlarged, bed-parallel, seismogram-type stylolites. These pores, which were due to the non-selective dissolution, now days form a poorly connected vuggy porosity in the Lower Jurassic limestones (Lucia, 2007). Differently, in the massive Cretaceous limestones, moldic porosity due to selective dissolution localize as intrafossil and intercrystal micropores. Overall, the study Mesozoic limestones show very weak poro-perm relations when high-angle microfractures are not present. In the latter plugs, we note that the oblique to bedding slickolites slightly affect the poro-perm relations forming a connected vuggy porosity due to their interactions with the bed-parallel solution surfaces. Ongoing XRT and NMR analyses will shed lights on the control exerted by both bed-parallel and bed-oblique solution surfaces on geometry, distribution, dimension, and connectivity of the pressure solution-related pore space.

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## Origin of bed-parallel mechanical interfaces affecting the fracture stratigraphy properties of Mesozoic platform carbonates, insights from the Viggiano Mt. of southern Italy

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*Keywords:* fracture stratigraphy, carbonates, pressure solution.

Depositional environments affect the formation of a variety of rock lithofacies in shallow-water carbonates, whose mechanical properties might be controlled by diagenetic processes such as cementation and physical-chemical compaction (Lucia, 2003). The stratigraphic architecture of carbonate platforms often includes laminations, bed surfaces, and bed-package interfaces which altogether might profoundly affect fracture compartmentalization. In this work, we focus on Mesozoic lagoonal-to-forereef platform carbonates exposed along the axial zone of the southern Apennines (Patacca & Scandone, 2007). We integrate field-based stratigraphic and structural analyses with mineralogical, petrographic, and microstructural investigations of selected specimens to unravel the control exerted by pressure solution on rock fracturing.

Lower Jurassic limestones are made up of well-layered beds arranged in single bed-packages. The single bed includes either mud- or grain-supported rocks. The bed packages show fining upward trends. On top of them, the oolitic limestones beds show a pronounced amalgamation. The aforementioned limestones include both isopachous and blocky cements. Cretaceous rocks consist of massive beds characterized by grainstone/rudstone (Dunham, 1971), which contain isopachous and radial fibrous cements. Considering the whole carbonate succession, the blocky cements were coeval to pressure solution, whereas both isopachous and radial fibrous cements predated both rock fracturing and pressure solution.

Independently of the bed thickness, higher values of fracture density (P20) and intensity (P21) characterize the well-cemented, coarse-grained carbonate beds at all study sites. We note that P20 and P21 show similar trends in the Lower Jurassic limestones. Differently, high values of P21 correspond to low values of P20 in the Cretaceous limestones. We interpret these results as due to the mechanical control exerted by the bed interfaces during the vertical growth of fractures throughout the Lower Jurassic limestones. Specifically, non-stratabound fractures (high P21 values) formed by linkage of pre-existing stratabound fractures localizing small-scale process zones (high P20 values) at the ruptured mechanical interfaces.

Focusing on mechanical interfaces, at small scales they are constituted by laterally continuous bed surfaces, along which undulated pressure solution seams localized. Within single limestone beds both undulated (wave-type) and rough (seismogram-type) solution surfaces are present (Koehn et al., 2007). The wave-type surfaces generally predate high-angle fractures, whereas the seismogram-type surfaces postdate them. At a larger scale, the mechanical interfaces bound the bed-packages, and include a pressure solution disjunctive cleavage due to anastomosing stylolites and elongated carbonate lithons. There, thrust-related S-C and S-C-C' fabrics are also documented.

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## Plug-to-outcrop scales DFN modeling of the storage and migration fluid properties of fractured platform carbonates

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Keywords: DFN modelling, limestones, storage properties.

The complex fluid saturation distribution in tight carbonates is a puzzling problem to solve for the researchers dealing with the production of geothermal and conventional energy, CCS, and management of water resources. Aiming at contributing to the better understanding how fractures affect fluid saturation, we conduct a multi-disciplinary investigation of the control exerted by matrix porosity, background diffuse fractures, and localized fault-related fractures on the storage capacity and migration properties of platform carbonates. Taking advantage of 3D outcrops exposing the Cretaceous limestones of the Altamura Fm. (Korneva et al., 2014), we first assess the geometry and multiscale distribution of the fracture networks crosscutting single beds (10's of cm-thick), bed-packages (a few m-thick), and bed-package associations (10's of m-thick), the structural elements affecting the fracture stratigraphy of platform carbonates at sub-seismic scales (Panza et al., 2016).

The field data are then employed for Discrete Fracture Network (DFN) modeling of multiple geocellular volumes representative of the study rock volumes. At small scale, the result of deterministic DFN modelling of a single limestone bed emphasizes the major control exerted by StrataBound fractures (SB) on the amount of fracture porosity, and shows the importance of detailed fracture connectivity analyses to fully assess the modalities of fluid saturation. At larger scales, DFN modeling of single beds and bed-packages is performed by including only stochastic SB fractures and Non StrataBound fractures (NSB). Results are consistent with the SB fractures affecting the values of fracture porosity, and with the most prominent NSB fractures exerting the major control on the values of equivalent permeability. At the scale of bed packages associations, the vertically persistent fractures affect the fluid migration paths, enhancing the fault-parallel flow.

In order to gather more information on matrix porosity and microscale fractures, we investigate the pore type, pore geometry, and overall textural anisotropy of selected rock plugs by mean of combined petrophysical and ultrasonic experiments. Results show presence of vugs along structural heterogeneities, and of stiff, sub-rounded primary pores within carbonate matrix (Panza et al., 2019). Microfractures are mainly oriented orthogonal to bedding, but do not significantly contribute on the values of total porosity. The carbonate matrix forms therefore a quite isotropic porous medium. In conclusion, we highlight the importance of integrated methodological analyses to the multiscale assessment of the storage capacity and fluid migration properties of fractured platform carbonates. For this reason, detailed field and laboratory analyses of surface analogs of subsurface reservoirs of geofluids are recommended to mitigate risks and increase environmental sustainability.

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## Structural and stratigraphic controls on epigenic karst in shallow marine carbonates, Crotes cave, Potiguar basin, Brazil: implications for karstified carbonate reservoirs

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*Keywords:* karst, fractures, reservoirs.

The interplay between sedimentary, diagenetic, tectonic, and hydrogeological processes in carbonate rocks influences the development of epigenetic karst (Bagni et al., 2020; Araújo et al., 2021). In this contribution, we present new structural, petrophysical and stratigraphic data to constrain the development of the Crotes cave in the Potiguar Basin, NE Brazil. The cave is ~120 m long and is developed in the Cretaceous Jandaíra Formation carbonate rocks. In the study area, the Jandaíra Fm. is 100 m thick and include peritidal dolostones topped by subtidal limestones, separated by a sub-aerial unconformity (Bagni et al., 2022). The Crotes cave mainly localizes along this unconformity.

Structural data were integrated with petrophysical data collected in situ, at increasing distance from the unconformity (uniaxial compressive strength UCS and gamma ray), and in the lab on 20 plugs (porosimetry and permeametry). The upper limestone succession is mostly affected by karstified through-going fractures. It is characterized by 1-6 m thick beds, UCS values of 58-78 MPa, permeability of 0.001-99 mD, and porosity of 3.1-16%. The lower dolostone succession is affected by strata-bound fractures and it is characterized by bed 2-10 cm thick, UCS values of 22-57.5 MPa, permeability 0.003-766 mD, and porosity 14-25%.

Field and laboratory data were integrated with digital structural data gathered through a 3D photogrammetric model of the cave using an in-house developed software (Mosis®), that allowed to reconstruct the fracture pattern in the upper limestone units. Our results show that dissolution is localized at the intersection between the major through-going clusters of NE-SW, NW-SE and N-S striking fractures. The selective dissolution along the thorough-going fractures favored the development of sub-vertical conduits for meteoric fluid percolation. Within the dolostones we documented the same three fracture sets, but mainly strata-bound fractures. Those fractures, below the unconformity, show lower connectivity thus favouring the horizontal spreading of fluids through bedding surface and primary porosity of the dolostone. We conclude that partitioning of fractures within the different stratigraphic units determined the permeability anisotropy (vertical versus horizontal), and hence controlled the cave geometry. This study provides useful templates for predicting karst features in fractured, subsurface carbonate reservoirs.

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## Exploring CCS feasibility on tight carbonate reservoirs: the relationship between facies and fractures

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Carbonate reservoirs represent potential CCS sites that can be deployed to contrast the increase of greenhouse gases in the atmosphere. The complex network of interconnected pores and fractures that often characterize tight carbonates, can make them highly permeable and potentially capable of storing large volumes of gas. However, the relationship between sedimentary facies and fracturing is still poorly understood.

In order to characterize potential carbonate reservoirs, we studied five outcrops in the Umbria-Marche Apennines, representative of two different carbonate depositional settings: shallow water platform and basin. For shallow water carbonates, we studied the Calcare Massiccio Fm. in 3 different outcrops: Campolarzo, Frasassi and Pioraco. where facies show a great laterally and vertically variety, ranging from mud-supported to grain-supported textures and a marked diagenetic (early and burial) overprinting. Facies are arranged into high-frequency, metre-scale, shallowing upward, peritidal cycles (thickness ranging from 0.3 to 3 m on average).

For the basinal lithofacies, we considered two outcrops: Colfiorito and Bottaccione Gorge (Gubbio). The first shows a particular facies of the Calcari Diasprigni Fm. characterized by alternation of thick and thin layers marked by different texture (respectively oolitic packstones and mudstones) with a tabular geometry. The second shows the Maiolica Fm. characterized by tabular, thinly to medium bedded limestones, mostly consisting of mudstone, and cherty nodules and layers.

A structural characterization has been performed by studying the fracture networks of the facies involved at different scales: starting from the outcrop, oriented scanlines were performed in order to extract fractures orientation and geometry. The scanlines were integrated with virtual outcrop models obtained with a TLS. For the regional scale, outcrops were digitalized using UAV. Hand-specimens and thin sections were used to obtain a spatial fracture analysis at smaller scales.

Fracture data collected at each considered outcrop will be integrated to build a Discrete Fracture Network, in order to define the relationships between different sets of fractures. The data were then compared to derive a proper scaling law.

The structural analysis has been combined to a detailed sedimentary petrographic study, aimed to describe the textures, the porosity types, and the distribution and nature of different cements.

Preliminary results shows that fractures mostly predates tilting and that the fracture spacing is strongly dependent on the thickness of the layer. Therefore, the sedimentation and diagenetic processes plays an important role in the formation and distribution of fracture pattern. Moreover, preliminary results confirm that the relationship between fractures and facies is typically scale-depending, highlighting the importance of a multiscale characterization to have a complete view on the fracture-facies-porosity interactions.

## Mechanical stratigraphy in Mesoproterozoic Morro do Chapéu sandstones combining field data and digital outcrop models in the Ferro Doido waterfall, Bahia, Brazil

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*Keywords:* mechanical stratigraphy, Morro do Chapéu, siliciclastic.

A wide variety of tectonic, structural, sedimentological and mineralogical studies were performed in siliciclastic rocks, but very few studies can be found on deformational features on Mesoproterozoic quartz-dominated arenites.

The sandstones of the Morro do Chapéu Fm., Stenian-early Tonian in age, together with the older (early Stenian) mixed siliciclastic-carbonatic deposits of the Caboclo Fm. (De Souza et al., 2019, Ferronato et al., 2021), form the vertical walls of the Ferro Doido waterfall, near Morro do Chapéu village, Bahia, central Brazil. The 100 m high walls of the waterfall, and the km-wide pavement above the cliff, were studied from a structural standpoint in order to quantify the brittle deformation pattern in this area.

A multidisciplinary approach was adopted, integrating field data with data extracted from a tridimensional digital outcrop model (DOM) of the waterfall and petrophysical data obtained from laboratory analyses on selected samples.

Structural data collected in the field and from DOM (extracted with the software Mosis Xp) were analyzed with the software Stereonet to characterize the fracture network geometry. Two major perpendicular sets were recognized from field data (N-S and E-W) together with two minor sets (NNW-SSE and NNE-SSW sets). The studied portion of the vertical waterfall wall was subdivided into 9 mechanical units (composed of several layers) and 5 sub-areas were selected for fracture analysis. Fractures oriented NNE-SSW and NNW-SSE sets are dominant respect N-S and E-W sets in the examined portion of the cliff. The porosity (in confining conditions) and permeability (Klinkenberg corrected, from Klinkenberg; 1941) in the 12 measured plugs (made from selected samples) range from 2.94% to 9.29% and from 8.87E-04 mD to 4.82 mD respectively. Samples from the Caboclo Fm., located at the bottom of the studied rock sequence, tend to have higher porosity and lower permeability than those from the Morro do Chapéu formation. The uniaxial compressive strength (UCS) was also measured, doing a conversion from field-measured Schmidt hammer rebound test data, and it ranges from 32 to 330, being overall lowest in the Caboclo Fm. and highest at the base of the Morro do Chapéu formation.

All the collected data are used to define the mechanical stratigraphy of the studied succession. The 9 mechanical units that were already defined (in the 3D model) using a visual criterion (based on color, amount of fracturing and thickness of the beds), will be subdivided in individual mechanical units in the future, in order to make scanlines and scan areas on the wall of the waterfall in a digital environment. The results will be compared with field data, to calibrate the digitally extracted information with field observations.

Approaching field analogs with a multidisciplinary study could help further understanding of fracture patterns in siliciclastic reservoirs and how brittle deformation develops in Mesoproterozoic siliciclastic rocks.

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## Integration of multiscale field and laboratory analyses for assessing the poro-perm relations of carbonate fault damage zones, Araxos Promontory, NW Greece

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*Keywords:* carbonate rocks, poro-perm relationship, Laboratory physical properties and digital image analysis.

We present the result of laboratory measurements of physical properties such as density, porosity,  $V_p$ ,  $V_s$ , and electrical resistivity performed in dry and in saturated conditions on 54 blocks of Mesozoic carbonate host rocks and fault breccias collected from outcrops of the Araxos Promontory, NW Greece. The goal is to assess the porosity and permeability properties of the studied carbonates. Host rocks consist of carbonate mudstones, wackestones, packstones, and sedimentary breccias pertaining to the Senonian and Vigla formations showing average density values, low values of porosity, and medium-to-high P- and S-wave velocities. Fault breccias derive from high-angle extensional and strike-slip fault zones, and are characterized by a wider range of density, porosity values up to 5-10 times higher than host rock, and low ultrasonic velocities. A slight textural anisotropy is documented in the carbonate host rocks, whereas a higher degree of resistivity values mirroring the increase of porosity. Independently on lithology, the carbonate host rocks might include vugs due to selective dissolution. Differently, the fault breccia samples include microfractures. Selected samples were also tested in pressure vessels with confining pressure up to 80MPa, showing that transport properties along microcracks in fault breccias can significantly increase with increasing depth.

In order to assess rock permeability and porosity-permeability relations, three main WorkFlows (WF) are carried out. Two of them are based on the Effective Medium Theory (EMT), so that permeability is computed by inverting ultrasonic measurements and assuming an array of penny-shaped cracks embedded in an impermeable host matrix, where aspect ratio and crack width are obtained by the seismic measurements. Two end terms have been modelled by assuming all cracks isolated and unconnected (WF1) or all cracks connected into the network (WF2). WF1 and WF2 are consistent with about 1-2 orders of magnitude difference between host rock and fault breccia permeability. WF3 is obtained by digital image analysis of selected thin sections (2D), taking in consideration pores and vugs as well as microcracks. WF3 provides higher values of computed permeability, and on the contrary does not exhibit systematic variation between host rock and fault breccia. We interpret this behaviour as due to the lower aspect ratio due to large fracture aperture (width) values measured from digital image analysis of the pore space, which affects the poro-perm relations.

**S40.**

**From macro- to micro-investigations in structural geology:  
methodological essentials and advances**

*CONVENERS AND CHAIRPERSONS*

*Costantino Zuccari (Università di Pisa)*

*Stefania Corvò (Università di Pavia)*

*Thomas Gusmeo (Università di Bologna)*

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## Structural and metamorphic evolution of the Valpelline Unit (Austroalpine Domain, Western Italian Alps)

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*Keywords:* high-temperature deformation, migmatite, lower continental crust.

High temperature (HT) processes culminating in granulitization and partial melting significantly contribute to the growth and internal differentiation of the continental crust. These processes may occur in different geodynamic contexts, under both extensional and compressional regimes, but are often difficult to study in the field due to the challenge of exhuming deeper crustal levels. The Valpelline Unit (Dent-Blanche Tectonic System) represents a fragment of pre-Alpine lower continental crust preserving both the regional Permian HT metamorphism and its associated structures. This unit comprises migmatite gneiss and granulites displaying heterogeneous mineral assemblages (i.e., Bt-Sil-Grt; Bt-Sil-Crd; Bt-Sil-Opx), together with minor amphibolites and marbles. The migmatitic structures of the Valpelline Unit, only intersected by late granitic-pegmatite dykes, testify the Permian HT extensional tectonics predating the Alpine convergence (Manzotti & Zucali, 2013). This work presents a detailed lithological, structural and geochemical analysis of the rock types, thus representing the necessary first step towards the implementation of a multidisciplinary study (e.g., P–T–D paths, geochronology and geochemical surveys) aimed to unveil the processes of crustal differentiation and shed light into Permian HT tectonics. Meso- and microstructural analysis allows the reconstruction of three deformation phases related to the HT evolution. The  $D_1$  is preserved as an  $S_1$  foliation in metabasite lenses and locally within metapelites; the regional foliation  $S_2$  developed during the  $D_2$  phase is related to widespread melt production and is locally transposed during the  $D_3$  into an  $S_3$  foliation which is sillimanite-rich and wraps garnet, cordierite and orthopyroxene. The P–T conditions of the Valpelline Unit during melt-production ( $D_2$ ) and melt-consumption ( $D_3$ ) range between 800–900°C and 0.5–0.8 GPa. Preliminary U–Pb zircon geochronology yielded Permian ages consistently older in Opx-bearing leucosomes ( $293 \pm 2$  Ma) than in Crd-bearing ones ( $285 \pm 2$  Ma) and late pegmatites ( $277 \pm 2$  Ma). Our work highlights spatial, compositional and chronological heterogeneities of this lower crust sector affected by lithospheric crustal extension during Permian times.

Manzotti P. & Zucali M. (2013) - The pre-Alpine tectonic history of the Austroalpine continental basement in the Valpelline unit (Western Italian Alps). *Geol. Mag.*, 150, 153-172. <https://doi.org/10.1017/S0016756812000441>.

## Quantitative combined multiscale structural and minero-chemical analysis to unravel the tectono-metamorphic evolution of cordierite-migmatite gneiss from the Valpelline Unit (Dent-Blanche Nappe, Western Italian Alps, Valle d'Aosta)

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Keywords: quantitative structural analysis, 3D outcrops, migmatites.

Migmatitic rocks represent one of the most fascinating types occurring along orogenic chains, due to their huge variety of mineral assemblages and complex meso- and microstructures resulting from the interplay between multistage deformation and melt production. For this reason, it is often difficult to reconstruct the relative chronology of the deformation events during the high-temperature (HT) tectono-metamorphic evolution through traditional structural analysis. The Valpelline Unit represents a fragment of pre-Alpine lower continental crust that underwent HT deformation and partial melting during Permian lithospheric extension and that is now exposed in the Austroalpine Domain within the axial sector of the Alpine chain. This unit is made by migmatite-gneiss, sillimanite-gneiss, acid granulites, amphibolites, marbles/calcsilicates and pegmatite dykes (Manzotti & Zucali, 2013). This work presents a multiscale and multidisciplinary approach aimed at reconstructing the tectono-metamorphic evolution of the Valpelline Unit (Dent-Blanche Nappe, Western Italian Alps) migmatites, by combining quantitative multiscale structural analysis and minero-chemical data, aimed at discriminating different generations of superimposed structures and tectono-metamorphic stages. In particular, mesostructural data have been extracted by processing 3D outcrop models acquired through an iPad Pro 11" equipped with a LiDAR (Light Detection and Ranging) sensor and a Parrot® Anafi drone on a smoothed surface, where Crd-migmatite gneiss and different families of leucosomes and pegmatites are well exposed. Our microstructural analysis combines quantitative microstructural data extracted through Micro-Fabric Analyzer tool (Visalli et al., 2021) and EMPA mineral analyses and X-ray maps processed through the Quantitative X-ray Maps Analyzer tool (Q-XRMA, Ortolano et al., 2018). Three main deformation stages have been defined at the meso- and microscale: the first ( $D_1$ ) is preserved as an  $S_1$  foliation within metabasite boudins; the second ( $D_2$ ) is related to the development of the regional foliation ( $S_2$ ), associated with cordierite and garnet growth, and melt production; (iii) the third deforms and locally transposes the  $S_2$  foliation forming an  $S_3$  sillimanite-rich foliation. Also, the described approach allows the reconstruction of the intersection relationships among the different pegmatite dykes systems cross-cutting all the HT migmatitic structures.

Manzotti P. & Zucali M. (2013) - The pre-Alpine tectonic history of the Austroalpine continental basement in the Valpelline unit (Western Italian Alps). *Geol. Mag.*, 150, 153-172. <https://doi.org/10.1017/S0016756812000441>.

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## **Fabric analysis in UHT granulites of Indo-Antarctic terrane: implications of micro-scale observations to macro-scale processes**

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*Keywords:* fabric, recrystallization, CPO.

The complexity of microstructure and its relationship with the metamorphism in the Ultra-High Temperature (UHT) terranes emphasizes the necessity of more fundamental understanding of the mechanical behaviour of UHT granulites following metamorphism, in response to the varying temperature and stress conditions. In this study, detailed megascopic field observations collated with microstructural and EBSD analysis of UHT granulites have been conducted in the southern Eastern Ghats Province, India and the Prydz Bay sector, East Antarctica. Microstructures in the UHT fabric include cusped and lobate boundaries between quartz and K-feldspar, along with chessboard extinction of quartz. The paucity of the low-angle grain boundaries ( $<10^\circ$ ) from the EBSD analyses signifies the strain-free recrystallized quartz ribbons with a high frequency of Dauphine Twin boundaries. Activation of the prism slip system in quartz with a KAM (Kernel Average Misorientation) values of 0.2-0.4, intracrystalline misorientation of  $0.06-0.8^\circ$  within a single quartz grain and recrystallization (grains  $<100$  pixels) of 18.43% with a moderately developed CPO (M index = 0.0159; Skemer et al., 2005) suggest rapid recrystallization and recovery under high-temperature conditions. Reworking of the UHT granulites within late fabric is characterized by sub-grain rotation in quartz and bulging in feldspar, and the segregation of quartz and feldspar due to plasticity contrast and high angles between quartz-quartz and quartz-feldspar grain boundaries (Culshaw & Fyson, 1984). Post-UHT reworking of the UHT fabric due to a late extensional (?) deformation is manifested by the truncation of sapphirine and sillimanite coronae against a late, low-temperature fabric, which supports the megascopic field observations in both terranes. Subsequently, reworking of the UHT fabric is inferred from the activation of basal and rhomb slip systems in quartz, with an extensional shear sense. Activation of basal slip system in ilmenite additionally supports the idea of late extensional shearing. The CPO analysis of sillimanite within the UHT metapelites reinforces the idea of passive rotation of the needles parallel to the late deformation fabric, rather than the activation of the intracrystalline slip system. Intracrystalline misorientation of  $2.9-3.8^\circ$  within a single quartz grain, KAM values of 1.4-1.8 in quartz, recrystallization of 9.04% with a strong CPO (M index = 0.0308) signify remnant strain and sub-grain formation in response to differential stress, corresponding to the late reworked fabric. This study documents the development of a stronger CPO in the post-UHT reworked fabric, which is governed by lower extent of recrystallization along with higher remnant strain. The contrasting response of the UHT and the late reworked fabric is further being investigated to develop a fundamental idea about the nature of strain accommodation, and ultimately, the rheology of high temperature granulites.

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## Microstructural and geochemical analyses on fibrous gypsum veins in a forearc environment: a study case of Pisco Basin (Peru) and San Joaquin Valley (California)

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*Keywords:* structural geology, forearc basin, gypsum veins.

The presence of fibrous gypsum in the form of veins in sedimentary successions has been observed and studied in various parts of the world. These veins often develop into fine-grained rocks and are commonly associated with evaporitic strata (Warren, 2006). Gypsum veins may form as a result of unloading during tectonic compression (Ferrill et al., 2022), or hydraulic fracturing due to fluid overpressure (Moragas et al., 2013; Rustichelli et al., 2016). By analysing the geochemical composition and the array and the geometry of the veins in the field it is possible to understand the geological and geodynamical setting of the precipitation environment. The East Pisco Basin (Peru) and the Western sector of San Joaquin Valley (California) are two areas where gypsum veins are present despite the absence of evaporitic layers. The two areas present some similarities: (1) development in forearc basin setting affected by subduction process associated with the presence of subducting aseismic ridges, and (2) the gypsum veins are associated with sand injection complexes. Structural survey allowed us to better understand the macrostructural setting of the areas. We collected data of gypsum veins and sandstone dykes and their relationship faults. Microstructural and geochemical analyses were performed on the samples collected both areas. Through the study of thin sections with optical and SEM microscopy, it was possible to enhance understanding of the kinematic conditions during the period of gypsum growth. Using XRD analyses we identified trace minerals which can be significant to conduct further analyses on the chemical composition of the original fluid. In addition, isotopic analyses will be decisive in understanding the possible origin of the gypsum. Results arising from the comparison of the samples from the two study areas have the potential to enhance our understanding of fluid circulation within forearc basins and the role of subduction zones dynamics.

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## Vorticity analysis of the bounding shear zones of the Rengali Province: implications for partitioning of transtensional deformation within a dilational step-over zone

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*Keywords:* vorticity, kinematics, transtension.

The oldest cratonic nucleus of the Indian Shield is the Singhbhum Craton, the southern part of which comprises Archean greenschist facies rocks, supposedly separated by the Barakot Shear Zone (BSZ) from Archean amphibolite to granulite facies rocks of the Rengali Province. Further south, the lithounits of the Rengali Province are separated from Neoproterozoic granulite facies rocks of the Eastern Ghats Province by the Kerajang Shear Zone (KSZ). The kinematics of the BSZ is disputed. One school of thought considers it as a strike-slip contact where the Rengali Province is a dilational step-over zone representing a rotated slice of the Bastar Craton (Misra & Gupta, 2014), while some believe it to be a thrust where the Rengali Province represents the exhumed root of the Singhbhum Craton (Mahapatro et al., 2012). Field observations indicate that the BSZ strikes ESE-WNW, with a subvertical foliation and is associated with an extensional component, instead of thrust-related signatures. Foliations in the BSZ exhibit two surface lineations - one oriented downdip while another is horizontal, complicating formulation of a simplified kinematic model owing to uncertainty about the maximum stretching direction. This study presents a macro- to microscale vorticity analysis based on megascopic field evidence and microstructures to deduce the direction of maximum stretching lineation and the vorticity vector. Sections perpendicular to foliation and parallel to the downdip lineation exhibit maximum asymmetry of the kinematic shear sense indicators, implying that it represents the possible vorticity normal section. This indicates the association of a subhorizontal vorticity axis of deformation, governed by an extensional component normal to the shear plane of the BSZ. The KSZ also strikes ESE-WNW with vertical to subvertical foliation planes. The KSZ is a strike-slip shear zone that can be traced into the interior of the Bastar Craton. Microstructural studies of lithounits from both the BSZ and KSZ indicate a strong dextral shear sense. In contrast to the direction of the vorticity vector observed in the BSZ, the maximum asymmetry of the shear sense indicators is observed in sections perpendicular to the foliation and parallel to the horizontal lineation, implying that the KSZ is associated with a subvertical vorticity vector governed by simple shear. Varied orientations of the vorticity vectors along the two bounding shear zones of the Rengali Province, and the association of an extensional component along with a prominent dextral shear sense provide evidence of a major strike-slip transtensional partitioning caused by localized deformation within a previously proposed dilational step-over zone. Hence, this study supports the proposition by Misra & Gupta (2014) that the BSZ is a strike-slip contact, with the Rengali Province representing a dilational step-over zone rather than an exhumed root of the Singhbhum Craton formed by thrusting or transpression.

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## The role of Dauphine twin boundaries in controlling fluid percolation through high-grade rocks: Insights from EBSD, AFM and Micro-CT analysis

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Keywords: AFM, grain-boundary, DTB.

Grain and phase boundaries are believed to play a significant role in fluid percolation through a 3-dimensional material framework under ductile and brittle conditions. But grain boundary domains in quartz-rich rocks are more resistant to fluid percolation in the granulite facies than in the greenschist facies (Dobe et al., 2021). This study aims to evaluate the nature of the random high-angle grain boundaries (RHAGB) in assisting or resisting fluid flow. One of the possible reasons for lower fluid percolation in high-grade quartz-rich rocks could be explained by the existence of Dauphine twin boundary (DTB) networks, which are the most common example of Coincident Site Lattice (CSL) relationships in quartz (Dobe et al., 2021; McLaren, 1986). Experimental evidence has confirmed that the resistance of materials to corrosion can be improved by increasing the proportion of CSL boundaries, which in turn enhances the resistance of grain boundaries to percolation (Aust., 1994). Using EBSD, the misorientation distributions of quartz grains from six high-grade quartzofeldspathic rocks have been calculated. Misorientation histogram data indicate that more than 70-80% of the quartz grains were misorientated by 60° along the [0001] axis, indicating the presence of the Dauphine twins. As the proportion of DTBs is significantly higher in these granulite facies rocks, these boundaries could influence the percolation pathways along the RHAGBs. Grain boundary maps reconstructed from these domains show that the DTBs terminate at RHAGBs, disrupting the high-angle grain boundary connectivity. Grain boundary width measurements using Atomic Force Microscopy (AFM) revealed that RHAGB domains with lower DTB frequencies have wider grain boundaries, with a maximum observed width of 780nm. On the other hand, RHAGBs in domains with higher DTB frequencies have a narrower width, ranging from 350-400 nm. AFM observations, used to evaluate the nature of the contact between the Dauphine twin boundaries and RHAGBs, manifest bridge-like structures perpendicular to the grain boundary. These bridge structures might be formed due to the higher degrees of coincidence of the DTB boundaries. They might serve as physical barriers inhibiting fluid percolation along the RHAGBs. X-ray Micro CT observations of these samples also indicate that the length of the connected pathways along the grain boundaries in high-grade rocks is less compared to the low-grade rocks. This study concludes that higher frequencies of DTBs in high-grade quartz-rich rocks might limit fluid percolation by disrupting the network of the connected pathways. Further understanding of the contact between DTBs and RHAGBs in quartz-rich rocks is in progress to explain why granulite facies rocks are essentially dry.

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## Hydrocarbon-bearing fluid migration produces brecciation at high pressure condition in subduction

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*Keywords:* hydrocarbon-bearing fluid, brecciation, EBSD.

It has been recently proposed that high-pressure genesis of abiotic hydrocarbon can lead to strain localization in subducted carbonate rocks (Giuntoli et al., 2020). However, the mechanical effects of the migration of these hydrocarbon-bearing fluids on the infiltrated rocks still need to be constrained.

In this study, we investigate omphacitite (i.e. omphacite-rich rock) adjacent to a high-pressure methane-rich fluid source from the Western Italian Alps (Italy) using a multiscale and analytical approach including petrographic, microstructural, X-ray compositional mapping and electron backscatter diffraction analyses (EBSD). In the field, omphacitite bands are 1-5 metres thick and tens of metres long and are adjacent to carbonate rocks affected by high-pressure reduction and methane-rich fluid production.

Hand specimens and thin sections display a brecciated structure, with omphacitite fragments ranging in size from a few microns to several centimetres, surrounded by a matrix of jadeite, omphacite, grossular, titanite, and graphite. X-ray compositional maps and cathodoluminescence images highlight oscillatory zoning and skeletal textures in jadeite, omphacite and garnet in the matrix, suggesting a fast matrix precipitation under plausible disequilibrium conditions. CH<sub>4</sub> and H<sub>2</sub> are found in fluid inclusions in the jadeite grains. This feature suggests a potential link between the genesis of CH<sub>4</sub> in the adjacent carbonate rocks and the brecciation event.

EBSD analysis was performed on omphacitite clasts close to their borders, where omphacite grain size varies between a few microns and a maximum of 100 microns. Those omphacite grains display no crystallographic preferred orientation, abundant low angle boundaries and low (< 5°) internal lattice distortion. We interpret these textures as formed by pervasive and diffuse micro-fracturing related to the brecciation occurring at high pore fluid pressure, reaching sub-lithostatic values. This study suggests that at high-pressure conditions in subduction zones, the genesis and migration of hydrocarbon-bearing fluids can trigger fracturing in adjacent lithotypes.

This work is part of project that has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (Grant agreement No. 864045).

Giuntoli F., Vitale Brovarone A. & Menegon L. (2020) - Feedback between high-pressure genesis of abiotic methane and strain localization in subducted carbonate rocks. *Sci. Rep.*, 10, 9848. <https://doi.org/10.1038/s41598-020-66640-3>.

## **Unravelling the tectonic evolution of an eclogitized “chaotic” complex: the Riffelberg-Garten Unit in the Breuil Dell (Upper Valtournenche, Western Alps)**

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*Keywords:* Riffelberg-Garten Unit, Zermatt-Sass Zone, ophiolitic mélange.

The Riffelberg-Garten Unit (RGU) is a tectono-stratigraphic unit that forms part of the Zermatt-Saas Zone (ZSZ) ophiolites of the Western Alps, which experienced peak metamorphism under eclogite facies conditions during alpine subduction. It is often referred to as a “chaotic” complex, since it is a mélange composed of a mixture of metasediments and metabasites with an extremely disordered appearance. Additionally, the RGU was pervasively deformed throughout the long, polyphase alpine subduction-exhumation history. Given its complexity, the exact origin and evolution of the RGU is still debated and unclear. Here, we focus on a portion of the RGU outcropping within the eastern Breuil Dell, in Upper Valtournenche (NE Aosta Valley, NW Italy). Through detailed geological-structural mapping carried out at the 1:5,000 scale (with 1:200, 1:100 and 1:50 scale outcrop maps) we were able to identify and describe seven different lithologic types composing the RGU, pointing out previously unreported evidence which provide new insights on its nature. We also defined its present structural architecture, recognizing four ductile deformation phases superimposed successively during the retrograde path from peak metamorphism to the final re-equilibration under greenschist facies conditions. Furthermore, combining the field results with microstructural and microchemical analyses (optical, SEM, EPMA), we could delineate for the first time the P-T-d(t) paths of both metasedimentary and mafic/ultramafic rocks. All the information gathered allow us to re-interpret such apparently “chaotic” mélange complex, providing a coherent genetic and evolutionary framework.

## MYflow – a practical Matlab toolbox for rheological modelling of mylonites

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*Keywords:* mylonites, matlab, modelling.

Mylonites form in a wide range of metamorphic conditions in mid- to lower-crustal shear zones and provide fundamental constraints to develop integrated Pressure-Temperature-Deformation paths. Mylonites are commonly composite rocks made of two or more mineral phases characterized by different physical properties, contrasting with the basic assumption of a monomineralic aggregate on which the paleopiezometry is made. The compositional heterogeneity of mylonites limits the applicability of piezometric relationships, even invalidating the derived stress-strain rate estimate. Besides, each mineral in the composite accommodates strain by variable grain size- stress- and temperature-dependent deformation mechanisms, making the rheological analysis of composite mylonites a challenging task. In this contribution, we analyze the microstructure of composite mylonites using MYflow, a Matlab-derived software package that includes several piezometric calibrations derived for the main mineral phases and evaluate, for each phase, the active deformation mechanism in stress-strain rate-temperature-grain size space. The code implements also several mixture models based on different mechanical constraints that allow to model the rheological behavior of composite rocks with heterogeneous grain size distribution. MYflow can be used to perform 0th dimensional rheological models or EBSD-based 2D models showing the grain-scale spatial variability of stress and strain rate as a function of composition, grain size and effective deformation mechanism. We present the main code application, starting from EBSD maps to modelling the grain-scale distribution of effective deformation mechanism, stress and strain-rate estimate. The code is benchmarked with selected mylonite samples collected from amphibolite to granulite facies shear zones from continental and oceanic crust.

## Earthquake nucleation and rheological transitions in the lower crust

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*Keywords:* lower crust, microstructure, shear zones and faults.

Field studies established that seismicity in the lower crust is linked to brittle failure of dry, strong rocks (Jamtveit et al., 2019). This implies build-up of differential stresses to gigapascal (GPa) levels (Campbell et al., 2020), but this requirement contrasts with the current models of continental lithosphere deformation, which typically favour a distributed flow of weak viscous lower crust. Thus, the magnitude of and the mechanisms capable of generating transiently high stresses in the continental lower crust are fundamental unknowns in structural geology and geodynamics. Recent advancements in micro-analytical techniques (i.e., high-angular resolution electron backscatter diffraction, HR-EBSD: Wallis et al., 2019) have proven successful at measuring the residual stress resulting from elastic strain retained in mineral grains, and have opened up new avenues in the research of crustal rheology. Furthermore, seismic slip (producing pseudotachylytes) may trigger fluid infiltration, weakening, and a transition to mylonitic viscous creep (produced during post- and interseismic creep) along faults initially characterized by frictional melting and wall-rock damage (Menegon et al., 2017). However, is the resulting weakening long-lived or short-lived, and what does it depend on?

The talk will present results from the study of exhumed networks of mylonites and pseudotachylytes that represent the geological record of the earthquake cycle in the lower crust, and discuss mechanisms capable of generating transient high stresses required to nucleate earthquakes in the lower crust, as well as the earthquake-induced rheological transitions. We investigated the preservation of high residual stresses resulting from dislocation interaction in the crystal lattice of seismically shocked minerals from the damage zone of pristine lower-crustal pseudotachylytes with HR-EBSD. The results reveal intragrain residual stress heterogeneities that reach GPa levels, and the talk will discuss the origin of such high stresses in the context of the earthquake cycle.

Using synchrotron micro-computed tomography, we have characterized the porosity evolution of lower-crustal seismogenic faults during the earthquake cycle by analysing a pristine- and a mylonitised pseudotachylyte, and considered the porosity network as a proxy for fluid-rock interaction. The results indicate a dramatic porosity reduction (on the order of 90%) in the mylonitised pseudotachylyte compared to the pristine one. We attributed this porosity reduction to dissolution-precipitation during the interseismic viscous creep. Such porosity reduction may eventually result in shear zone hardening, and in the development of new pseudotachylytes overprinting the mylonites, as commonly observed in the field. Therefore, earthquake-induced rheological weakening of the lower crust is intermittent, and occurs only as long as a fluid can infiltrate a transiently permeable shear zone, thereby facilitating strain localisation.

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## The origin of neofomed clay minerals in fault zones: an example from the Carboneras Fault, Betic Cordilleras, Spain

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*Keywords:* brittle-structural-facies, x-ray diffraction, hydrogen isotope analysis.

Multiple brittle deformation episodes localizing within one single fault zone increase its structural complexity by commonly developing tightly juxtaposed, although not necessarily always coeval, distinct structural domains, referred to as Brittle Structural Facies (BSF). BSFs may form at different time and depths and determine an irregular distribution of inherited and neofomed minerals along faults and in fault rocks. Hence, BSFs represent an archive of faulting and faulting conditions through time and space. In clay-rich fault rocks, the study of neofomed clay minerals associated with the fluid-assisted development of BSFs allows us to reconstruct the temperature conditions of deformation and the origin of fluids involved during deformation.

We combine X-ray diffraction (XRD) analyses of whole-rock composition and <2 $\mu$ m grain-size fraction with H isotope data from 46 samples of different BSFs collected from three structurally well-characterized strands of the Carboneras Fault (Betic Cordilleras, SE Spain), to (i) constrain the formation temperature of neofomed clay minerals, (ii) determine the depth at which deformation occurred, and (iii) unravel the origin of fluids involved during tectonic processes.

Whole-rock samples are composed of quartz, phyllosilicates, carbonates, Fe-Ti oxides, feldspars, chlorides, and sulphates. The <2 $\mu$ m grain-size fraction is composed of both detrital and neofomed minerals: illite/muscovite, chlorite, kaolinite, paragonite, mixed layers illite-smectite (I-S) and chlorite-smectite (C-S), and smectite. The coexistence of randomly ordered (R0) and short-range ordered (R1) mixed layers I-S indicate the occurrence of distinct deformation events at different temperature conditions, ranging from <120°C for R0 I-S to 120-150°C for R1 I-S. Furthermore, the occurrence of mixed layer C-S indicates that hydrothermal fluids circulated within the fault zone.

Bulk samples display  $\delta^2\text{H}$  values (V-SMOW) between -35‰ and -60‰, except for a few samples characterized by high content of mixed layers I-S reaching -100‰. Their respective <2 $\mu$ m fractions show  $\delta^2\text{H}$  values between -10‰ and -50‰ and reach -65‰ in samples with high content of I-S. The low  $\delta^2\text{H}$  values (< -65‰) suggest a contribution from meteoric-hydrothermal waters, and the large variations in  $\delta^2\text{H}$  values testify for a mixing between waters of different origin, and/or more likely water-rock interaction at different temperatures and depths resulting in different isotopic fractionation between fluids and mineral phases. Future O isotopes investigations will allow us to (i) strengthen the interpretation of hydrogen isotopes, for which fractionation processes must be also evaluated in detail, and (ii) further constrain the origin of fluids and mixing processes.

## **Architecture, fluid rock interaction and implication for seismic slip along a carbonate-hosted low-angle normal fault (Agri valley, Southern Apennine, Italy)**

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*Keywords:* low-angle normal faults, fluid rock interaction, seismic deformation.

Low-Angle Normal Faults (LANFs) consist of shallowly dipping extensional structures that require the activation of strain weakening mechanisms to allow slip. However, unravelling if LANFs can host seismic deformation in the brittle crust still remain a debated question. In order to better understand the mechanical behavior of these structures, the detailed structural investigation along exhumed faults represent a key tool to gain insights that can be applied to subsurface conditions. Here we present the preliminary results of a multiscale structural analysis carried out along a carbonate-hosted LANF cropping out along the eastern flank of the Agri Valley (Southern Apennine). The study LANF is exposed discontinuously for ~3 km, strikes N120-160E, and dips 20-35° towards NE. This fault juxtaposes Jurassic dolomitized limestones of the hanging wall onto Triassic dolomites along its southern portions, while it cuts through the Triassic dolomites along the northern one. The LANF includes a principal slip surface (PSS), encompassed by 10's of cm-to- 1 m-thick fault core, and numerous secondary slip surfaces (SSS) arranged as low-angle synthetic splays, and R-shear structures. As reported below, such a structural configuration is also recognized at the microscale within representative samples of the fault core.

Focusing on the fault core, it consists of cataclastic rocks assemblages characterized by different degrees of maturity and cementation. The most striking structural element is a cm-thick ultracataclastic layer localized along the PSS. This layer shows, at different scales, corrugated contacts, injection bands, convoluted and flame-like structures. In some cases, white and dark (red to grey) ultracataclastic layers are mutually interdigitated simulating a flux where protusions are inclined coherently with the shear sense.

The internal texture of the ultracataclastic layer consists of few dolomitic clasts, some of which sharply truncated by slip surfaces, and sub-angular ultracataclastic relicts, surrounded by highly cemented calcite matrix. A foliated cataclasite, consisting of dark laminae within a white matrix, locally occurs in overlapping domains between PSS and SSS.

The first result of this work hence highlights that deformation along the study fault was mainly accommodated by fracturing and cataclastic processes, which took place within m-thick volumes flanking the PSS. There, slip was partitioned along R-shear structures, and synthetic low-angle faults, as well as along the PSS, which possibly reactivated an original bedding interface. However, strain localization characterized by fluidized layers and truncated clasts suggest a coseismic deformation. The fractured Triassic dolomites at the footwall might have acted as confined reservoir sealed between shale-rich formations of the underlying Lagonegro Succession and the highly cemented fault zone, where transient peaks of overpressured fluids may have triggered fault rupture.



## **Tectonic escape of Sicily microplate in the framework of the Tyrrhenian-Apennine system evolution**

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*Keywords:* plate kinematics, Sicily Channel, Tyrrhenian-Apennine system.

The aim of this work is to reconstruct the kinematic evolution of Sicily, considered as an independent plate starting from 4.5 Ma ago, and its role in the framework of the Tyrrhenian-Apennine System. The new microplate is located in an area where complex geodynamic processes work together, these are: the Tyrrhenian-Apennine System evolution, the African-Ionian slab subduction and Africa-Europe collision. Sicily is involved in a process of escape towards east-southeast induced by the African plate acting as an intender pushing northward, during its convergence with the European plate, and by the Malta escarpment STEP fault, due to the retreat of the African-Ionian slab that created space eastward.

The plates and microplates involved during the evolution of the last 4.5 Ma are Europe, Africa, Calabria and Tunisia. This last microplate is strictly related to the evolution of Sicily. The boundaries of Sicily and Tunisia microplates are identified observing at the macro-scale lithospheric structures known from the literature and identifiable from geological and geophysical datasets.

Sicily-Europe margin is along the Drepano-Elimi chain, a E-W trending morpho-structure with a general transpressive kinematic; the margin with the Calabrian microplate is along the Taormina and the “Aeolian-Tindari-Letojanni” lines; the margin with Africa is expressed along part of the Malta Escarpment and along the Sicily Channel, where a series of troughs (Pantelleria, Linosa and Malta troughs) were interpreted in literature as rift basins or pull-apart basins related to a dextral shear zone. The margins of Tunisia instead follow the N-S and NE-SW structures that characterize the Central Atlas.

Several attempts have been tried to obtain the Euler pole of rotation between Sicily and Africa, starting from the structures in the Sicily Channel and using the GPlates software. Then, also Sicily-Europe, Sicily-Calabria and Sicily-Tunisia poles and the respective velocity vectors have been derived and compared with the geological data.

The method used in this work involves a continuous comparison of data at different scales; often this is made difficult by the overlapping of several deformation phases, for example along the area of the current convergence of Africa and Europe where structures show a prevailing compressive kinematic.

## Tectono-metamorphic constraints on shear deformation of the Monte Grighini dome (Sardinia): implications for the Southern European Variscan belt

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Keywords: transpression, EVSZ, shear zone.

Dome-shaped structures, characterised by a high-grade metamorphic or granitic core surrounded by low-grade rocks, provide tectonic windows into deep crustal levels. Their origin and setting are often debated and several different mechanisms have been proposed for their exhumation (Cao et al., 2022). Unveiling the evolution of shear zones that drive their exhumation requires detailed reconstruction and correlation between petrochronology and structural analyses at different scales. This work presents an integrated structural, kinematic, and petrochronological study of the Monte Grighini dome within the Variscan hinterland-foreland transition zone of Sardinia (Italy). The area is characterised by pervasive pure shear-dominated non-coaxial transpressive deformation (i.e., the Monte Grighini shear zone). Geothermometry of mylonitic sillimanite-bearing metapelite shows that the shear zone developed under high-temperature (~625°C) and low-pressure (~0.4-0.6 GPa) conditions. In-situ U-(Th)-Pb monazite geochronology reveals that the shear deformation initiated at ~315 Ma and continued until up to ~300 Ma. Whilst previous studies have invoked a transtensional regime driven by the Monte Grighini shear zone at ~305-295 Ma (Musumeci, 1992; Cruciani et al., 2016), this work shows that it has striking similarities to dextral ductile transpressive shear zones in the framework of the Southern European Variscan belt (e.g., Simonetti, 2021). This sector could be ascribed as one of the youngest and most external transpressive shear zones active in the framework of the East Variscan Shear Zone (Simonetti, 2021), not only restricted within migmatites or at the boundary between medium- and high-grade complexes but also affecting the hinterland to the foreland transition of the Variscan chain.

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## **Shedding the light on shear zone development, evolution and rheology: Case studies, opportunities and challenges**

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*Keywords:* shear zone, rheology, fluids.

Strain localization in zones of weakness is central to how Earth deforms. Many studies have shown that strain is easily localized in a polyphase rock, especially if the rock undergoes syn-tectonic metamorphism and associated weakening. Accordingly, to study shear zones, we need to integrate information derived from a range of disciplines including material science, structural geology, metamorphic petrology and geochronology. This necessity offers new insights, opportunities but also pose challenges. Here, a range of recent case studies is used to highlight how our understanding of high strain zones is changing as interdisciplinary and multi-technique studies become more prevalent, how such studies offer new exciting opportunities and to discuss potential challenges and future avenues of investigation.

Rheology, i.e. the flow behaviour of rocks, of both the high strain zone and the less deformed surrounding is important to derive. Shape changes observed in the field (e.g. foliation deflection, pinch & swell structures) provide estimates of rheological contrast, while deformation mechanism derived by in-depth microstructural analysis using electron backscatter diffraction (EBSD) analysis provide flow laws relating stress and strain rate. Recent work has shown that not only grain size and stress but the presence and/or absence of fluid can be critical in determining which mechanisms are dominant. In a “wet” environment dissolution precipitation creep may play a more dominant role than previously thought. Similarly, it has become clear that it is important to assess if deformation occurred in the presence of melt; its distribution as seen by 3D tomography has major implications on the shear zones’ rheological behaviour. To quantify rheology and constrain availability of fluids, the pressure-temperature-fluid conditions at the time of deformation must be known. Here, thermodynamic modelling combined with microstructurally controlled mineral and bulk chemistry are main contributors to our ability to estimate PT conditions. Interesting questions of local variations governing local assemblages and potential rheology arise.

Our ability to perform in-situ geochronology represents a major step in defining timing of shear zone activity. However, the interplay between deformation structures, fluid related modifications at the grain and subgrain scale and robustness of geochronometers is critical in our assessment of geochronology results. Even if we can provide an age for the deformation of a particular part of a high strain zone at certain PT-fluid conditions following a certain flow law, it remains difficult to assess the activity of a shear zone in space and time. Numerical simulations combined with field based studies along with in-depth analysis of local small scale chemical changes may shed light on this problem and help resolve how Earth deforms.

## **Antitaxial calcite veins in shales associated with normal fault systems: evidence from the central Southern Alps (N Italy)**

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*Keywords:* antitaxial fibrous veins, fluid overpressure, extensional tectonics.

Antitaxial fibrous veins are commonly found in low permeability strata in sedimentary basins worldwide. Many studies refer to those veins as “beef” since they are bedding-parallel veins of fibrous material (Cobbold et al., 2013). Recently, Delogkos et al. (2022) suggested in their work that extension is accompanied by bed-parallel slip (BPS), especially in rift systems with low-moderate basin extensions. This study aims to provide more clues on the formation mechanism of bed-parallel antitaxial calcite veins associated to a normal fault system, since they have significant impacts on the mechanical properties and fluid flow behaviour of the host shale.

This work concentrates on the late Norian succession of the Seriana Valley area (central Southern Alps, N Italy), characterized by the Riva di Solto Shale. Here, the unit is in the footwall of the Amora Fault System, a N-S trending rift-related normal faults system that formed during the Early Jurassic as a consequence of the opening of the Alpine Tethys. It consists of black, thin laminated organic rich shales, marls and limestones arranged in asymmetric cycles. At the mesoscale, E-dipping normal faults synthetic to the Amora Fault System can be observed offsetting the shale layers. These are characterized by the widespread presence of calcite veins, that developed parallel to the bedding or on low-angles N-dipping planes, which often show successive folding and thrusting. The microstructural analysis of 8 sampled veins allowed their classification as antitaxial calcite veins, as described by Bons et al. (2012), and revealed the presence of three antitaxial growth stages in most of the samples, confirmed by the cathodoluminescence analysis.

The O-C stable-isotopes analyses shows that the antitaxial calcite veins precipitated from a fluid with  $\delta^{13}\text{C}$  buffered from the host-rock, and  $\delta^{18}\text{O}$  shifting towards more negative values in the latest growth stage, possibly due to change in the temperature of the fluids. The U-Pb dating gave an Early Jurassic age, confirming that this system is contemporaneous and related to the Amora Normal Fault System.

According to the structural and geochemical analyses, we suggest that the antitaxial calcite veins in the Riva di Solto Shale formed during the Early Jurassic by hydraulic fracturing in a mechanically anisotropic rock with a tensile failure normal to the maximum principal stress ( $\sigma_1$ ). Fluid overpressure enabled the development of temporary fluid-flow pathways that were subsequently sealed to form mineral vein networks with a “crack-seal slip cycle” repeated several times.

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Cobbold P.R., Zanello A., Rodrigues N. & Løseth H. (2013) - Bedding-parallel fibrous veins (beef and cone-in-cone):

Worldwide occurrence and possible significance in terms of fluid overpressure, hydrocarbon generation and mineralization. Marine and Petroleum Geology, 43, 1-20. <https://doi.org/10.1016/j.marpetgeo.2013.01.010>.

Delogkos E., Roche V. & Walsh J.J. (2022) - Bed-parallel slip associated with normal fault systems. Earth-Science

Reviews, 230. <https://doi.org/10.1016/j.earscirev.2022.104044>.

## **Tectono-stratigraphic, isotopic, and geochronological constraints on the Amora Fault System, central Southern Alps (BG)**

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*Keywords:* Jurassic rifting, geochronology, paleo-fluid flow.

The central Southern Alps (N Italy) preserve stratigraphic evidence of the Early Jurassic rifting related to the opening of the Alpine Tethys, despite its later involvement in the Alpine orogeny. Here, the extensional tectonics produced rapid facies and thickness changes of the Liassic succession, interpreted as syn-rift deposits, documenting a horst and graben architecture postdating a Rhaetian shallow-water homogeneous succession. Despite the identification of several extensional syn-depositional faults bordering structural highs, no geochronological constraints were until now available to confirm the Early Jurassic age of these faults. In this work geochronological constraints obtained by LA-ICP-MS U-Pb dating on syn-tectonic carbonate veins associated with extensional faults are presented for the first time.

Field work (Seriana Valley, N Italy) led to the identification of N-S trending syn-depositional faults, the Amora Fault System, that borders a deep half-graben filled with Lower Jurassic cherty limestones (Moltrasio Limestone). The syn-depositional activity of these faults is documented by stratigraphic evidence, different thickness of the hangingwall and footwall successions, and facies association (such as abundant slump overfolds and mass flow deposits).

In the study area, clear cross-cutting relationships between structures and middle Eocene magmatic bodies document three main tectonic events: 1) the E-W oriented extensional phase; 2) a N-S oriented extensional phase characterized by the emplacement of andesitic dikes; 3) the N-S oriented Alpine compression. The relative age constraints permitted to focus on the E-W extensional phase, related to the opening of the Lombardian basin.

Carbonate syn-tectonic veins and slickenfibers were sampled in the Norian to Lower Jurassic successions, both in the footwall and in the hangingwall of the Amora Fault System.

O-C stable-isotopes analyses and U-Pb dating were performed on 21 samples, based on previous microstructural analyses with transmitted light and cathodoluminescence microscopy. The data revealed the occurrence of several precipitation events, related to polyphasic and chemically heterogeneous fluids circulation. Specifically, it is possible to distinguish two types of fluid circulation events: the first, Early to Middle Jurassic age, with a  $\delta^{13}\text{C}$  signature buffered by the host-rocks, the second, starting from the Late Cretaceous, with meteoric affinity associated to a negative  $\delta^{13}\text{C}$  and dedolomitization processes.

Finally, our analyses demonstrate that the Amora Fault System developed in the central Southern Alps in the Early Jurassic and was re-activated during the Alpine compression.

## **Construction of post-collisional magmatic complexes: an integrated field, microstructural and EBSD approach on the granitoids from the late Variscan Serre Batholith (southern Italy)**

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*Keywords:* microstructures, CPO, granites.

Over the past several years, electron-back-scattered diffraction (EBSD) analysis has been extensively applied to evaluate kinematics in tectonically deformed rocks and, more specifically, to unravel the interplay between magmatism and tectonics, which is often poorly constrained. The Serre Batholith, in central Calabria, is a 13-km thick composite batholith representing the intermediate portion of a continuous and nearly complete cross-section of late Variscan continental crust. The construction of the batholith began with the emplacement of strongly to moderately foliated deep-seated quartz-diorites and tonalites (c. 297 Ma), followed upward by weakly to non-foliated strongly peraluminous porphyritic to equigranular granodiorites and granites (c. 295 Ma) and, finally, by shallow-seated non-foliated weakly peraluminous granodiorites and granites (c. 292 Ma). Microstructures reveal deformation starting at magmatic conditions for the lowermost granitoids and from submagmatic to low-temperature solid state conditions for all the overlying rocks, suggesting that a tectonic stress was active before the complete crystallization of the different magmatic bodies and continued long after their solidification. Quartz CPO data for 8 granitoid samples from the different crustal levels, indicates deformation dominated by the activation of rhomb slip and, in some cases, a combination of basal and rhomb slip, indicative of dominant medium to low- temperature deformation. The asymmetry of quartz CPO indicates top-to-west sense of shear in the samples from the lowermost levels and top-to-east sense of movement for the deep-intermediate rocks. Symmetrical and very scattered data do not convey any clear information on deformation for the intermediate-shallow granitoids. On the whole, obtained data point to synkinematic intrusion for the deep to intermediate granitoids. For the upper magmatic levels, a possible late kinematic scenario or, alternatively, a stage of relative tectonic quiescence is implied. Finally, while the emplacement of the lower-level granitoids might have been driven by the activation of regional-scale shear zones, there is no clear structural evidence to conclude the same about the upper-level granitoids where a tectonic stress is recorded at a later stage. A further integrated approach with AMS (Anisotropy of Magnetic Susceptibility) will allow more in-depth investigations of the relationships between regional tectonic structures and the emplacement of the late-Variscan Serre Batholith granitoids, contributing, ultimately, to the general understanding of build-up mechanisms of post-collisional batholiths.



## **Extensional faulting in the pleistocenic basins of Basilicata region (Southern Italy): kinematics and activity investigated by space-borne SAR interferometry**

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*Keywords:* Bradanic Foredeep, St Arcangelo Basin, extensional tectonics, SAR interferometry.

The Pleistocene basins of the Basilicata region, Bradanic Foredeep and St Arcangelo Basin (Southern Italy) are the filling with huge mainly regressive sediments, of tectonic trough dissected by other tectonic lineaments. Starting from Pleistocene age, the entire region underwent a distensive tectonics towards West, whose effects can be seen through the morphologies of both the Mesozoic carbonate basement and of the above more recent fillings. Particularly, NW – SE lineations border flat surfaces at the edge of big soil masses, tilted along direct faults. The loss of continuity of the prevailing clay masses produces other significant processes concerning underground fluids flow and several mud volcanoes. The process has been verified and confirmed also from some deep underground works (long tunnels in the region). Availability of geomatic tools, like high resolution DEMs of the ground surface and of the top of the Mesozoic basement allows us to retrieve through simple rules the kinematics of the faulting of the quaternary filling, i.e. the horizontal and vertical displacement around the fault tracks and the rotation of the old flat terraced surfaces. Fault shear surfaces on the East border of the Bradanic trough develop tracks parallel to the direction of the buried basement, and this is a relevant correlation to analyze to evaluate causes and type of the local tectonics.

This study should be relevant for a new reading of the regional geodynamic, since previously those landforms were interpreted as an effect of local erosional processes. The 3D-representation of the detached masses helps to identify the stress field which originates the direct faulting. The feasibility of using space-borne multi-temporal SAR interferometry to support the displacement analysis has been investigated. The interest of this methodology is in the extended time and space span of the existing data, covering over 15 years, and the capability of detect sub-millimetric displacements availability owing of permanent scatterers.

## Post late-Miocene exhumation history of the Northern Apennines fold-and-thrust belt constrained by detrital apatite thermochronology in the Epiligurian wedge-top basins

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*Keywords:* Northern Apennines, thermochronology, Epiligurian wedge-top basins.

The Northern Apennines fold-and-thrust belt results from the Cenozoic convergence and collision between the Adria and Europe plates. Previous thermochronological studies have been performed on the lowermost structural units of the Northern Apennines to unravel the style and timing of thickening and later dismantling of the belt. The wealth of available data suggests exhumation in the late Miocene-Pliocene interval for these units with increased exhumation rate up to 1 mm/yr in the Pliocene. However, a systematic thermochronological study of the Epiligurian wedge-top basins, which is necessary to understand the Cenozoic exhumation history of the Northern Apennines, is still missing. Here, we combine apatite fission-track (AFT) and (U-Th)/He (AHe) thermochronological data with a new structural characterisation of the Epiligurian stratigraphic succession in the axial domain of the Northern Apennines. We investigated the coarser sandstone units of different middle Eocene to the upper Miocene Epiligurian formations (Loiano, Antognola, Pantano and Cigarello Fms) in the Marzabotto Basin with the goal to constrain the tectono-thermal history of the Epiligurian Units below and above the Burdigalian unconformity. This unconformity represents an abrupt shift from a deep marine (pre-Burdigalian) to platform (post-Burdigalian) environment during progressive uplift of the orogenic wedge. None of the AFT samples pass the  $\chi^2$  test, indicating the presence of different population of detrital grains. However, not all the detrital populations are older than the depositional age of the hosting formation suggesting only a minimal resetting of the AFT system post deposition (i.e. maximum T < 120°C). In addition, the detrital populations are consistent with multiple source regions located in the Alps and Apennine. A spatial-temporal shift of the source is recorded by a sudden change of the lag time trend for the AFT ages with an increase at 22-17 Ma (corresponding with the Burdigalian unconformity) followed by a decrease during the Langhian-Serravallian. AHe ages show a more variable single grain age distribution ranging from 104 to 7 Ma (Late Cretaceous-late Miocene) suggesting partial thermal resetting of the AHe system post deposition. Thermal history modelling of the base of the Epiligurian sedimentary succession (Loiano Fm), constrained by stratigraphic data, suggests a maximum burial temperature for the Epiligurian Units of ca. 85-90° C and subsequent cooling starting at ca. 10 Ma in response to the propagation of the Northern Apennines fold-and-thrust belt. These results are consistent with the existing previous data of the lowermost units that compose the orogenic building.

## Thrusting and negative inversion along the Circeo thrust, central Apennines

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*Keywords:* U-Pb dating, thermal modeling, balanced cross-section.

The evolution of the Apennine wedge has seen the migration of the thrust wedge and back-arc extension phases over time and space, in response to the Eastward rollback of the subducting Adria slab. In this framework, thrusting and post-orogenic extensional faulting have occurred in two parallel forelandward-migrating ribbons, with extensional deformation overprinting or partly exploiting anisotropies of the inherited thrust system. Here, we explore the tectonic framework and the timing of thrusting and subsequent negative inversion of the Circeo thrust, one of the major thrusts in the inner portion of the central Apennines, with the main aim to constrain the timing and mode of the compression to extension switch. Field surveying, structural analysis, carbonate C and O and clumped isotopes analysis, X-ray diffraction of clay minerals, and U-Pb dating of calcite slickenfibers have been integrated with seismic interpretation, cross-section balancing, and 1D burial and thermal modeling.

The hanging wall of the Circeo thrust involves the lowermost portion of the sedimentary succession of the Mesozoic Circeo pelagic basin and exposes Jurassic extensional faults with ~ 1 km displacement. The thrust, which is domed and at places show evidence of slip reversal, puts in contact the Jurassic Calcare Massiccio Fm. and the Miocene Circeo Flysch. We show that the thrust developed as a thin-skinned structure during Langhian-Serravallian time, likely reactivating part of the Jurassic extensional system. Post-thrusting negative inversion of the thrust is dated at the Middle Miocene, long before back-arc extension. Our data show that both thrusting and subsequent negative inversion occurred in a closed fluid-circulation system, with TD47 temperatures of both events being about 100-120°, consistent with the maximum burial temperatures of nearly 120°C as derived from mixed layer I-S data. We propose that the negative inversion of the Circeo thrust resulted from the activation of an underlying thrust, which folded it and steepened its ramp, triggering its syn-compressional negative inversion. The thrust stack was later affected by Pliocene extensional tectonics associated with the opening of the Tyrrhenian back-arc basin.

## **High-resolution multidisciplinary studies of fault zone architectures: A futile exercise or a necessary insight into fault mechanics and seismogenesis?**

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*Keywords:* fault architecture, fault mechanics, seismotectonics.

Long-lived, multiply reactivated faults can be architecturally complex, with each new deformation episode adding to this complexity by forming new brittle structural facies, altering the bulk and local permeability and steering the rheological/mechanical characteristics of the deforming rock volume. This impacts on the overall seismogenic style associated with faulting, with phases of coseismic rupturing and aseismic creep variably occurring in time and space. Recent studies of crustal-scale fault zones have documented that this complexity is the norm rather than the exception and that it may result from deformation histories lasting many millions of years. Outcrops, therefore, only represent snapshots of this long history and rushed interpretations of their complexity and/or its downplaying may have negative consequences on conceptual models of deformation localization, fault mechanics and seismotectonics. To better understand the architecturally complex geometry and evolution in time and space of mature fault zones, we present the methodological approach to- and the first results from an ongoing study of the Carboneras Fault (CF) in the Betic Cordilleras of Spain. The CF is a NE-SW striking, 100 km long, upper crustal sinistral strike-slip fault that is described as accommodating c. 40 km offset. It belongs to the Africa–Iberia diffuse plate boundary and tectonic activity along it spans the mid Miocene -Present time interval, with still ongoing distributed seismicity. In its archetypal outcrops, the CF exhibits a complex architecture defined by strands of phyllosilicate-rich fault gouge enveloping domains of variably reworked host rock. We studied three key outcrops, aiming at elucidating the fine details of its spatial and temporal evolution to derive constraints upon its seismogenic style and mechanical evolution. Up to 14 brittle structural facies have been identified and characterized by a multidisciplinary approach including structural analysis, X-ray diffraction and isotopic analysis of fault rocks. Sampling of each facies made it possible to define their mineralogical composition, the maximum temperature they were subjected to during faulting, their isotopic signature and the deformation mechanisms responsible for their formation. *In-situ* outcrop air-permeametry helped constrain the present-day permeability and its heterogeneity at the scale of the fault zone. K-Ar illite dating of eight gouge samples associated with different brittle structural facies will constrain, in an unprecedented fashion, the temporal dimension of faulting and provide a comprehensive timeline for deformation localization down to the microscopic scale. Results from this high-resolution approach are key toward a realistic analysis of the faulting history of the CF, and offer a comprehensive work protocol to untangle the spatiotemporal evolution of the mechanics and seismogenesis of long-lived mature fault zones elsewhere.

## **Low-grade tectono-metamorphic overprint in the Carboniferous Badstub Formation as Alpine convergence record in the shallow crust of the Drauzug-Gurktal Nappe System, Upper Austroalpine basement nappes**

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*Keywords:* Alpine pumpellyite–prehnite riebeckite, Palaeozoic sequences, geodynamic modelling.

Within the Carboniferous of Nötsch, the Badstub Formation is a clastic sequence in the topmost Drauzug-Gurktal Nappe System of the Upper Austroalpine basement nappes exposed few kilometres north of the Gailtal line (e.g., Piller, 2014), an eastern segment of the Periadriatic Fault System (Carinthia, Austria). This sequence consists of conglomerate, breccia, sandstone and siltstone, and fossil-rich carbonatic schists that form a south-dipping monoclinical stratigraphy. The prevalent clastic rock type is metabasite. Although these Palaeozoic sequences preserve pristine sedimentary features clearly detectable at a first glance and are even famous for the outstanding fossil records, multi-scale structural analysis disclosed a syn-metamorphic foliation in fine-grained rocks, sets of mineralised faults, veins, and corona textures. Vein fillings and coronas within intraclast space contain equilibrium mineral assemblages characterised by prehnite, pumpellyite, chlorite, phengitic mica, winchite, and riebeckite. Thermodynamic modelling based on mineral assemblages and chlorite geothermometry constrain metamorphic conditions at 260 - 310°C and 0.25 - 0.50 GPa that are consistent with a temperature / depth ratio of about 20°C km<sup>-1</sup>. This ratio falls in the maximum term of the range of the pressure and temperature estimates of the Eo-Alpine metamorphic peak in the Upper Austroalpine basement nappes (e.g., Janák et al., 2015; Schulz, 2017). Therefore, we set a 2D thermomechanical model that simulates a generic ocean-continent convergence and that shows the fitting of this thermal state at different time steps in the upper and lower continental plate either during oceanic subduction or continental collision. Without any radiometric age constraint, we envisage that the tectono-metamorphic record of the Badstub Formation was recorded during the Alpine times by ablation of upper continental plate operated by the subducting oceanic plate or in the passive margin of lower continental plate because of collision. Anyhow, during the Alpine convergence, the Badstub rocks were buried from the shallow crust at depths between 13 and 18 km and eventually stacked into the orogenic wedge at the Adria margin. During the downward and upward path, the Badstub rocks were translated as a coherent poorly strained block according to the scarce possibility of mylonite development in a low-grade metamorphic environment, as predicted by numerical modelling (Regorda et al., 2021). This is the first quantitative constraint on metamorphism for these Carboniferous rocks and is consistent with the Upper Austroalpine basement nappes being a tectonic system that recorded the Alpine convergence under eclogite to prehnite-pumpellyite facies conditions.

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## Processes and fabrics in metamorphic basements from the map to the atomic scale in space and time

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*Keywords:* rock memory, fabric evolution, reaction progress.

In this contribution, we will discuss the methodological essentials to be pursued for comprehending processes active in metamorphic rocks (but not exclusively), that control the rock memory. Heterogeneous and multiphase tectono-metamorphic evolutions need a mapping strategy to track the finite strain features and metamorphic signatures (the rock memory) to be represented in foliation trajectory maps Gosso et al., 2015.

The proposed procedure calls for an analytical approach that integrates structural, petrological, lithostratigraphic, and, wherever possible, geochronological data, while strongly maintaining the reference to the structural framework resolved by fieldwork activity.

Indeed, the quantitative estimation of the development of the concurrent deformation and metamorphism at any scale, produces a matrix of rock types expected in a metamorphic terrain, which sheds light on decrypting the tectono-metamorphic evolution (theoretical rock matrix). The evolution recorded by a specific rock type (e.g., granite) is mostly controlled by the evolution in space and time of chemical, shape, and crystallographic properties, which control the production of rocks that can record strong differences in the Degree of Fabric Evolution-DFE (deformation gradients) and Degree of Reaction Progress-DRP (metamorphic transformation gradients). The interplay of DFE and DRP produces the actual rock matrix. DFE and DRP can be mapped, and such maps become the fundamentals to guide the selection of the “right” samples for subsequent and more resolved analyses (e.g., geochronology, strain analysis, 3D quantitative imaging).

The efficacy of the combined method has been tested on various Alpine terrains, aiming at i) exploring the influence of thermal regimes; ii) studying the influence of inherited textures, DFE, bulk rock, and mineral compositions on DRP; iii) quantifying the 3D architecture of deformation and metamorphic transformation gradients; iv) individuating the critical thresholds making “strain rate” the dominant factor over metamorphic reactions.

Nowadays, new, and very promising digital tools have been introduced. We need to make them a real advance in understanding tectonics and geodynamics through modern, solid, and quantitative structural geology.

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## Preliminary results of a crustal-scale, fault-controlled, paleofluid circulation, Contursi Terme (southern Italy)

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*Keywords:* fluid-rock interaction, fluid inclusion, noble gases.

The study of fault-related vein mineralization is key to unravel the modalities of paleofluid circulation in the Earth's crust in association with crustal deformation and earthquake faulting. This information is crucial to better assess the present day hazard associated to the seismically active fault. Detailed field and microstructural observations are therefore important to select representative vein samples for a subsequent laboratory investigation. In particular, the analysis of fluid inclusion (FI) trapped in minerals reveals geologically important information such as composition, temperature, pressure and salinity from the mineralizing fault fluids (Randive et al., 2014). Accordingly, the results of this work might provide a direct information of environmental conditions at which the vein minerals precipitated. Integration of these results with data regarding isotopic composition and noble gases (He, Ne, Ar) of the vein minerals can shed lights into the temporal evolution of fault fluid geochemistry, origin (i.e., meteoric, crustal, mantle), and eventually assess post-genetic processes that modified its original isotopic signature.

In this work we present the first results of an ongoing works aimed at investigating the Contursi Terme area of southern Italy, which is characterized by a well-known hydrothermal activity. A recent study of both warm and cold spring waters (Gori et al., 2023) highlights degassing of a deep-derived fluid, and that the free gas in the area are characterized by a crustal component, which is about 80% of the total. The remaining 20% is related to a mantle component. For this reason, we analyze the mineralogy and geochemistry of fault-related veins to compare and contrast the current fluid degassing with the paleofluid. The study area lies in between the two regional-scale, high-angle faults, respectively the Marzano (epicentral area of the 1980 Irpinia earthquake) and the Cervialto faults. In detail, the area exposes two main fault sets respectively striking NW-SE and ENE-WSW. There, we selected representative fault-re-related vein samples, and coated slickensides as well. The vein infill consists of calcite and dolomite minerals, as documented after XRD diffractometry. Current FI and geochemical analyses focus on these precipitates to decipher the modalities of circulation of deep-derived fluids through the crust.

Gori F., Paternoster M., Barbieri M., Buttitta D., Caracausi A., Parente F., Sulli A. & Petitta M (2023) - Hydrogeochemical multi-component approach to assess fluids upwelling and mixing in shallow carbonate-evaporitic aquifers (Contursi area, southern Apennines, Italy). *Journal of Hydrology*, 618, 129258. <https://doi.org/10.1016/j.jhydrol.2023.129258>.  
Randive K., Hari K., Dora L., Malpe D. & Bhondwe A- (2014) - Study of Fluid Inclusions: Methods, Techniques and Applications. *Geological Magazine*, 29, 19-28.

**S41.**

**Data and Questions on the deformation history of the  
southern Apennines of Italy: from long-term tectonics to  
seismogenic faulting**

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## **Deep boreholes stratigraphic and palaeoenvironment studies to reconstruct quaternary tectonic evolution of Bojano intramountain basin (Southern Apennines)**

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*Keywords:* borehole data, fault detection, Quaternary infilling.

Several deep boreholes were retrieved from the Bojano basin, one of the largest intermountain tectonic depressions of the central-southern Apennines. Stratigraphical and paleoenvironmental studies allowed investigating the entire Quaternary succession, deposited in unconformity on claystones, silstones and marls of the Sannio Unit (Early Miocene), thrust on sandstones and siltstones of the Molise Flysch (Upper Miocene). Facies analyses on alternating of fluvial marshy, palustrine and alluvial fan deposits, allowed characterizing the Quaternary paleoenvironmental evolution of the basin and hypothesizing the causes of the recorded environmental changes to the tectonic history of the axial sector of the Central-Southern Apennines chain. In the sector of the Campochiaro alluvial fan, new paleomagnetic and morpho-stratigraphical data allowed identifying that the beginning of the Quaternary sedimentation started shortly before 1.07 Ma and then, between the end of Early Pleistocene and the beginning of the Middle Pleistocene, interested by a first cycle of alluvial fan sedimentation. During Middle Pleistocene, between 600 and 400 ky, the sedimentation occurred newly in palustrine environment, witnessing the enhancement of the subsidence rate within the basin. The upper part (Late Pleistocene-Holocene) of the infilling succession refers mainly to alluvial fan and secondly to fluvial-marshy environments. The Quaternary succession was mainly accommodated within a half-graben structure, controlled by an E-W oriented N-dipping, master normal fault, localized on the Matese slope and interpreted as an active and capable fault, as well as by NW-SE oriented, NE dipping, high angle faults intersecting the alluvial fan system, in agreement with the NE-SW tectonic extension, acted on this sector of the Apennine chain since the Middle Pleistocene. Morpho-stratigraphical and tephro-stratigraphical data allowed hypothesizing that the fault intersecting the alluvial fan system is the prosecution toward SE of the Bojano fault and that it was also active during late-Pleistocene-Holocene. Starting from the available data on several historical earthquakes and seismicity that have struck the Bojano basin, producing huge damage, further deepening of the issue appears essential in order to fully understand the role of this fault in generating strong earthquakes.

## Evaluations and processing of kinematic classifications for the integration of seismological and geological-structural data in active tectonic contexts

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*Keywords:* earthquakes, seismotectonic, kinematic classifications.

With the progress of geological and geophysical contributions to the study and description of the deformation of the Earth's crust due to seismic events, scientists have developed numerous models of representation and kinematic analyses to assign a tectonic regime to the fault structures. Authors have attempted to develop classification criteria that reflect the actual rupture mechanism of the seismic source, using seismological data of focal mechanisms (Frohlich, 1992; Zoback, 1992) or the kinematic slip data of the fault (Aki & Richards, 1980).

Most of these classifications suffer from several problems: 1) there are different classification criteria that can be applied to a data set, each of which gives its own result, often very different from each other, 2) the information obtainable from a focal mechanism (deformation axes and nodal planes) must be attributable to the same tectonic regime, 3) in the kinematic analysis it is important to consider not only pure "Andersonian" movements but also intermediate fields, 4) part of the focal mechanism data set is defined as "unknown", thus subtracting information from the seismotectonic analysis.

Based on these assumptions, we have developed a system capable of combining a type of classification based on geological data (slip vector rake) with a classification that takes into account seismological data (deformation axes P, T and B).

In this work we analyze the quality and the problems related to the application of different methods of classification of focal mechanisms of an integrated seismic catalog of different authors. Through the creation of scripts in the MATLAB environment, the dataset was represented in ternary diagrams, useful for describing and schematizing the kinematic characteristics of a seismically active area. Then, on the same seismic database, different kinematic classifications were tested, using both the fault rake value and the orientation values of the deformation axes, in order to obtain the best relationship between the two different methodologies and to be able to assign to each mechanism the same kinematic regime. At the end of these tests, a classification by slip rake and a classification by deformation axes based on 10 kinematic fields are proposed, able to attribute the same results to 90% of the data used in terms of classification of the tectonic regime.

These classification methods limit the gap on high quality data, integrating the geological data and seismological data present in the focal mechanism, and describe in more detail the deformation processes of the Earth's crust related to fault structures and seismic sources.

Finally, as an applied hypothesis of the work carried out, it was chosen to compare the Italian seismicity, discriminated on the basis of the classification proposed in the work, with seismotectonic zoning models from the literature, to highlight a good compatibility between the two data.

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## **Revision and analysis of macroseismic data of some strong Calabria earthquakes (Italy) for seismotectonic purposes**

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*Keywords:* earthquakes, faults, Calabria.

In tectonically active areas, such as the Italian peninsula, identifying the faults responsible for the strong earthquakes is often challenging, especially when they occurred in historical times. In such cases, geoscientists need to integrate all the available information from historical reports (Guidoboni et al., 2019), surface geology and geophysics to constrain the seismogenic faults. This is the case of the southern Calabrian arc, in the area between the Catanzaro and the Messina Straits, that after a paroxysmal activity with six  $M_w$  6.5-7 events in 125 years from 1783 to 1908 and other two  $M_w$  6 events in 1791 and 1894, has only released small shocks with a few minor isolated sequences ( $M_w < 4.5$ ). Despite the strongest Calabria earthquakes have been largely studied, robust and commonly accepted seismic sources are still missing. To contribute to the debate, we reviewed and updated, according to EMS scale (Grüntal, 1998), the macroseismic fields of the five main events of the 1783 Calabria sequence (5, 6 and 7 February, 1 and 28 March,  $M_w$  5.9 to 7.1), two other destructive events located in the same epicentral area of the 1783 sequence (1791,  $M_w$  6.1 and 1894,  $M_w$  6.1), along with the Messina Strait 1908 earthquake ( $M_w$  7.1). The new macroseismic fields were analyzed using a series of MATLAB algorithms to identify 1) the unitarity of the field or its partitioning in sub-sources and 2) the field and sub-fields main elongation. By using a collection of earthquake scale laws (e.g., Wells & Coppersmith, 1994) from literature and calculating the equivalent magnitude of seismic events (Gasperini et al., 2010), average source parameters (Length, Width, Area), with their range of variability, were evaluated. From these data, the MATLAB algorithm processes and produces an elliptical map-view representation of the source geometry for each earthquake analyzed. We also elaborated an updated map of the major late Quaternary-Pliocene extensional fault systems of the Calabrian Arc and a new catalogue of coseismic effects of the main events. We compared the computed source parameters with the geometry and dimensions of the mapped faults and advanced new alternative hypotheses on the earthquake/fault associations with respect to the models available in the literature, and in the case of multiple proposed solutions, we helped identify a better-constrained source. In particular, we have suggested new seismotectonic hypotheses for the 1908 earthquake and the 28 March shock of the 1783 sequence, based on the new shape of their macroseismic fields and comparing our results with the clues obtained studying the seismogenic behaviour of faults from recent instrumental sequences in central Italy. Finally, we reconstruct the time-space evolution of the seismicity along an ideal transect across the axis of southern Calabria during the last fifth centuries.

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## New insights in the Val D'Agri structural framework: reprocessing of vintage 2D seismic lines to better frame the Western flank of the Valley

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*Keywords:* 2D vintage seismic lines reprocessing, Monti della Maddalena fault system.

The Val D'Agri Basin is a northwest-southeast trending extensional to transtensional sedimentary basin, located in the Campania-Lucania sector of the Southern Apennines. The present-day structure is the result of a complex tectonic evolution where different deformation events superimposed through time. Two different fault arrays controlled the opening and long-term evolution of the Val d'Agri Basin since the Late Pliocene (D'adda et al., 2017): to the east, the East Agri Fault System (EAFS) characterized by NW-striking, SW-dipping fault segments; to the west, the Monti della Maddalena Fault System (MMFS) characterized by NW-striking, NE-dipping extensional fault segments. In the last decades these Quaternary faults have been deeply investigated mainly to define which segments are active and potentially responsible for large magnitude earthquakes such as the 1857 one (Bello et al., 2022 and references therein).

According to seismic interpretation and modelling, and to geochemical data (Cello et al., 2001; D'adda et al., 2017) along the eastern flank of the valley, normal faults cutting the allochthonous sequence appear decoupled from deep-seated faults cutting the Apulian platform.

On the other hand, to the west, the MMFS, identified as main seismogenetic structures, have been investigated mainly by means of surface, near-surface data (Improta et al., 2017 and references therein). Thus, the deep geometry of these faults is still uncertain.

To better define the structural framework of the South-Western flank of the valley, five 2D seismic lines acquired by Eni in the 90's have been selected. The original dataset has been reprocessed with an ad-hoc sequence. In particular, the static corrections and the denoise sequence applied, permit to overcome the biggest problem over the area: Signal/Noise (S/N) ratio. After this pre-conditioning on the data, an accurate velocity model building and Pre-Stack Depth Migration were performed. The favourable cut-crossing of the chosen lines, the highest S/N ratio on the seismic, and the available geological information on the main rock units of the valley, helped in building an accurate pseudo-3D velocity model. This model was the input of both Kirchhoff and Reverse Time Migration algorithms to produce the final imaging on the lines providing a more valuable definition of the structural asset in the investigated area.

The interpretation of these reprocessed lines has been supported by the knowledge of the surface geology and the information coming from the closest wells. Based on the seismic interpretation a pseudo-3D structural model has been built to quality check the interpretation and reconstruct major fault planes.

The interpretation carried out on the available data allows to: i) describe NW-SE Pliocene reverse faults within the Apulian platform ii) characterize NW-SE segments of the MMFS cutting through the Apulian Platform and Allochthonous system iii) identify minor NNE-SSW faults.

*The authors acknowledge Eni and Shell Italia E&P management for the permission to publish this paper.*

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## **Tectonically-deformed archeological remains at Lilybaeum in Western Sicily as possible footprints of missed large earthquake in the area**

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*Keywords:* deformed archeological remains, active faulting, seismic hazard.

Archaeoseismic analysis performed in Western Sicily point to deformed archeological remains at Lilybaeum, a Punic coastal city founded in 397 B.C. at the Island's westernmost edge. Long-lasting archeological excavations and geophysical prospecting have revealed a quadrangular-shaped urban setting of the city with an internal checkboard road fabric of main roads (decumanus) orthogonally-joined by secondary ones (Cardines). In this frame, one of the most suggestive archaeological remain is the Decumanus Maximus, a NW-SE trending stone-paved monumental avenue connecting the harbor to the *civitas*. As epigraphically attested, the Decumanus Maximus is dated from the 2<sup>nd</sup> to the 4<sup>th</sup> century AD. Starting from the direct observation of deformed ruins, an interdisciplinary approach, which has included field-structural analysis, drone-shot high-resolution aerial photogrammetry and DSM, and geophysical prospecting, was followed to understand whether the recognized deformations may represent the ground effects of a previously unknown large earthquake in the area. An unusual NE-SW trending step, in particular, has been found to displace transversally the Decumanus Maximus of about 10 cm. High-resolution profiling over the acquired DSM, revealed how the raised block is gently folded to create an anticline coaxial to the fracture, whereas the lowered block is somewhat tilted toward the SE. Folding and tilting on the blocks separated by the fracture are consistent with a deformation having a tectonic origin. This is also confirmed by sub-surface geophysical imaging in the area. A cardines NE of the Decumanus is tilted toward the NW as result of rotation along its NE-SW trending longitudinal axis. Considering the Romans' civil engineering expertise in roads construction, the one-side tilting of the road suggests it may also be involved in tectonic folding. Deformed ruins have been also found in the NE sector of the investigated archeological site where Hellenistic floor mosaics are characterized by rippled to asymmetrically folded surfaces. NE-SW trends of thrusting and folding affecting the archeological remains (Decumanus, cardines, and mosaics) are all consistent with the NW-SE oriented max stress axis to which Western Sicily is currently undergone. In this contest, a coseismic origin of the displacement affecting the Decumanus Maximus is here proposed. According to the amount of dislocation measured along well-dated archeological features and to age-constrained directional collapses, a back-verging reverse fault ruptured in the area possibly in the VI century AD producing a highly-energetic ( $M \sim 6.5$ ) earthquake. This founding may provide additional constraints in redefining the seismic hazard of Western Sicily, a region where recurrence-time intervals for large earthquakes are still unknown. High-resolution geophysical explorations are also planned in the adjacent marine setting to search for a possible offshore prosecution of the identified tectonic features.

## Inspecting Late-Quaternary active extension along the outer sector of the central-southern Apennines (Abruzzo-Molise border, Italy): preliminary results from the topographic analysis

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Keywords: topographic analysis, active extensional tectonics, central-southern Apennines (Italy).

Identification, geometric characterization, and deformation rates of active faults are basic inputs and crucial data for correct seismic hazard assessment.

Central Apennines are one of the most seismically active areas of Italy. Historical and instrumental high-energetic events are mostly related to Late-Quaternary active (W-dipping) normal fault systems which cross the bulk of the chain. However, Quaternary extensional tectonics across the Abruzzo-Molise border is poorly documented.

In the south of Abruzzo, displaced glacial deposits (Giraudi & Giaccio, 2017) provide constraints on the post-Last Glacial Maximum (LGM) activity of some normal faults dissecting the carbonatic ridges belonging to the sector (e.g., Mt. Arazzecca). Recently, Faure Walker et al., 2021, provided post-LGM throw-rate estimates of 0.2-0.3 mm/yr (Mt. Pizzalto), rather lower than the rates known for the neighbouring sectors (0.7-1.0 mm/yr). However, the structural continuity of the above lineaments and others located in more external positions (e.g., Mt. Porrara) breaks down towards the Molise. Moreover, the sector was the locus of the 1984 Mw 5.9 Val di Sangro-Barrea earthquake (Rovida et al., 2019) and hints on ongoing extension and inconsistencies between geodetic- and geological/seismological records are also remarked by Carafa et al. (2020).

Based on these arguments, we inspected the occurrence of recent extensional tectonics across the Abruzzo-Molise border by computing: 1) topographic derivatives (slope-, aspect- and curvature) to ease the detection of discontinuity along geomorphic markers, and 2) topographic analysis (local and residual relief maps, swath profiles) to assess even subtle topographic signals of unbalance between rock uplift and erosion.

Moreover, to increase the availability of deformation rates, we drew serial topographic profiles across the Mt. Pizzalto and Mt. Rotella faults and we computed post-LGM throw rates by exploiting a 10m-px res. DEM (<https://tinitaly.pi.ingv.it/>) and, where available, DTMs built starting from topographic data (<http://opendata.regione.abruzzo.it/>) and 1m-px res. LiDAR data ([www.pcn.minambiente.it](http://www.pcn.minambiente.it)).

Preliminary results allowed us to identify key areas to investigate more in depth and located 1) between Pizzoferrato and Valle del Sole villages 2) on Mt. Secine, and 3) in the Mt. Campo-Mt. S. Franco sector and 4) east of Vastogirardi village. Here the discontinuities along the markers and topographic anomalies show coherence with rock uplift. Throw-rate computation provided estimates between 1.2 and 1.4 mm/yr, the latter coherent with deformation rates reported in the literature.

If these preliminary data will be supported by more in detail investigations (e.g., field survey, InSAR data analysis), it will be possible to provide constraints on the southern prosecution of the extensional deformation across the Abruzzo-Molise border, thus increasing the knowledge on new potentially seismogenic faults.

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## The 1857 Basilicata earthquake ( $M_w$ 7.2): is the trans-ridge Caggiano-Montemurro en-echelon normal fault the responsible?

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Keywords: trans-ridge normal faults, 1857 Basilicata earthquake, active tectonics.

Identifying still unrecognized surface evidence of faults capable of releasing moderate-to-strong earthquakes is especially relevant for seismotectonic and seismic hazard purposes. This is the case of the Basilicata 1857 earthquake ( $M_w$  7.2), which, in a time-lapse of ~3 minutes, released two distinct subevents generating devastation and victims (10.000 to 19.000 casualties) in a large area of the southern Apennines, between the Vallo di Diano and the Val d'Agri (Mallet, 1862). There are many open questions regarding this earthquake, such as the causative fault, the possibility of a hidden source fault, the lack of surface faulting events during the earthquake, the size and depth of the seismogenic fault segments and the dip-angle and dip direction (NE rather than SW) within the Val d'Agri. Answering these open questions is crucial due to the study area's social and economic structure and heritage and the related seismic and anthropogenic hazards.

Through an initial phase of satellite image interpretation, we delineated an alignment of morphostructural elements, which we considered clues to guide field surveys. About 370 punctual structural data (fault plane and striation) were acquired over an area of ~900 km<sup>2</sup> and used to delineate a ~65 km-long SSW-dipping en-echelon fault system connecting the Auletta, Vallo di Diano, and Val d'Agri basins between the Caggiano and Montemurro villages. The fault system develops transversally across a portion of the Monti della Maddalena NNW-SSE striking ridge; therefore, it is referred to as Caggiano-Montemurro (CMF) trans-ridge fault (Bello et al., 2022).

Most commonly, normal faults bound major Quaternary basinal depressions. However, the strong 1980 Irpinia earthquake ( $M_w$  6.9) had already proven that faults capable of generating strong earthquakes can run in the highest portions of the massifs, generating small along-strike elongated intramountain basins (i.e., a few tens or hundreds of meters; Bello et al., 2021). The similarities between the structural style of the fault-controlled small basins in the highest portion of the Monti della Maddalena massifs in the study area and the small basins along the Irpinia fault, can then be interpreted as similar evidence of recent fault activity. Furthermore, formal stress field inversion of fault/slip data surveyed along the CMF provides a N032-trending near-horizontal  $s_3$ -axis, which is coaxial to that computed for the neighboring Irpinia area (Bello et al., 2021), highlighting a deviation of the intra-Apennine tensional axis from a regional SW-NE trend to a WSW-ENE trend in the Campania-Lucania sector.

Considering the continuity of the CMF, we hypothesize that the whole system may represent the master fault of the area and we speculate on its maximum expected magnitude (between 7 and 7.3), making the CMF a possible responsible for the 1857 earthquake. In the CMF, we find the simplest possible explanation, supported by literature data (Galli et al., 2006).

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## Studying fault scarps with geochemical and topographic analyzes to understand past earthquakes: an example from the southern Apennines of Italy

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**Keywords:** Rare Earth Elements analysis, past earthquakes, fault scarps.

Systematically studying the active faults that released strong earthquakes in the past is the new challenge for seismic hazard assessment. A methodology developed in recent years informs on the slip and number of earthquakes released by a fault. This consists in sampling and analyzing portions of the fault plane in order to determine the rare earth elements (REE) concentrations possibly correlated to seismic cycles and slip history (Carcaillet et al., 2008). Sedimentary limestones are generally REE-poor, while the pedogenic environment (soil) they are in contact with is generally enriched during its development. In the uppermost part of the soil, REE forms organic complexes preventing their leaching and transferring to the deeper part of the soil. Thus, REE+Y enriches the organic richer soil portion (Carcaillet et al., 2008 and references therein). Primary (*i.e.*, limestone) and secondary (*i.e.*, cement) carbonates easily dissolve in the presence of any fluids acidified by dissolved CO<sub>2</sub>. Fault planes developing in limestone produce breccias subject to dissolution by rain and circulating (vadose) waters. As explained in detail by Carcaillet et al. (2008), the dissolution of the carbonate along the exposed fault plane produces REE+Y enrichment in the runoff waters. These waters reach the pedogenized colluvial wedge at the base of the fault scarp where REE+Y forms organic complexes and/or are taken up by specific bacteria enriching the topsoil and its fluids. These fluids produce re-precipitation of carbonates on the fault plane. The exchange process stops at the time when the fault plane is exposed due to exhumation (slope erosion processes or surface faulting). We apply this methodology to the Caggiano normal fault (southern Apennines, Italy), cropping out southeast of the Irpinia 1980 earthquake fault (M<sub>w</sub> 6.9), which was responsible for both the 1561 and partly the 1857 Basilicata earthquakes (M<sub>w</sub> 6.7 and 7.1) (Galli et al., 2006; Bello et al., 2022). We integrate the REE analysis approach with a high-resolution topography analysis along 98 serial topographic profiles to measure vertical separations (Bello et al., 2021) attributable to post Late Glacial Maximum (LGM) faulting. The asymmetric scarp height profiles suggest fault lateral propagation and along-strike variations in the fault evolution. This integrated and multidisciplinary approach highlights the occurrence of seven-to-eleven earthquakes with variable slip between ~40 cm and ~70 cm within post-LGM times. We speculate on the magnitudes of the respective earthquakes obtaining magnitudes to be between 5.5 and 7.0, and most commonly between 6.3 and 6.5. The results suggest a recurrence time between 1.6 and 2.3 ka and a slip rate ranging between 0.6 and 0.9 mm/yr and offer an approach useful to be applied on carbonate fault planes in similar worldwide tectonic.

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## The clustered microseismicity in Benevento high seismic risk area (Southern Apennines) - a template-matching approach

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Keywords: template-matching, spazio-temporal clustering, Benevento seismic risk area.

Benevento province is a high seismic risk area struck in historical and early instrumental times by moderate-to-large earthquakes that caused severe damage (1456, 1688, 1694, 1702, 1732, 1805, 1930, up to X–XI MCS). The study area is located in the southern Apennines in a sector undergoing extension at a rate of a few mm/yr. The available focal mechanisms of the major earthquakes show an SW–NE trending nearly horizontal T-axes consistent with the regional stress field and the active normal fault pattern. In addition to the aforementioned major earthquakes, in the 60s, a moderate complex seismic sequence occurred northeast of Benevento town. It was characterized by two major normal fault seismic events 10 minutes apart (21 August 1962,  $M_L$  5.7 at 18:09, a mainshock with  $M_L$  6.1 at 18:19) that involved small foreshocks and aftershocks (Westaway, 1987).

Close to the 1962 earthquakes, on 27 September 2012, the Benevento area was hit by a seismic event with  $M_L$  4.1 (Adinolfi et al., 2015). Unlike the previous upper crust earthquakes associated with the normal fault pattern, the seismic source of this event showed right-lateral strike-slip kinematics. It was located at depths between 16 and 20 km, highlighting seismotectonic complexities previously unknown.

The seismicity observed in the last 40 years is mainly characterized by low-energy sparse events or swarm activities. To gain insight into the seismotectonic framework of this area, we analyzed the seismic activity reported by the new release of the Italian seismic catalog (CLASS, Latorre et al., 2022) in the time interval spanning from 2012 to 2022, in which the seismic network configuration can be considered stable.

We enhanced the catalog by template matching technique using the open-source seismological package PyMPA (Vuan et al., 2018), obtaining a significant increment of the output catalog of ~ 6-8 times the Italian Seismic Bulletin and CLASS.

We detected 3 seismicity clusters close to the 2012 strike-slip seismic sequence and 2 others southwestern Morcone localities (north of Benevento) at depths greater than 12 km ( $M_{L,max}$  3.0).

We detected the foreshocks of the seismic sequences of 2012 and characterized the seismic activity in foreshock, mainshock and swarm-like seismic sequences.

The non-homogeneously distributed seismicity extends for about 40 km. It is mainly composed of spatially complementary seismic swarms highlighting a slow deformation sector below the base of the seismogenic layer of the southern Apennine extensional domain. A future study on earthquake kinematics may add some other critical seismotectonic constraints.

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## **Late Miocene-Quaternary structural evolution of the northern Calabrian Arc: new insights from marine geophysical data**

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*Keywords:* lithospheric discontinuities, crustal shear zones, Calabrian Arc, marine geophysical data.

The Calabrian Arc has developed in the frame of the Tyrrhenian-Ionian subduction system since the Neogene. Its structural evolution is controlled by lithospheric discontinuities (e.g., STEP and slab-tear faults) and regional-scale crustal shear zones. Polyphase subsidence and inversion tectonics in basins developed along the Calabrian Arc and its offshore suggest rapid changes of direction and magnitude of stress induced by the frontal accretion of the Apulian and Ionian domains. In the last decades, many studies were carried out on the tectono-stratigraphic reconstruction of sedimentary basins located both at the western (Paola, Amantea, Crati and Sant'Eufemia basins) and eastern side (Sibari Plain, Crotona and Squillace basins) of the northern Calabrian Arc. However, the role of contractional, extensional, and strike-slip tectonics is debated. Consequently, contrasting models have been proposed for explaining the tectonic evolution of basins since the Middle Miocene. This talk presents an overview of the late Miocene – Quaternary structural evolution of the northern Calabrian Arc, focusing on studies of the Tyrrhenian and Ionian offshore.



## Active tectonics in the Calabrian Arc: Insights from the structural pattern of the Squillace Basin (offshore eastern Calabria)

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*Keywords:* active tectonics, Ionian Sea, Calabrian Arc.

This research aims to reconstruct the evolution of the Squillace Basin (Ionian offshore of the Calabrian Arc) from the Late Miocene to Recent times and recognise active shallow and deep structures using a multiscale approach. The latter is based on interpreting high-penetration and high-resolution seismic reflection profiles, calibrated with well-log data coupled with bathymetric data and the distribution of instrumental earthquakes. Data highlight three steps in the evolution of the Squillace Basin. A Late Miocene extensional event led to the formation of WNW-ESE oriented horst and half-graben structures. During the Pliocene, deformation was localised in the central and northern sectors of the basin and expressed by a WNW-ESE oriented strike-slip fault and NW-SE normal faults, respectively. A transpressional event started in the Early Pleistocene, causing the positive inversion of deep (> 3 km) extensional faults and the formation of NW-SE to WNW-ESE oriented transpressional/reverse faults and related anticlines. The kinematics of these faults agree with the NW-SE oriented left-lateral Albi-Cosenza, Lamezia-Catanzaro and Petilia-Sosti crustal fault zones developed in north Calabria. The results of this work suggest that the transpressional structures in the northwestern sector of the basin likely represent the offshore prolongation of the Albi-Cosenza fault zone. NW-SE to WNW-ESE trending, shallow (<2 km) high-angle normal faults offset the younger deposits. Their depth and direction indicate that these faults are secondary structures formed in the extrados of the anticlines associated with the transpressional faults. The distribution of earthquakes shows events with  $M > 3$  and depth <15 km located in the hanging wall of transpressional faults. The integrated data suggest that these structures are active and probably responsible for the major earthquakes that affected the Ionian offshore. Conversely, shallow normal structures (depth <2km), formed in the extrados of anticlines associated with the transpressional faults, are inconsistent with hazardous seismicity based on their length and depth.

## **The Campania-Lucania Extensional Fault System, Southern Italy: an analog modeling perspective**

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*Keywords:* Southern Apennines, extensional fault system, analogue models.

The Italian Apennines Quaternary extension was accommodated by the formation of both high-angle (west-dipping) and moderate- to low-angle (east-dipping) normal and normal-oblique faults that cross-cut and offset Mio-Pliocene fold-and-thrust structures.

This extensional (east-dipping) detachment structure in Northern Italy is known as Etrurian Fault System (EFS). The EFS represents a regional NNW–SSE fault alignment, which has less-evident field expressions (cropping out along the western border of the Apennine belt), and extends from north to south from the extensional Lunigiana–Garfagnana basins to the Mugello–Casentino ones to the western border of the Eastern Tiber basin.

The counterpart Central Italy structure, known as Latium-Abruzzo Extensional Detachment (LAED; Lavecchia et al., 2017), crops out in the Sabini-Eastern Simbruini (SES) and it is supposed to continue at mid-crustal depths beneath the L'Aquila 2009 (Mw6.3) epicentral area. The LAED would represent a regional right-lateral en echelon arm of the EFS.

Potentially seismogenic moderate- to low-angle east-dipping normal faults are also located in Southern Italy, along the Campania-Lucania Extensional Fault System (CLEFS; Brozzetti, 2011). These faults were responsible for the 1980 Irpinia earthquake (Mw6.8). In the Central and Southern Apennines eastward of the extensional belt, also active E–W strike-slip faults are recognized.

Previous studies investigated how a newly-formed normal fault interacts with structures inherited from a previous contractional phase (Bonini et al., 2015). Here we present the preliminary results of analogue models carried out aiming to reproduce the formation and the downward propagation of a moderate-to low-angle normal main regional fault. Both with the genesis and the evolution of this kind of structure, we investigated also the progressively activation of antithetic normal faults sole to the main east-dipping plain. Models were executed using a device composed by two rigid blocks juxtaposed along sloping sides, which represent the plane of the master fault. The footwall block is fixed, whereas the hangingwall block is allowed to slide downward along the sloping plane (30°); the displacement of the moving block is controlled by a stepper-motor at a constant velocity. Wet clay (kaolin) was used as analogue of the rocks above and below the master fault; the use of wet clay allows to insert mechanical discontinuities that simulate pre-existing faults or thin layers of weaker rocks. Then a set of several experiments was performed in order to find the best fitting setup able to reproduce the main extensional (east-dipping) detachment structure.

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## Fluids and tectonic loading controlling the time-3D space relationships among background seismicity, swarms, major events, and active faults – a case study from the central-southern Apennines of Italy

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*Keywords:* background and clustered seismicity, active tectonics, Central-southern Apennines transition zone.

Distributed and localized seismic deformations represent two end-member models. Transient aseismic processes, caused by fluid flow, fault creep, and slow slip events, can further influence the earthquake distribution making the seismotectonic framework even less clear.

The 3D spatiotemporal seismicity analyses can help discriminate the background and clustered seismic activity components and consequently discern tectonic and transient aseismic processes. This differentiation, jointly with geological and geophysical information, can help gain insight, especially into the seismotectonics of areas with low seismicity rates in instrumental times.

We focus on the Abruzzi-Molise-Northern Campania extensional domain located in the transition zone between the Umbria-Marche and the Southern Campania-Lucania Apennines, struck by Accumoli-Visso-Norcia 2016 (M<sub>w</sub> 6.5) and the Irpinia 1980 (M<sub>w</sub> 6.9) seismic sequences, respectively.

The seismic catalogs (1980-2022) show that in instrumental times the study area is predominantly characterized by a low level of seismicity, relatively stable in the size and time domains, and low-energy seismic clustering. The only relevant earthquakes are Barrea, 1984 (M<sub>w</sub> 5.8) and Matese, 2013 (M<sub>w</sub> 5.0) seismic events. Conversely, it was struck by eleven events among the largest historical-early instrumental earthquakes (M<sub>w</sub> ≥ 6.5) of the Italian territory since 1349. Accordingly, it is considered one of the highest seismic risk zones of the peninsula, characterized by (1) complex fault patterns able to release moderate-to-large earthquakes, (2) a base of a seismogenic layer of ~ 10-11 km deepening from north to south, down to 12-14 km (Chiarabba & De Gori, 2016), (3) a variable heat flow increasing from east to west (0.04-to-0.1 W/m<sup>2</sup>) (e.g., Carafa et al., 2015), and (4) the presence of significant CO<sub>2</sub> flux (Fron dini et al., 2019) west-southwestward.

With the main aim to define spatial relationships among background, clustered seismicity, and Quaternary geological structures, we analyzed 42 year-record of seismicity (0.0 ≤ ML ≤ 5.8, from 1980 to 2022) occurring at different crustal depths. We divide the dataset into three time periods with homogeneous completeness magnitude (1980-2005, 2005-2011, and 2012-2022). We applied the filter matching technique to enhance the catalog only to the last period 2012-2022 in which the seismic network configuration can be considered stable. We identified 45 spatiotemporal clusters and defined the background seismicity rate.

We further discriminated the seismic sequences and swarm activities and studied the relationships between the seismic spatial distribution with the active faults, the Vp/Vs, and the CO<sub>2</sub> anomalies.

The spatiotemporal distribution of seismicity suggests that the faults system in the southern-central Apennines is characterized by heterogeneous rheology where small fault patches systematically release strain through swarms and other parts are to date locked.

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## Earthquake catalog enhancement through template matching: an application to the Southern Apennines (Italy)

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*Keywords:* enhanced earthquake catalogs, southern Apennines (Italy), fault geometry.

Improving the capability of seismic networks to detect small-magnitude seismicity, near or below the network detection threshold, is the prerequisite to study the seismotectonics of an area in terms of fault geometry, kinematics and mechanics. Thus, leading to an improved comprehension of the physical mechanisms behind small and large earthquakes.

In the framework of the MUSE-4D project of PRIN 2017, we applied a template-matching algorithm (a cross-correlation based technique for the detection of hidden low-magnitude earthquakes) to the entire scale of the Southern Apennines of Italy. Here, the ongoing extension of the Mio-Pliocene Apennine thrust-belt poses a major seismic hazard, as testified by several Mw~7 earthquakes that struck this area in the past 300 years. No clear consensus exists on the seismotectonic models related to some of these strong earthquakes, particularly in terms of characterization of the fault structure and crustal rheology that can thus largely benefit from the application of template-matching.

We use ~4000 earthquakes recorded at ~200 stations of the INGV National Seismic Network between 2009 and 2015, as templates. We scan six years (2009-2015) of continuous recordings with the template-matching algorithm, ending up with ~3 million (possible) detections. Only 3% (~88.000 events) comply with the minimum quality thresholds that we set (at least four P and four S picks, recorded at least at five stations). For determining earthquake locations we used the fully-probabilistic non-linear code NonLinLoc, with an ad-hoc 1D velocity model and corrections for station residuals.

The final catalog comprises ~26.000 new seismic events, showing a mean horizontal and vertical error of 1.5 and 2.8 km, respectively, and a mean RMS of 0.14 s. These values are only slightly higher than those of the template catalog, mainly due to the lower number of phase arrivals that usually constrain the detected events. Given the small magnitude (ML<1) of the majority of the newly detected events, the new catalog shows a decrease in magnitude of completeness from 1.6 to 0.5 or 0.6 using the Max-curvature or the MC90 methods, respectively.

The main NW-SE trending seismogenic structures of the axial zone of the chain are illuminated by abundant microseismicity, with evident gaps delineating the along-strike boundary of such structures. In addition, the new catalog unravels distinct E-W oriented clusters in the external zone of the seismic belt, likely related to shear zones developed in the deeper crystalline crust of the Adria plate. Finally, we show the improvement in the recovery of the missed seismicity, during the 2013 and 2014 Mw5 Matese seismic sequence.

## Crustal structure and last 15 years instrumental seismicity distribution in the Marzano-Irpinia area

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*Keywords:* seismic reflection profiles, instrumental seismicity distribution, Marzano-Irpinia.

The crustal structure in the area including the Picentini, Marzano and Alburni mountain ranges and the Irpinia hills (Campania-Lucania Apennines) was reconstructed using largely unpublished seismic reflection profiles (commercial lines and a re-processed segment of the CROP-04 deep crustal line), exploratory well logs and geologic-structural relations among the lithostratigraphic units.

This area is one of the most seismically active in Italy and hosted destructive historical earthquakes. Several NW-SE striking normal faults have been considered active in this area. The best-constrained seismogenic structure is the Irpinia fault, which slipped during the Mw = 6.9, 1980 earthquake. The main rupture nucleated between 12-13 km depth and caused ~40 km long discontinuous surface faulting across the Marzano massif and in the NE part of the Picentini Mountains.

We used a dataset of seismicity recorded in the Irpinia region compiled by merging different sources, including the Bollettino Sismico Italiano-INGV (time range: 2009-2021) and the ISNet Network from 2007 to 2021. A portion of the BSI catalog events occurring between 2009 and 2014 were used as master events for the detection of small-magnitude seismicity through template-matching, over the same period. This technique allowed the retrieval of that portion of seismicity that usually falls below the detectability threshold due to the low signal-to-noise ratio.

For all catalogs, earthquake locations have been determined with a common 1D average velocity model (mostly based on commercial sonic logs) and using the probabilistic, non-linear code NonLinLoc.

The epicentral distribution of the final 2083 selected events (magnitude range between -0.3 and 3.7) on the depth converted seismic profiles shows that most of the 2007-2021 seismicity falls within a crustal volume broadly coincident with the hanging wall of the Irpinia fault and limited to the northeast by its antithetic fault. The deeper events could follow a curved projection of the Irpinia fault at depths between 8-13 km b.s.l.

Few shallow events appear to follow the basal thrust of the Apenninic platform on the Lagonegro-Molise basin unit or are hosted within the latter unit between 3-5 km depth. Most of the events are host within the Apulian platform unit, where they tend to cluster downward.

Based on deep well log data and rheological modelling, we infer that the increase in number and the clustering of event hypocentres beneath Mt. Marzano corresponds to the transition in the Apulia unit from the carbonate-evaporite sedimentary sequence to the Verrucano-equivalent layer and the crystalline basement starting from ~10 km depth.

## **Paleoseismology in the southern Apennines: when the icing on the cake of active tectonics is tastier than the cake itself**

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*Keywords:* paleoseismology, active tectonics, earthquakes.

When California geologists in the 1970s realized that the time intervals between strong earthquakes were longer than their colonial history, they had to migrate from paper to geologic archives to find traces of past earthquakes, inventing paleoseismology. The first trenches in Italy were opened in the late 1980s in a small intramontane basin of central Apennines on behalf of the former Italian Committee for Nuclear Energy (CNEN), followed in the 1990s by many other governmental and private institutions who began excavating active faults all along the peninsula. To date, I believe at least two hundred trenches have been opened across about 30 fault systems, almost all with dip-slip kinematics. Most of these faults are not found in the southern Apennines because of an objective impediment in identifying active faults there. The high erodibility of the siliciclastic units outcropping at the top of the seismogenic belt do not allow the preservation of short-term and low-velocity (< 1 mm/yr) tectonic indicators, as fault scarps or slickensides. In spite of this, the results obtained in the southern Apennines, including the Calabrian Arc, have often been excellent, allowing 1) to ascertain the late Pleistocene activity of structures for which regional studies of active tectonics did not lead to unambiguous results, and 2) to derive conclusive information on the age and magnitude of unknown prehistoric events or poorly parameterized historical earthquakes in terms of energy and location. For instance, excavations across the *Aquae Iuliae* and the northern Matese faults allowed the most enigmatic and powerful medieval earthquake sequences to be associated with them (1349 and 1456, respectively). Trenches on the 1980 Mt. Marzano fault revealed that it was responsible for all the historical earthquakes on record in its hanging wall over the past two millennia. Those on the Mount Pollino fault have confirmed the existence of a seismic gap in the last millennium, in the face of earlier destructive events. In the Calabrian Arc, the Cittanova and Serre faults were unambiguously linked to the catastrophic events of Feb. 5 and 7, 1783, whereas paleoseismological trenches have identified the unknown Lakes fault on the Sila Plateau, responsible for the disastrous June 1638 earthquake, as well as many others in historic and prehistoric times. As a rule, we consider paleoseismology the last step in a study of active tectonics, which cannot disregard from previous extensive analyses on the Quaternary deposits, on the geomorphology and tectonics of the area. In other words, paleoseismology is just the icing on the cake, the litmus test that our hunches and skill have proven correct. However, sometimes the icing is tastier than the whole cake, as it alone provides unexpected results that go beyond just active tectonics, trespassing into the world of historical seismology, archaeology, seismic hazard and urban planning.



## Multidisciplinary analysis for 3D seismotectonic modelling: the case study of Serre and Cittanova faults in Southern Calabrian Arc (Italy)

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*Keywords:* Calabrian Arc, active tectonics, 3D modelling.

Active normal faulting and uplifting, consistent with a WNW-ESE oriented regional extension, dominate the Quaternary tectonics of the southern Calabrian Arc (Monaco & Tortorici, 2000). The main tectonic structures of this extensional domain are considered to be the source of numerous historical and recent strong earthquakes, among which the 1783 seismic sequence (M 6.5-7) was one of the most destructive ever recorded in Southern Italy (Jacques et al., 2001). Previous works on the seismotectonic of the Calabrian Arc indicate a disagreement on the attitude (E-dipping vs W-dipping) of the main seismogenic sources slicing across Southern Calabria, whereby the seismotectonic framework remains still debated. Following a multidisciplinary approach, based on morpho-structural and seismological data, the geometry at depth of the most reliable sources (i.e. Cittanova and Serre faults) was firstly modeled in a 3D environment to retrieve information about their seismic potential. GNSS data of the permanent stations of RING/RDN and TopNetlive Italy networks have been processed in order to visualize the velocity field affecting this area. Then, the inversion of these data allowed us to document a predominant WNW-ESE active extensional strain orthogonally to the modelled faults, consistent with the regional dynamics. The reliability of the model was tested using empirical relation and fault response modeling simulation. Furthermore, Slip Tendency analysis (Morris et al., 1996) revealed the propensity to slip of the modelled planes by applying a remote stress state obtained from the structural survey on the faults.

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## QUaternary fault strain INDicators database (QUIN 1.0 and 2.0) – a release of more than 7000 fault/slip data with strain parameters from the Extensional Belt of Peninsular Italy

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Keywords: fault/slip data, QUIN database, Apennines of Italy.

Strain and regional stress databases of active deformation patterns are largely available in the literature but are almost exclusively derived from earthquakes and geodetic data. However, in areas such as Italy, where the regional stress field has remained unchanged over the last few million years, the analysis of structural data relevant for seismogenic purposes can be extended at least to the overall Quaternary time interval. QUIN was born with this assumption. It is a “QUaternary fault strain INDicators database” designed to integrate, unify and elaborate published and new high-detailed geologic information on potentially seismogenic faults. It provides data on the location, attitude, kinematics, and deformation axes of Fault Striation Pairs (FSPs) measured on Quaternary faults, together with an original shapefile of the faults hosting the FSP. The first QUIN release provides data on FSP exposed along the intra-Apennine Quaternary extensional faults of Central Italy (Lavecchia et al., 2021). The second QUIN release will focus on the southern Apennines of Italy and Calabria.

The two combined databases provide data on more than 7000 FSP Pairs surveyed in about 700 structural sites along the extent of Peninsular Italy for about 1000 km from northern Tuscany to southern Calabria. Up to now, the QUIN research project has involved CRUST researchers working in the PRIN Project MUSE-4D (UniCatania, UniChieti, UniPerugia) with colleagues from the University of London and Roma INGV. In the future, the QUIN project may be extended to other areas to integrate with geological data contemporary geometric and kinematic deformation patterns that might be scattered and incomplete whenever exclusively derived from earthquake data. Researchers interested in collaborating for future project extensions to other areas of the world are invited to contact us!

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## Multi-scale 3D Geometric-Kinematic Fault Modeling in High Seismogenic Areas of Southern Italy through MUSE-4D

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Keywords: 3D fault model, PRIN MUSE-4D, Southern Italy.

The MUSE-4D project of PRIN 2017 is a comprehensive investigation aimed at studying and constraining the geometric, kinematic, and dynamic setting of the Quaternary, active, and seismogenic fault systems in the Campania-Lucania and Calabria extensional belt of Southern Italy. The project has a special focus on the structural control on the time-space release of multiple magnitude 7-class earthquakes. In particular, it investigates, from a seismotectonic point of view, the fault system responsible for four destructive earthquakes that occurred in the southern Apennines of Italy: Reggio Calabria-Messina 1908 (Mw7.1), Irpinia 1980 (Mw 6.9), Basilicata 1857 (Mw 7.1), and South Calabria 1783 (Mw 7.1). These events released similar cumulative magnitudes over a variable time-lapse, ranging from instantaneous to a few months.

To understand the behaviour and characteristics of the complex fault pattern associated to the above events, the MUSE 4D project utilizes a multi-scale, interdisciplinary approach. Active and potentially seismogenic deformation patterns are reconstructed in a long-term tectonic perspective, spanning the Quaternary time and at different scales, from outcrop to regional. This approach allows for a better understanding of the evolution of tectonic processes and earthquake dynamics over time.

One of the project's key outcomes is developing an original 3D nonplanar fault database for two large areas of the Southern Apennines of Italy, with associated geometric and kinematic parameters constrained by high-quality and detailed geological data, hypocentral locations, and focal mechanisms. This tridimensional approach helps limit the number of possible alternative fault models built for any fault, imposing restricted boundary conditions. Any fault surface has to be admissible, integrating the overall available geological, geophysical, and seismological interpretation, and spatially adequately connected and kinematically compatible with the neighboring ones.

The results of the MUSE-4D project offer new possible seismotectonic interpretations and reconstruct new 4D seismogenic scenarios, providing a deeper understanding of the evolution of tectonic processes and the factors that control earthquake dynamics in the study area. This work demonstrates the importance of multi-scale, integrated approaches in understanding complex fault systems and mitigating their impact on local communities.

## Testing the MCMTpy waveform inversion method for moment tensor estimations in the Calabrian Arc region

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*Keywords:* moment tensor, error estimation, Calabrian Arc.

Earthquake focal mechanisms have been revealed as essential in seismotectonic studies, being fundamental to investigate the relationships between earthquakes, seismic faults, and active tectonics. The classical methods of focal mechanism computation based on P-wave first motions may be biased by several factors (like e.g., an inadequate distribution of seismic stations), whereas the more recent techniques using waveform inversion have so far demonstrated as being much more stable and reliable (Presti et al., 2013). The improvements achieved with the waveform inversion techniques enable increasingly accurate comparisons and evaluations, thus needing also a more accurate estimation of the related errors.

In this work we present the application in the Calabrian Arc region of a new Python package (MCMTpy, Yin & Wang, 2022), that exploits the Cut-And-Paste waveform inversion algorithm (CAP, Zhao & Helmberger, 1994; Zhu & Helmberger, 1996) and Bayesian inference, using Markov Chain to implement the source location and focal mechanism inversion in a single workflow. The main functions included in MCMTpy package are source parameters inversion (i) under double-couple assumption with Markov-Chain Monte Carlo (MCMC) method, (ii) under double-couple assumption with a grid-search method and (iii) for the full moment tensor solution with MCMC method. The combined approach implemented by MCMTpy may improve the inversion accuracy of source parameters by also providing a way to quantify uncertainties by statistical inference.

In order to explore the effectiveness of this package in computing moment tensor solution and related errors also in non-optimal network geometry, we applied the MCMTpy algorithm to two earthquakes occurred in the Calabrian Arc region. We performed several tests by varying the starting solution, number of chains and iterations, and the type of computation (e.g., MCMC, grid-search method) and we compared the obtained results with moment tensor solutions obtained by applying different waveform inversion methods.

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## Geometrical and structural characterization of earthquake surface ruptures

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*Keywords:* coseismic ruptures, structural analysis, seismotectonics.

Surface ruptures associated with moderate to strong earthquakes are frequent structures forming in different tectonic settings. They constitute the primary geologic datasets useful for quantifying coseismic slip and have important implications for understanding fault-zone mechanics and for characterizing seismogenic structures. The survey of the magnitude and direction along-strike slip distributions permits the description of the permanent displacement that occurs during an earthquake at the ground surface and may be an important proxy for slip magnitude at depth. Surface rupture linked with active faults represents an important hazard assessment tool, especially in populated areas. The increasing availability of high-resolution remote sensing and surveying methods enables unprecedented analysis of ground rupture offsets. High-resolution point cloud 3D digital outcrop reconstruction allows us to not only measure offsets but to quantify uncertainties more precisely and rigorously than has been previously possible.

We present several examples from two regions quite different in terms of geological features and seismotectonic where central Italy is a mountain area, sparsely populated, while M. Etna's slopes have a much higher population density and many man-made structures. The first one is Mts. Sibillini in central Italy where a sequence of strong earthquakes ( $M_w > 6$ ) with extensional kinematics occurred in August–October 2016, astride which remote sensing and field survey outcomes highlighted quite accurately the field displacement of extensional faults in the Mt. Vettore – M. Bove area. Here the geological effect of the earthquake is represented by more than 35 km of ground ruptures with a complex pattern. They are composed of subparallel and overlapping synthetic and antithetic fault splays where the geometry and structural features of the coseismic ruptures can be easily surveyed. Different methodologies including remote sensing and field surveys permit to calculate along-strike slip distribution and the data can be compared in terms of uncertainties in measurement. The second case is relative to the Mt. Etna volcano in Sicily, where a shallow and low–moderate magnitude earthquake ( $M_w \sim 5$ ) with strike-slip kinematics, associated with a summit eruption, occurred on 26 December 2018 and generated several ground ruptures. Here, anthropic activity has greatly changed the landscape. A coseismic set of ruptures for more than 13 km extending in an arcuate alignment from the village of Fleri, in the northwest, to Aci Trezza in the southeast, largely corresponding to the Fiandaca fault. The geometry and structural features of the coseismic ruptures can be recognized especially in the man-made linear markers, such as walls, and paved roads. The surveys, using different methodologies, permit the reconstruction of the geometry and the areal distribution of the rupture zone including the kinematic of the fault.

**PRIN Project 2017 “Overtime tectonic, dynamic and rheologic control on destructive multiple seismic events - Special Italian Faults & Earthquakes: from real 4D cases to models - MUSE 4D”: onshore and offshore active fault architecture of central-southern Calabria from seismological, geodetic, structural-geological data and interpretation of seismic lines**

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*Keywords:* active tectonics, Calabrian Arc, seismogenic faults.

This contribution illustrates the results of UniCT Research Unit in the PRIN Project 2017, which focused on active fault architecture of central-southern Calabria from seismological, geodetic, structural-geological data and interpretation of seismic profiles. Our research included: 1) interpretation of seismic lines from Videpi database and other marine geological data, e.g. SCS, MCS, sparker, multibeam, acquired in the Gulf of S. Eufemia, in the Squillace Basin and in the Strait of Messina; 2) new morpho-structural survey and dating of active faults and marine terraces in the onshore sectors; 3) redefinition of instrumental seismicity; 4) revision and analysis of macroseismic data of some strong earthquakes; 5) evaluation of deformation rates from GNSS data; 6) 3D modelling of major faults. The integration of our data set confirms the extension along the axis of the Calabrian Arc, accommodated by normal faulting (e.g. Aspromonte and Serre Mts. and Messina Straits) and oblique strike-slip displacement along the W-E striking Lamezia-Catanzaro fault system and the NW-SE trending faults of the Squillace Basin, forming the active northern limits of the subducting Ionian slab and along the NW-SE striking Tindari fault system, representing the southern boundary of the Calabrian Arc. Data interpretation of the new dataset of sub-seafloor geophysical soundings with unprecedented resolution, relocated seismicity and geodetic data, together with morphotectonic investigations and inverse modelling of available levelling data, provide additional constraints on the deformation mechanisms and seismotectonics of the investigated areas (Barreca et al., 2021; Corradino et al., 2021; Giuffrida et al., this volume; Pirrotta et al.; 2021). New alternative hypotheses on the earthquake/fault associations with respect to the models available in the literature, have been also proposed (Andrenacci et al., this volume).

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## **Extensional Quaternary faulting and basin development in the southern Campania-Lucania arc (Italy): architecture and kinematics constrained by field and seismic reflection data**

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*Keywords:* Campania-Lucania Apennines, seismic section interpretation, 3D modeling.

A well-known evolutionary feature of the Italian Apennines is the superimposition of Quaternary extensional deformations on the Mio-Pliocene orogen. The Campania-Lucanian area is no exception, and both west and east-dipping Pleistocene normal faults, with the associated continental basins, have been recognized to dissect the thrust and fold belt.

Most of these faults have been investigated in detail in their geometric parameters (attitude, length, and dip-angle at the surface), associated stratigraphic omission, chronology of deformation, and Quaternary slip rates. The association with recent strong earthquakes (e.g., the Irpinia Faults) or low to medium-magnitude instrumental seismicity (e.g., the Mercure-Morano Calabro fault alignment) demonstrates that some of them are presently active and seismogenic. Nevertheless, uncertainties about some significant aspects remain unsolved as f.i.: i) the subsurface geometry of extensional faults, ii) the depth and sense of dip of their decollement level, iii) the hierarchy between conjugate faults (i.e., which structures - the west- or the east-dipping - represent the master faults?), and iv) the relationships occurring at depth between the normal faults and the major thrust surfaces (the former throughout displace the second or locally invert them?).

In addition, most of the known faults have been described as individual structures, without being contextualized in the framework of a crustal-scale regional array related to the geodynamics of the Tyrrhenian-Apennine system.

In this work, the above crucial issues are addressed by studying a ~4400 square km wide sector of the Campania-Lucanian Apennines, bordered to the north by the Sele Valley and to the south by the Mt Cervati-Montemurro transect.

In this area, we have studied a grid of 12 seismic lines, for a total length of ~380 km, constrained at the surface with original field data, and calibrated at depth with the available well logs.

The depth-conversion of the lines, which show quite good quality down to 5sec twt, was the base for the drawing of a series of geological transects across the entire area.

The whole set of geological and seismic sections, interpreted down to the top of the Apulian platform, allowed the building of a three-dimensional subsurface geological model. This latter is mainly focused on the geometries and amount of displacement of the extensional faults but also takes into account their relationships with the main thrust sheets.

The model also defines the reciprocal interplay between the antithetic boundary faults of the quaternary depressions (Auletta, Vallo di Diano, and Agri Valley), the geometry of the sin-tectonic sedimentary infill, and the locations of their depocenters.

The 3D Quaternary faults here reconstructed for the Campania-Lucania area are an integral part of a larger tri-dimensional geological model extended to the entire southern Apennines, which is one of the main expected products of the MUSE 4D PRIN project.

## Characterization of the Castelsaraceno microearthquake sequence (High Agri Valley, Southern Apennines, Italy) through a semi-automated template matching and machine-learning based approach

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*Keywords:* seismic sequence, microearthquakes, fault imaging.

The accurate characterization of microearthquake sequences occurring in tectonically active areas enables the imaging of seismogenic faults at depth and works for seismologists as a magnifying glass in shedding light on the physical and mechanical processes involved in earthquake nucleation and in rupture activation and propagation. In this context, the improvement of the current standard procedures for earthquake detection, phase-picking – mainly manual-based - and accurate location, currently requiring a huge amount of work from expert seismologists especially in the case of noise-contaminated microearthquakes signals, is essential for the more efficient analysis of these seismic sequences.

Here we show how the investigation of a low-magnitude sequence, occurred in August 2020 close to Castelsaraceno village (High Agri Valley, southern Apennines) benefited from the application of a semi-automated template matching and machine-learning based workflow. The study area is a NW-SE trending quaternary basin located in the axial zone of the Southern Apennines, bordered by fault systems capable of producing large earthquakes (e.g., the 1857 M7 event). The analyses were performed on seismic data mainly recorded by a local seismic network belonging to the High Agri Valley geophysical Observatory (HAVO) located at a maximum epicentral distance of ~20 km from the seismicity cluster.

First, we applied a semi-automated single-station template matching technique (Stabile et al., 2021) to continuous data-streams recorded at the two nearest stations of the HAVO network (from 28th July to 12th October 2020), thus detecting more than twice the number of microearthquakes previously identified by standard manual detections. Then, the phase-picking step was automatically performed through a deep-learning algorithm (Phasenet; Zhu & Beroza, 2018) on the 202 ultimately detected microearthquakes. Finally, an automatic multi-step absolute and relative earthquake location procedure was carried out.

At the end of the procedure, a total of 72 accurately relocated events were identified as belonging to the Castelsaraceno sequence, which occurred in a short time span (7-12 August) and confined at depth (10-12 km). The M<sub>L</sub> 2.1 foreshock doublet and the M<sub>L</sub> 2.9 mainshock – both occurred on 7 August - ruptured the same seismogenic patch, thus suggesting a persistent asperity. The integration of the seismological data (aftershocks distribution, focal mechanism of the mainshock, source parameters) and the geological framework of the study area allowed us to identify the seismogenic fault as an anti-apenninic (strike 190°), left-lateral NNE-SSW strike-slip fault with normal component kinematic (rake -34°), which would be activated in a brittle portion of the crystalline basement. We hypothesize that the fault is an ancient Lower Pleistocene thrust re-activated in the current extensional regime.

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## Neotectonics of the Catanzaro Trough (Central Calabria, Italy): recent E-W extension and implications for the March 28, 1783 earthquake

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*Keywords:* Calabrian Arc, active faults, seismotectonics.

We performed a multidisciplinary work, integrating morphometric, structural, geodetic and seismological analyses in the Catanzaro Trough (central Calabria, southern Italy) for seismotectonics purposes. The Catanzaro Trough is a seismically active structural depression that developed transversally to the Calabrian Arc during the Neogene–Quaternary (Ghisetti & Vezzani, 1982). This area experienced some of the strongest historical earthquakes of Italy, such as the last shocks of the 1783 seismic sequence (the March 1 and March 28, 1783 earthquakes) (Rovida et al., 2021) whose seismogenic sources are still not well defined.

The main investigated fault system is the WSW–ENE to WNW–ESE trending, south-dipping normal-oblique Lamezia-Catanzaro Fault System, bounding to the north the Catanzaro Trough. This system has displaced upper Pleistocene deposits and alluvial fans, creating triangular and trapezoidal facets. Morphometric analyses reveal that some fault segments of this system are active since they perturb the modern drainage basins. Additionally, the analysis of instrumental seismicity indicates that some clusters of earthquakes have nucleated on the Lamezia-Catanzaro Fault System. GPS data confirm that slow left-lateral motion occurs along this fault system (Pirrotta et al., 2021).

In the southern sector of the Catanzaro Trough, we mapped minor north-dipping normal faults. They show eroded fault scarps with weak seismic activity and negligible geodetic motion. Additionally, the morphometric analysis indicates that the fluvial basins intercepted by these faults don't show evidence of tectonic disturbance.

Morphometric data highlight the presence of a newly detected normal NNE–SSW-trending, WNW-dipping fault system, the Caraffa Fault System, representing the northern prosecution of the Serre Fault (Pirrotta et al., 2022). Seismological data confirm the activity of the Caraffa Fault System along which an alignment of instrumental earthquakes is observed. Geodetic investigation indicates that this system contributes to accommodate the extension that occurs orthogonally to the Calabrian Arc.

Our study highlights that the Catanzaro Trough is a Plio-Quaternary half-graben developed in the frame of the tear-faulting occurring at the northern edge of the subducting Ionian slab. The high number of seismic events evidenced by the instrumental seismicity, the macroseismic intensity distribution and the scaling laws, relating to earthquakes and seismogenic faults, support the hypothesis that both the Lamezia-Catanzaro Fault System and the Caraffa Fault System may have been responsible for the historical earthquakes of this sector of the Calabrian Arc. In addition, given its location, geometry and kinematics, the Caraffa Fault System could be responsible for the March 28, 1783 event.

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## Moment tensor analysis of the 1947 earthquake in the Calabria Ionian offshore area (Southern Italy)

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*Keywords:* historical earthquake, moment tensor inversion, Calabria.

The 11 May 1947 earthquake occurred in the Gulf of Squillace area (Southern Italy) is the largest instrumental seismic event,  $M_w$  5.7 ever recorded in the Ionian calabrian offshore (Parametric Catalogue of Italian Earthquakes CPTI15; Rovida et al., 2022). Based on the macroseismic data reported on the CPTI15 catalogue (Rovida et al., 2022) the earthquake is located on the Ionian coast of central Calabria; otherwise, the instrumental location reported in literature suggests an offshore epicenter even if the lack of a proper azimuthal coverage of the seismic networks operating at that time prevented estimation of the hypocentral depth (Valle et al., 1948). No proper estimates of moment magnitude are available from databases and literature, the value reported in the CPTI15 catalog (Rovida et al., 2022) is obtained by combining macroseismic data with the conversions of instrumental estimates of  $M_s$  and  $m_b$ . In this work we computed the first moment tensor solution for the 1947 earthquake by using a time-domain waveform inversion algorithm properly implemented for analog seismic data (Stich et al., 2005). We collected the original seismograms recorded by long-period seismographs available from the official database of the SISMOS project (<https://sismos.ingv.it/>) and directly furnished by european seismic agencies. Each selected analog seismogram has been manually digitized, then interpolated and corrected for geometrical distortions by using the Teseo GIMP software. We also recovered the instrument response parameters from the original station bulletins and computed the specific transfer functions for the purely mechanical and electromagnetic collected sensors. Moreover, a careful reanalysis of the arrival times data available from the International Seismological Summary ISS bulletin and from the collected station bulletins has been carried out.

Our results indicate that the 1947 earthquake was characterized by an almost pure strike-slip faulting activity occurred on about WNW-ESE trending fault plane, and a moment magnitude  $M_w$  value of 5.1. The obtained result has been accurately checked by performing several inversion tests (e.g., changing the epicenter location, the weighting factors, and velocity model) and interpreted in the frame of the regional seismotectonic scenario (Orecchio et al., 2021 and references therein). The results prove the invaluable and irreplaceable role of information coming from old seismograms to furnish new constraints to local and regional seismotectonic modelling in regions characterized by high seismic risk, such as the Calabrian Arc.

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## Fault structure of the Lake Pertusillo reservoir induced seismicity (Southern Italy) highlighted by an enhanced template-matching catalogue

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*Keywords:* enhanced earthquake catalogs, southern Apennines (Italy), reservoir induced seismicity.

The Val d'Agri basin in the southern Apennines seismic belt is one of the central Mediterranean regions with highest seismic hazard, testified by the strong 1857 M7.1 Basilicata earthquake. The Val d'Agri is also a natural laboratory for studying anthropogenic seismicity related to two well-documented cases of induced seismicity: the first is a wastewater-injection induced seismicity case observed at the Costa Molina injection well; the second case, which is investigated in this study, is the protracted reservoir induced seismicity (RIS) related to the seasonal water level oscillation in the medium-size Pertusillo water reservoir (PWR).

Protracted RIS has been associated with destructive earthquakes, as testified by the 1967 M6.3 earthquake in the Konya region (India), followed by persistent moderate-magnitude M5+ events. In recent years, many other M4+ RIS earthquakes have been observed worldwide, fostering the seismological community to better understand the physical mechanism behind this process and its repercussions on the seismic hazard. The PWR seismicity is characterised by low energy with largest events around  $M_L 3$ . However, a deeper understanding of this phenomenon is compelling due to the presence of active faults, potential source of M6+ earthquakes close to the lake, in an area where the source of the large M7.1 1857 Basilicata earthquake is still debated.

We study the PWR induced seismicity through a very-high resolution earthquake catalogue computed by applying template-matching detection techniques to seismic data recorded during a 1-year-long dense passive survey. Template-matching (TM) uses cross-correlation between continuous seismic data and known earthquakes (templates) to detect previously unidentified events. This method is very useful in areas characterised by dense clusters of small-magnitude seismic events to compute enhanced earthquake catalogues with low completeness magnitude ( $M_c$ ), allowing to image the geometry of faults and fractures and to track the spatio-temporal seismicity evolution.

We use about 400 local earthquakes as templates and we applied the template-matching algorithm to a 13-month-long dense passive survey. We obtain a final double-difference catalogue of 5,070 earthquakes ( $-0.7L < 2.6$ ;  $M_c = 0.1$ ), allowing us to perform a detailed investigation of the spatiotemporal distribution of the swarm-seismicity and to map the *b-value* of the Gutenberg-Richter law. We combine seismicity data with available subsurface geophysical data, fostering an improved interpretation of the RIS.

Space-time earthquake distribution clearly shows that seismicity is organised in four distinct clusters, indicating a progressive southward activation in response to loading/unloading phases of the Pertusillo reservoir. Seismicity unravels new km-scale faults and/or better defines faults partially-illuminated by the previously available earthquake catalogues. All earthquakes are confined within a brine-saturated fractured carbonate reservoir, reactivating with extensional kinematics pre-existing reverse/transpressional faults favourably oriented in the present-day extension. In particular, seismicity is strongly controlled by inherited rock properties (i.e., rock fracturing; geometry of inherited faults; pore-fluid-pressure). In agreement with these observations, *b-value* shows a significant spatial variability, with very-high *b-value* (up to 2.2) within areas of distributed seismicity, while lower ( $\sim 1.2$ ) *b-value* are associated with on-fault larger magnitude seismicity.

**S42.**

**Magma storage, transport, fragmentation, and dynamics of  
deposition: advances in understanding magmatic processes  
and eruptive behaviors**

*CONVENERS AND CHAIRPERSONS*

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## Study of magmatic degassing processes at Campi Flegrei caldera (Italy): insights from the Baia–Fondi di Baia eruption

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Keywords: Campi Flegrei, caldera.

The Campi Flegrei caldera (CF) is considered the most dangerous volcano in Europe and is currently affected by a new phase of unrest, ongoing since 2005. The aim of this study is reconstructing the degassing and crystallization processes and timescale during magmas ascent in volcanic conduits in Baia-Fondi di Baia eruption (9525-9696 BP). This event marked, after 1000 years of quiescence, the beginning of Epoch 2 of post-Neapolitan Yellow Tuff volcanism (last 15 ka of activity) and was fed by multiple vents aligned along a north-south trending fissure in the western sector of CF. The eruption sequence was described in detail by Pistolesi et al. (2017) and Voloschina et al. (2018). The stratigraphic succession is related to two distinct eruptive episodes (Baia and Fondi di Baia), separated by a short interval of time, each of them characterized by different eruptive phases. The eruptive episode of Baia began in a shallow water environment with an opening phase that formed a breccia deposit (Unit I), quickly followed by a fallout activity alternated by pyroclastic density currents (Unit II). This peak phase set in turbulent activity, probably associated with Vulcanian explosions and characterized by a progressively lower intensity (Unit III). After a short phase of quiescence, a second eruptive episode (Fondi di Baia) occurred. The erupted products from both events showed a wide range of groundmass glass compositions. They indicated the involvement of at least two different magma batches that interacted during various phases of the eruption. The proportion of highly evolved (phonolitic-trachytic) and mildly evolved (tephriphonolitic-latitic) end-members varied, with an increase in the latter during the Fondi di Baia stage. This new study was conducted on 12 samples of the proximal pyroclastic sequence of Baia, Fondi di Baia and the distal deposit of Baia. The samples were representative of the different phases of the eruptions (magmatic and phreatomagmatic phases), with particular attention to the initial phases as these are indicative of the processes and timing of opening of the volcanic conduits and therefore of the appearance of early warning signals. On representative samples new geochemical and 2D and 3D textural investigations are in progress on the matrices (microlites, residual glasses, and bubbles), in order to estimate pressures of microlite crystallization, magma degassing and fragmentation, and the durations of magma ascent.

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## **Geochemical and isotopic constraints on the recent magmatic activity of the Dilo-Dukana and Mega volcanic fields (Ririba rift, South Ethiopia): implications for rift evolution**

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*Keywords:* continental rift evolution, Sr-Nd-Pb isotopes, alkaline-basalt magmatism.

The Late Pleistocene-Holocene Dilo-Dukana and Mega volcanic fields (Ririba rift, South Ethiopia) formed through monogenetic eruptions of variable volumes of alkaline-basalts rich in mantle xenoliths. This activity postdated the emplacement of voluminous Pliocene subalkaline basaltic lavas related to the main rifting phase. Both volcanic fields display vent alignments and lava flows that abruptly cut inactive rift-related features, suggestive of an emplacement after rift abandonment.

We provide new petrological, geochemical and isotopic data on these still poorly studied basaltic products aimed at investigating the nature and temporal variation of the mantle source compared to the previous Pliocene activity, and the main differentiation processes involved.

Petrological and geochemical data clearly discriminate the younger alkaline lavas from the Pliocene products, indicating a variation within the mantle source during the two activities possibly related to the local rifting evolution. In detail, the Dilo-Dukana and Mega products show porphyritic textures, with mainly olivine and clinopyroxene as phenocrysts, minor oxides and rare plagioclase, which dominate in the microcrystalline groundmass. Crustal and mantle micro-xenoliths are commonly observed dispersed within the lava samples. From the compositional point of view, the analyzed samples overlap both in major, trace elements and radiogenic (Sr-Nd-Pb) isotopes. However, well-defined trends are displayed by incompatible trace elements and by major elements, indicating the prominent role of fractional crystallization (dominated by olivine and clinopyroxene) driving magma differentiation. The negligible amount of plagioclase among the fractionating assemblage and the presence of large xenoliths, suggest that these magmas rapidly ascended without stopping at shallow storage levels. No clear geochemical correlation is evident with respect to location, xenoliths content or eruptive style. Light-REEs roughly discriminate between the products erupted at Dilo-Dukana and Mega, pointing to possible variations in the degree of melting and/or crystallization conditions of different magma pulses in the two areas.

Overall, these data indicate that the volcanic fields are fed by two different systems of deep structures, unrelated to rifting but associated to old inherited fabrics, directly transferring mantle melts to the surface. The isotopic signature suggests a decreasing though time of the Sub Continental Lithospheric Mantle contribution, consistent with a general cooling of the lithosphere following the abandonment after the rift-related Pliocene effusive phase.

## **Patterns of tilt deformation and volcanic tremor reveal changing dynamics during the 2020-22 fountaining activity at Mt. Etna**

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*Keywords:* Etna paroxysms, volcanic tremor, tilt deformation.

The paroxysmal sequence that occurred during December 13-14, 2020 - February 21, 2022 at Mt. Etna volcano is constituted of 62 lava fountain events. In this work, we propose a multidisciplinary study based on tilt deformation and volcanic tremor RMS amplitude time series using data registered, throughout the whole sequence, by the permanent seismic and tilt networks run by Istituto Nazionale di Geofisica e Vulcanologia – Osservatorio Etneo. We retrieved the amount of deflations associated with the fountaining activity, inflations related to the intra-event time, the maxima peaks of volcanic tremor RMS amplitude and a slope parameter to quantify the evolution velocity of each of these phases. We have identified 3 sub-periods based on the deformation patterns and volcanological data. Analysis of the calculated data for both deformation and volcanic tremor RMS amplitude signals showed meaningful differences among the three sub-periods, reflecting magma storage and transport dynamics. During the first period, associated to the February - April 2021 activity, overall medium-high values have been registered for the complete set of parameters considered, indicating higher volumes of volatile-rich magmas transferred from the deeper to the upper portions of the plumbing system. During the second period (May - June 2021) lava fountains were characterized by lower durations, on average, and the lowest values registered during the whole eruptive sequence, with lower volumes and deformations and with slower development of the phenomena. This behavior during the May – June 2021 period could be strictly related to minor amounts of undegassed magmas in the uppermost feeding system, as also confirmed by SO<sub>2</sub> data acquired through the continuous gas monitoring network. During the third period (July - October 2021) an increasing trend of the above cited parameters, coupled with decreasing inflation velocity, has been observed. Detailed elaborations of tilt signals and volcanic tremor RMS amplitudes have revealed peculiar behaviors for episodes belonging to the second period, which are characterized by marked inflations right before the onset of lava fountains and periodic RMS amplitude patterns. This approach allowed the investigation of differences in the eruptive style and evolution of the paroxysmal episodes observed at Mt. Etna during the 2020-2022 sequence, inferring some of the magmatic processes and magma transfers dynamics that have determined the distinct features observed during the summit eruptions.

## Trajectories of ballistics and assessment of the hazard in the summit area of Mt. Etna (Italy) related to the 2020-22 sequence of lava fountains

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*Keywords:* Mt. Etna, lava fountains, hazard from ballistics.

Basaltic volcanic systems are particularly acknowledged for producing predominantly effusive activity, chiefly due to the physical and chemical properties of magmas. However, even basaltic volcanoes can produce explosive activity, which is often characterized by the production of energetic lava fountains. In the recent decades, Mt. Etna has given rise to several sequences of lava fountains, also known locally as paroxysmal eruptions. The last sequence began on December 13, 2020, and ended on February 21, 2022, producing sixty-two paroxysmal episodes from the South East Crater (SEC). Some lava fountains, among those occurred during the 2020-2022 paroxysmal sequence, have reached considerable, although variable, heights and intensities, occurring under largely different wind speeds and producing sometimes eruptive columns rising up to 15 km above sea level (a.s.l.). During such kind of events, several ballistics fell around the summit craters, sometimes reaching touristic areas. The rather frequent activity poses primary questions on how the impact associated with the fallout of these particles can be estimated. In this work, we present field data collected soon after the lava fountain of February 21, 2022. This event produced high lava fountains (>1000 m above the crater edge) and a volcanic plume about 10 km a.s.l. which was directed toward southeast. Several large ballistics fell in the area of the Barbagallo Craters (just southeast of the summit area at around 2900 m a.s.l.), which is one of the most popular touristic areas on Mt. Etna. Hence, we collected several samples and performed laboratory analyses in order to retrieve their size, shape and density. Values obtained, together with the quantitative analysis of lava fountain, have been compared with results acquired through a calculator of ballistic trajectories ejected during explosive eruptions, which is named “Eject! software” (Mastin, 2001) and is free-available to the volcanological community. We have therefore estimated the main eruption conditions occurred during this lava fountain event and compared them with other data obtained by other remote sensors, including weather data and the relative height of the incandescent jet region of the lava fountain (Mereu et al., 2020) during the paroxysmal phase of this eruptive event. A similar approach has been hence applied to other lava fountains of the 2020-22 sequence, which were characterized by different eruptive and meteorological conditions with respect to that of February 21, 2022 and for which the fallout of large clasts was reported. This work is a first step to identify a real-time and free available system capable of assessing the possible impact by fallout during the Mt. Etna lava fountains, in order to mitigate the risk associated with the fallout of large ballistics, especially close to areas densely affected by tourists and hikers.

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Mereu L., Scollo S., Bonadonna C., Freret-Lorgeril V. & Marzano F.S. (2020) - Multisensor Characterization of the Incandescent Jet Region of Lava Fountain-Fed Tephra Plumes. *Remote Sens.*, 12, 3629.

## High-resolution compositional mapping reveals degassing dynamics during major explosions at Stromboli

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*Keywords:* Stromboli, degassing dynamic, major explosions.

Major explosions at Stromboli volcano encompass a wide range of medium to high intensity eruptions. Since the paroxysmal explosions in the summer 2019, these events have occurred with a frequency of about six per year, therefore posing significant hazard on the island, in particular on the upper flanks of the volcano. Nevertheless, their intermediate nature between ordinary and paroxysmal volcanic activities make them more elusive to pinpoint in terms of eruptive dynamics and associated precursors.

To better understand the mechanisms that trigger and accompany the evolution of the major explosions at Stromboli, we have linked compositions of erupted products and measurements of gas composition in the plume to numerical modeling of gas-magma transfer in the upper part of the plumbing system.

High-resolution compositional mappings of residual melts were performed, by means of FE-EMPA, on Stromboli products emitted during different explosive events, ranging from ordinary activity (11 April 2022 and 29 June 2022) to major explosion (13 May 2022) to paroxysms (3 July and 28 August 2019). Preliminary results suggest complex bubble-melt interaction dynamics during major explosions, evidenced by chlorine and potassium patterns dictated by bubble growth, coalescence, and ascent. Syn- and pre-eruptive magma degassing during major explosions at Stromboli seems to be characterized by partial gas-melt decoupling and gas escape through permeable pathways, followed by a partial collapse of the bubble channels, which leaves well-preserved trails of Cl and K in the elemental maps. Similar elementary distributions aren't found in residual glasses of products from ordinary and paroxysmal activities.

The results of FTIR analyses on gas plume composition allowed to identify an increase of SO<sub>2</sub>/HCl ratio after the major explosion occurred on 13 March 2022. This increase can be associated with a variation of magma volume in shallow sector of the plumbing system which results in a reduction in chlorine degassing.

In order to better understand the measured and observational data, we used bubble growth and dynamics models to identify the decoupling time scales and physical parameter (viscosity, volatile contents) ranges leading to the observed distributions characterizing intermediate-intensity eruptions.

## Detection of near-surface fault systems in the Casamicciola area (Ischia, Italy) through Electrical Resistivity Tomography

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*Keywords:* electrical resistivity tomography, Ischia Island, faults.

The Ischia Island hosts a resurgent caldera, which volcanism has been correlated with the dynamics of a shallow magma body and its volcano-tectonic configuration (e.g. Di Giuseppe et al., 2017). Since the caldera-forming eruption, which laid down the Mt. Epomeo deposits about ~50-60 ka, the central part of the island has undergone approximately 800-900 m of intermittent uplift, accompanied by deformation and faulting affecting the northern rim of the Mt. Epomeo resurgent structure. The edges of the resurgent block are marked by a system of sub-vertical faults with NW-SE, NE-SW, and N-S strike (e.g. Sbrana & Toccaceli, 2011) which also facilitate the development of an intense hydrothermal circulation. The hydrothermal circulation and the related geological structures can be reliably characterized through geophysical prospecting. Electrical Resistivity Tomography (ERT) in the structural modelling of relatively complex geological areas has been demonstrated as a technique capable of reconstructing the contact between different geological formations and the flexure structure produced by faulting in terms of electrical resistivity contrasts.

Here we present the results of an ERT survey performed in the northern sector of Ischia, including the most damaged zones of Casamicciola Municipality during the August 21, 2017 earthquake. Detected resistivity anomalies range between a few  $\Omega\text{m}$  up to about 10000  $\Omega\text{m}$ , and sharp contrasts between them, are well consistent with the rock sequences reconstructed from the geological survey and the borehole logs available in the neighbourhood of the study area. Specifically, the lowest resistivity values are likely correlated to the occurrence of significant fluid circulation and/or highly fractured deposits, whilst the high resistive zones are ascribable to the presence of a bedrock constituted of more cohesive tuffs and lavas. The net lateral contrast between the resistive and conductive zones, observed approximately in all investigated sections, could be associated with the presence of differently oriented fault systems. Some of the detected discontinuities correlate with structural elements that develop up to the maximum investigated depth, reaching, in some cases, the proximity of the current ground level.

The presented results allow an affordable geometrical reconstruction of the main structural lineaments characterizing the shallow substrate of the investigated area.

Di Giuseppe M.G., Troiano A. & Carlino S. (2017) - Magnetotelluric imaging of the resurgent caldera on the island of Ischia (southern Italy): inferences for its structure and activity. *Bulletin of Volcanology*, 79, 85. <https://doi.org/10.1007/s00445-017-1170-4>.

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## Unravel the effect of stirring and undercooling on the crystallization kinetics and solidification path of a phonotephritic melt

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*Keywords:* crystallization kinetics, magma rheology, thermorheological modeling.

In active volcanic environments, magmas that ascend within the conduit and erupt at the surface as lava flows experience physico-chemical perturbations related to temperature changes and convective mass transport. We have conducted experimental investigations to examine the concurrent effects of undercooling and stirring on the crystallization kinetics of a leucite-bearing phonotephrite from Somma-Vesuvius (Italy). Two sets of undercooling experiments have been carried out within the same temperature range of 1300-1150°C. The first set involved classical static undercooling (SU) experiments with no stirring applied to the melt, while the second set involved dynamic undercooling (DU) experiments with a shear strain rate of 1 s<sup>-1</sup> applied. For both SU and DU experiments, we observe that the degree of crystallization and the textural evolution of leucite and clinopyroxene progress with increasing the degree of undercooling. The effect of melt stirring in DU experiments shortens the timescale of crystal nucleation and growth by raising the melt liquidus temperature up to ~28 °C compared to SU experiments. As a result, the solidification process is more pervasive and takes place at higher temperatures in DU experiments, accompanied by a substantial increase in the crystal nucleation density and growth rate. Thermorheological modeling indicates that stirring-induced crystallization increases the melt viscosity by a factor of ~1.5-4.5 depending on the system temperature. At a given temperature, convective mass transport can therefore produce higher crystallinity (and higher viscosity) suspension. We document that if subsequent cooling occurs, the existing crystal cargo in such suspensions may promote the onset of non-Newtonian rheological response, causing a transition from homogeneous viscous flow to shear localization and magma/lava rupture.

## **Emplacement mechanisms of the high-grade Kencherra Ignimbrite (Central Main Ethiopian Rift)**

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*Keywords:* ignimbrite, field vulcanology, emplacement mechanism.

High grade, welded ignimbrites result of utmost interest for the understanding of the mechanisms and processes involved in the emplacement of these deposits. In this view, the Central sector of the Main Ethiopian Rift represents a highly valuable study area, since it hosts numerous examples of these deposits dispersed over a wide area and particularly well exposed along the numerous scarp faults of the rift.

In the present work we focus on the Lower Pleistocene “Kencherra Ignimbrite”, which can be considered an important marker bed within the volcanic stratigraphy of the investigated area. No detailed presentation of this ignimbrite deposit has ever been reported and within the present study we conducted field investigations, microscopic observations, density measurements, geochemical and geochronological analyses to provide a description of the stratigraphy and the characteristics of this Ignimbrite, shedding new light on the potential source and on the peculiar emplacement processes producing its diagnostic features. This rhyolitic ignimbrite crops out along the eastern margin of the rift, covering a minimum area of 1000 km<sup>2</sup> with a nearly constant thickness between 10-20 m. Its internal stratigraphy is defined by a characteristic sequence of facies, typified by lower and upper vitrophyres enclosing the main body of the ignimbrite. This is characterized by a pervasive, sub-horizontal foliation defined by laterally discontinuous parting planes clearly indicative of progressive aggradation and strain from a sustained current. Macro- and micro-scale strain indicators are abundant and well preserved in this facies of the ignimbrite, although in the absence of folding.

Being emplaced on a relative flat topography, with the main fault escarpments which now characterize the eastern margin postdating the Kencherra Ignimbrite emplacement, we can exclude the effects of topographically-induced rheomorphism in determining the well exposed deformative structures. Therefore, since all the observed structures can be attributed to the shearing imparted by the overriding particulate flow, the Kencherra ignimbrite represents an interesting and peculiar case to study the syn-eruptive sequence of agglutination, deposition and deformation which characterize the emplacement of high-grade ignimbrite deposits.

## **Formation and emplacement of a clastogenic lava flow: a case study from the May 18<sup>th</sup>, 2016 eruption at Mt. Etna volcano**

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*Keywords:* clastogenic lava.

On May 18<sup>th</sup>, 2016, Mount Etna was the scenario of an explosive eruption from the Voragine crater, which produced vigorous lava-fountaining. Following the filling of the Voragine and Bocca Nuova summit craters by the ejected pyroclasts, clastogenic lava overflowed from the lowered crater western rim, flowing down on the western flank of the volcano, and stopping at about 1800 m a.s.l. The rheological behavior of this clastogenic lava flow was described through a suite of high-temperature (1075 to 1100°C), uniaxial deformation experiments at a constant strain rate of  $10^{-4} \text{ s}^{-1}$  on selected natural samples (i.e., crystal- and vesicle-bearing), collected both in the crater area (loose scoriae samples) and in various portions of the lava flow (channels and lateral levees). The lava flow was also sampled at its front for what regards either the flow core or autobreccia clasts. Through textural analyses, a progressive change in the rheological behavior was recognized in agreement with the progressive increase in the vesicle content, which shows a maximum value for pyroclasts (56%) and varies from the inner part (18%) to the upper part (25%), reaching a minimum value in the intermediate portion (10%) of the lava flow. Preliminary rheological results show that samples deform within the brittle regime at a lower temperature, as a function of the internal vesicle texture of the collected samples. In contrast, with a minor temperature increase (25°C), ductile deformation dominates independently from textural features. Combined textural and rheological data confirm field observations of the 2016 clastogenic lava flow: due to sintering and compaction, a marked decrease in vesicle content from the pyroclasts to the overflowing zone promoted the lava viscous flow. Subsequently, the downflow porosity increase has favored the brittle behavior and autobreccia formation.

## The ballistic bomb field of the 1888-90 eruption of La Fossa volcano (Vulcano, Eolian Islands)

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*Keywords:* Vulcano island, eruptive dynamics, bread crust bombs.

Vulcanian eruptions are typically associated with the launch of different types of cm-to-m sized ballistic ejecta and, in particular, with the well-known breadcrust bombs. Consequently, these products represent not only a significant source of hazard affecting communities located in the volcano surroundings, but they are also a source of crucial information to interpret the complex dynamics of such eruptions. In particular, the study of the textural features of vulcanian bombs can help to solve the time-space evolution of the conduit stratigraphy and to shed light on the complex interplay between conduit processes (i.e. magma vesiculation, crystallization and fragmentation) that actively controls the unsteady dynamics of such eruptions.

In this study, we conducted extensive fieldwork and sampling in order to describe nature, grain size, and distribution of the ballistic products related to the 1888-1890 eruption at La Fossa volcano (Vulcano island, Aeolian archipelago). The whole summit of the Vulcano crater was investigated with a dedicated strategy aimed at reconstructing the spatial dispersal of the different types of bombs within each sector of the crater area.

As a result, the ballistic products showed significant variability in the morphological and textural characteristics, and six main types of bombs were identified: Dense blocks [D]; Breccia bearing Dense blocks [DBr]; three different sub-categories of Breadcrust bombs (thick crust [BcB-Tk], thin crust [BcB-Tn], vesicular rind [BcB-Vr]); Black Scoria bombs [S]. The different types show a not homogeneous dispersal across the crater area of La Fossa volcano. Moreover, the poorly vesicular lithotypes (D-blocks and DBr) largely dominate the total amount of ballistics (around 80 wt% of deposit), while the BcB only represent less than 20 wt% of the deposit.

All the bomb types were described in terms of external morphology, density, crystal content, vesicle size distribution, presence of glassy rind, internal foliation and type of vesicularity gradients.

These data were used to reconstruct a possible pre and syn-eruptive stratigraphy of the magma conduit of Vulcano and to monitor its time-space evolution throughout the long-lasting stage of ballistic production, that occurred during the 88-90 eruption at La Fossa volcano. This allowed us to interpret the dynamics of this long-lasting stage as mostly controlled by the repeated, partial failure of a high-viscosity and degassed magma plug, only occasionally punctuated by the occurrence of discrete pulses involving variably vesicular and deeper material.

## **A 4D reconstruction of magma movements into the Etna plumbing system throughout a decade of eruptions at the volcano**

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*Keywords:* Etna, paroxysmal eruptions, plumbing system dynamics.

The Etna South East Crater produced during December 2020 – February 2022 a sequence of sixty-two episodes of powerful lava fountains after nearly two years of continuous, though weak, explosive activity at the summit. With regard to the eruptions of the last decade, the observation of frequent changes in the eruptive style and shifts in the location of volcanic activity in the summit area poses the need of defining how the conditions of storage, transfer and interaction of magmas have changed over time. In this contribution, the whole rock, crystal and glass chemistry of tephra from the 2020-22 paroxysmal sequence have been inspected in the framework of the previous post-2011 volcanic activity in order to document the plumbing system evolution throughout the last decade. Thermodynamic modeling on whole rock has been combined with micro-analytical data on volcanic crystals and glasses to investigate the physical and chemical conditions of magmas involved and the kinetics of magma movements among the different levels of the plumbing system. The Fe-Mg compositional zoning of olivine crystals have been also analyzed and modelled by diffusion chronometry with the aim of identifying the ascent pathways of magmas through the volcano plumbing system and inferring temporal changes in conditions of magma accumulation, recharge and ascent driving the eruptions. Our constraints on the whole rock major element distribution over the whole decade indicate significant changes in storage and transfer dynamics starting from the eruptions at the crater Voragine on December 2015. The whole rock composition also highlights that the 2020-22 eruptions have been fed by the most basic magma emitted since 2011. Olivine zoning confirms the activation, during the first months of 2021, of the most basic magmatic environments characterizing the feeding system of Mt. Etna. This basic magma entered the intermediate (170 – 250 MPa) plumbing system of Mt. Etna throughout the 2021, driving volcanic periods of more frequent eruptions, as during February 16 – April 1 and May 19 – July 14, 2021. The entire dataset for the 2020-22 activity suggests patterns of magma ascent similar to those observed during the 2011-13 sequence, yet very different kinetics of processes. Indeed, timescales of magma movements associated to the first months of the 2020-22 paroxysmal eruptions are significantly faster than those registered during the 2011-13 for almost all the connections between magmatic environments (days to weeks vs. weeks to months, respectively), presenting conversely great similarities with the timescales of transfer leading to the powerful eruptions at Voragine during 2015-16 (days to weeks).

## Effect of magma–carbonate interaction on the viscosity of a phonotephrite melt from Vesuvius (Italy)

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*Keywords:* melt physics/chemistry.

The effects of crustal contamination on magma evolution and differentiation have been well documented, particularly during the assimilation of carbonate/dolomite where a multi-reaction zone advances from the carbonate wall-rock towards the innermost of the magma chamber.

Here we present a set of viscosity measurements exploring the effect of variable degrees of carbonate assimilation on the melt viscosity ( $\eta$ ) of a phonotephrite from Vesuvius (Italy). The starting material was doped with different amounts of CaO and CaO+MgO to mimic the effects of progressive limestone and dolomite assimilation, respectively. The high and low temperature liquid viscosity of the investigated melts were measured by concentric cylinder viscometry (CC) and differential scanning calorimetry (DSC), respectively. Melt fragility ( $m$ ) was also measured using Brillouin technique.

The viscosity data show non-Arrhenian trends, well described by both Vogel-Fulcher-Tammann (VFT) and Mauro-Yue-Ellison-Gupta-Allan (MYEGA) equations, with trends differing between high-T, low- $\eta$  and low-T, high- $\eta$  conditions. In the high-T regime, all contaminated melts show lower viscosity than the pristine melt, with the effect being more pronounced when only CaO is added. The opposite trend is observed in the low-T regime, due to different fragility of the investigated melts.

Recent predictive viscosity models reproduce the high-T, low  $\eta$  or low-T, high  $\eta$  regimes well, but do not perform simultaneously well over the entire temperature range investigated. This discrepancy seems to be due to the fact that the calibration data used to constrain viscosity models do not include Si-poor, Ca-Mg-rich compositions as those arising from extensive calcite and dolomite assimilation.



## The deep volcano-tectonic structure of the Campi Flegrei caldera by magnetotelluric survey

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Keywords: Campi Flegrei Caldera, volcano-tectonic features, magnetotelluric survey.

Electromagnetic imaging can proficiently detect deep structures in volcanic environments. A short-period magnetotelluric (MT) survey has been performed in the central-eastern Campi Flegrei volcanic environment, crossing the caldera through the main, recent volcano-tectonic structures and intersecting the most active sector of the Solfatara-Agnano zone (Isaia et al., 2021; Troiano et al., 2022). The survey involved about 100 measurement sites whose inversion produced a 3D resistivity imaging, which identified the electrical pattern of the investigated structure down to a depth of 2.5 km below sea level, highlighting several electrical resistivity anomalies related to distinct processes and physical conditions in the system. The model represents the first three-dimensional image of the first few kilometers of the central sector of the Phlegraean area. Results have been interpreted taking into account the geological, volcanological and structural features reconstructed through field and borehole data, highlight the main volcano-tectonic structures partly hypothesized by previous shallower electrical surveys by describing their development in depth. The electromagnetic reconstruction of the volcano's internal structure points out the geometry of the main structures for the ascent of magma and magmatic fluids, at least below a large continental portion of the caldera. The preliminary picture of the electrical resistivity distribution with depth suggests that the CF caldera was formed by distinct volcano-tectonic collapse structures with a shallower geothermal system well developed below the Solfatara-Agnano area fed by a deeper source. The primary fault system, acting as a preferential pathway for magmatic fluids, is also identified. The resistivity model allows (i) to constrain the main electromagnetic features of the caldera and (ii) to delineate significant clues about its structural setting. This new picture represents a relevant contribution furnished by MT observations for hazard assessment at Campi Flegrei and can enhance the modeling of the driving mechanisms of the ongoing unrest as well provided crucial information for the formulation of scenarios related to possible impulsive events such as hydrothermal and phreatic explosions in the Solfatara-Pisciarelli area.

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Troiano A., Di Giuseppe M.G. & Isaia R. (2022) - 3D structure of the Campi Flegrei caldera central sector reconstructed through short-period magnetotelluric imaging. *Scientific Reports*, 12, 20802. <https://doi.org/10.1038/s41598-022-24998-6>.

## Geochemical and petrological characterization of two large silicic ignimbrites from the Main Ethiopian Rift (Ethiopia)

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*Keywords:* Main Ethiopian rift, large silicic eruptions, Daly gap.

The Plio-Pleistocene volcanism in the Main Ethiopian Rift (MER) is characterized by distinctive bimodal compositions with basalts and rhyolites as the most abundant and scarce or absent intermediate terms (i.e., Daly gap). The mafic products are associated with cinder cones and lava flows while the felsic magmas produced large explosive eruptions often resulting in the formation of large calderas. This work focuses on these highly evolved compositions, the genesis of which still represents a matter of debate, with interpretations ranging from pure fractional crystallization to more complex scenarios involving magma mixing and crustal melting. We conducted analyses of two Central MER large silicic units with similar age and petrological characteristics: the 1.16 Ma Golja ignimbrite (GI) and the 1.3 Ma Kencherra ignimbrite (KI). The two units are remarkably crystal-poor with less than 10% of K-feld, qtz, pl, cpx, aen and Fe-Ti oxides and contain different types of juvenile material including white and banded pumices and fiamme, as well as dark scoria.

In GI detailed analysis of matrix glass and melt inclusions from all juvenile types reveal a broad compositional spectrum ranging from basalts (found only in the pl-hosted melt inclusions) to rhyolites, with intermediate compositions (basaltic trachyandesites to trachydacites) present in the mingled pumices and dark scoria. Trace element plots show distinct evolutionary trends, not visible in major element compositions, while in-situ <sup>87</sup>Sr/<sup>86</sup>Sr analyses of feldspars display wide isotopic variation ranging from mantle-like to crustal values, akin to the Pan African crust. In the KI welded pyroclastic sequence, matrix glass and fiamme have rhyolitic composition while scoriaceous clasts, increasing in size and abundance up-sequence, range between trachybasalts and trachytes. Two different groups of rhyolites can be distinguished based on incompatible trace elements and REE concentrations.

Overall, geochemical and isotopic data suggest involvement of fractional crystallization, assimilation of old crustal material and magma mixing in petrogenesis of the intermediate and evolved composition from KI and GI. Our data represent the first geochemical characterization of these large ignimbrites and contribute to a better understanding of silicic magmatism in the Central MER.

## A deep CO<sub>2</sub>-rich magma reservoir beneath Fogo volcano

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**Keywords:** un-degassed mantle source, Cape Verde Archipelago, magma plumbing system.

Volatile components play a critical role in the control of physical and chemical characteristics of magma (e.g., density, viscosity). Understanding the pre-eruptive volatile contents in the magma is critical to volcano monitoring and volcanic hazard assessment and risk mitigation. Here we use the silicate melt inclusions (MIs) hosted in olivine phenocrysts (Fo<sub>80-85</sub>) of basanitic (SiO<sub>2</sub> ~42 wt.%, MgO ~5 wt.%) and alkali-rich (Na<sub>2</sub>O + K<sub>2</sub>O ~7 wt.%) tephra samples of Fogo volcano, Cape Verde Archipelago, to (i) quantify parental melt volatile contents, and volatile evolution along the different magma plumbing system levels; (ii) constrain the magmatic source, and the rates/modes of magma ascent prior and during the eruptions; (iii) model magmatic degassing.

Our results reveal high concentrations of dissolved volatiles in the parental un-degassed magma, in particular the CO<sub>2</sub> content, averagely 2.0 wt.%. The ratios between CO<sub>2</sub> and trace elements (CO<sub>2</sub>/Nb = 224-558; CO<sub>2</sub>/Ba = 24-52; CO<sub>2</sub>/Sr = 18-43) are representative of an un-degassed mantle source signature. We used different H<sub>2</sub>O-CO<sub>2</sub> solubility models to model melt-volatile contents along the decompression path at T-fO<sub>2</sub> conditions relevant to Fogo volcano. Converting total CO<sub>2</sub> contents into saturation pressures, we obtain the deepest saturation pressures of 1388 MPa (42465 ppm), that combined with previous independent barometric results, highlights a deep magma reservoir at ~40 km depth where the CO<sub>2</sub> saturation starts beneath Fogo. Our novel results are the first to demonstrate (i) the deepest Fogo magma reservoir and (ii) an unusual CO<sub>2</sub>-rich mantle source, which feeds the alkali-rich mafic melts of the intraplate volcanism at Cape Verde.

## **Dynamics of Campi Flegrei caldera (Italy) after the 1538 AD eruption**

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*Keywords:* Campi Flegrei, subsidence, eruption.

Understanding how shallow magma transfer occurs at volcanoes is important to have a conceptual model of how a volcano works and, possibly, to forecast where and when an eruptive vent may open. However, shallow magma transfer is difficult to detect at poorly monitored volcanoes, and particularly at calderas, characterized by areal volcanism. Magma transfer before the last 1538 eruption at Campi Flegrei caldera (Italy) was previously studied using historical, archaeological, and geological data. Here, we extend that dataset to 1650, to uncover any magma transfer during overall post-eruptive phase. Results highlight two post-eruptive subsidence phases, separated by a previously undocumented uplift during 1540-1582. Uplift highlights the pressurization of the central (~3.5 km depth) and peripheral (~1 km depth) pre-eruptive sources, suggesting an aborted eruption. The subsidence events are explained by the depressurization of the central source and pressurization of a deeper magmatic layer (~8 km depth). Therefore, despite the overall post-eruptive deflation, after 1538 the deeper reservoir experienced continuous magma supply, with magma almost erupting between 1540-1582, challenging the common assumption of post-eruptive relaxation. This underlies the importance of monitoring the deeper magmatic systems, also after eruptions, to properly assess their eruptive potential.

## Pre-eruptive conditions of the Tajogaite cone eruption in Cumbre Vieja ridge (La Palma, Canary Islands)

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*Keywords:* Canary Islands, eruption, magmatic chamber.

Tajogaite is a monogenetic volcano located in the municipality of El Paso in Cumbre Vieja ridge of La Palma in the Canary Islands. Its latest eruption, characterized by Strombolian activity, is the longest historical eruption recorded on the island. It started on September 19, 2021, and lasted for 85 days until it stopped on December 13, 2021. In order to constrain the pre-eruptive conditions of the shallow reservoir of Cumbre Vieja volcanic ridge, located between 8 and 12 km depth (D'Auria et al., 2022), thermodynamic simulations and phase equilibria experiments were combined. The starting materials used are a combination of a natural rock from a lava flow that erupted on October 2, 2021 (Romero et al., 2022) and a series of analogous synthetic compositions with variable water content (1, 3, and 5 wt% H<sub>2</sub>O). The experiments were performed in the temperature (*T*)/water content (wt% H<sub>2</sub>O) space at 275 MPa, and the results show that i) olivine crystallizes between 1175 and 1150°C and clinopyroxene between 1125 and 1100°C for water contents up to 1 wt%; ii) olivine crystallizes at lower temperatures for higher water contents. More specifically, in experiments with 3 wt% H<sub>2</sub>O, olivine crystallizes between 1125 and 1100°C, whilst for experiments with 5 wt% H<sub>2</sub>O at temperatures less than 1000°C; iii) clinopyroxene crystallization is always in the temperature interval 1125-1100°C, and remains unaffected by the changing water content; iv) water contents play a significant role in the crystallization of oxides (Cr-spinel and Ti-magnetite), as Cr-spinel is stable at high temperature and water contents up to 3 wt%, whereas Ti-magnetite is present in the run performed with the highest water content added, as well as in the one performed at 1000°C with 1 wt% H<sub>2</sub>O added; v) amphibole and apatite crystals were solely observed in the sample obtained at temperature of 1000°C and water content of 1 wt%. The mineralogical assemblage produced in the experiments is similar to the natural one (Pankhurst et al., 2022). The experimental results and the observed natural mineralogical assemblage were partially reproduced with Rhyolite-MELTS simulations. Additionally, the Rhyolite-MELTS simulations places the stability field of amphibole at pressures higher than 400 MPa. Thus, the reaction rims observed in the natural amphiboles, as described by Pankhurst et al. (2022), are indicative of the disequilibrium conditions during magma ascent at pressures lower than 400 MPa. Moreover, the formation of natural plagioclase microlites (<50 μm) in the groundmass is expected at low pressure (<20 MPa) and temperature in the range 1050-1140 °C, suggesting that plagioclase microcrystals are associated with magma ascent within the shallow part of the conduit, and/or with the cooling of the erupted lava outside the vent.

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## Highly explosive ancient eruptive activity at Stromboli (PaleoStromboli I, 85-75 ka) triggered by sudden changes in the pre-eruptive dynamics

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*Keywords:* basaltic explosive eruptions, collapse-drive eruptions, magma plumbing systems.

The trigger and explosivity of a volcanic eruption are mainly related to the relationships between regional tectonics, volcano-tectonic activity and the magma input rate from depth. At mainly constant magma input rates, the occurrence of some shallow dynamics such as sector collapses, landslides, caldera-forming eruptions and the opening/closure of conduits are able to generate and regulate eruptive mechanisms finally leading to an increased explosivity of eruptions (i.e., top-to-bottom trigger mechanisms). A variable magma input rate from the source is also able to regulate eruptive dynamics, as it can promote extreme differentiation processes and/or magma mixing/mingling in the shallow portion of the magma feeding system, finally leading to an increased explosivity and energy of eruptions (i.e. bottom-to-top trigger mechanisms). This is the case of the ancient volcano-stratigraphic succession at Stromboli, where is noticed in literature a period of unusual high-energetic explosive eruptions, likely to be associated to (partially/totally) closed conduit dynamics.

Here we present a new detailed and stratigraphically-constrained study of the Petrazza eruptive cycle, belonging to the PaleoStromboli I eruptive epoch (85-75 ka) and outcropping on the south-eastern flanks of the island of Stromboli. A multi-disciplinary approach embracing whole rock, mineral compositional and textural studies and geobarometry confirm initial conditions of closed conduit system, allowing an extensive differentiation of magmas and the crystallization of amphibole. High-intensity explosions are then triggered by the input of hotter and more mafic magma, which partially and gradually substituted the residing one in the intermediate/shallow portions of the feeding system, leading to “classical” open-conduit eruptive dynamics. At the end of the sequence an event of extreme decompression of the magma feeding system, here related to a structural collapse of the volcanic edifice whose deposits are still visible within the sequence, triggered a rapid magma ascent at water undersaturated conditions and an high-energetic explosive eruption, assumed as the larger for the Stromboli volcanic system.



## CO<sub>2</sub> and magma remobilization

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*Keywords:* CO<sub>2</sub>, mush, magma.

Magma remobilisation is the process by which magma is reactivated and mobilised within a mush system. A mush system is a partially molten mixture of a solid crystalline matrix and interstitial liquid, typically involving the solidification of a magmatic system. Magma remobilisation can occur in a variety of ways, including the injection of new magma into an existing system due, for example, to the upward migration of hot buoyant magma from deeper levels, or the mechanical deformation of the solid matrix that allows previously trapped interstitial liquid to become mobile. Another mechanism may involve volatile fluxing, mainly CO<sub>2</sub> exsolved from larger depths. In a mush system, the process of magma remobilisation can lead to changes in the system's crystal content and texture, as well as changes in the chemical composition of the magma. Overall, understanding the processes involved in magma remobilisation in mush systems can shed light on the complex dynamics of magmatic systems and their associated hazards.

Here I show under which thermodynamic and chemical constraints CO<sub>2</sub>-fluxing may promote remobilization of shallow magma batches, such that volcanic hazard may be extremely high because associated with the remobilization of apparently inactive magma batches. In contexts where discharged fluids come essentially from deep magma reservoirs, the possibility of rapid and abrupt remobilization of shallow magma batches in a mush system cannot absolutely be discarded, even if such shallow batches do not appear to be involved in melt-fluid exchanges and are then ruled out as possible sources of the fluid either discharged at surface or infiltrating hydrothermal systems. The implications of rapid shallow magma remobilization are then discussed with reference to Campi Flegrei, where the active source of magmatic fluids is shown by many research groups to be at least 8 km deep. Any scenario which considers that the eruptible magma is the deep magma sourcing CO<sub>2</sub>-rich fluids upward may seriously be underestimating the volcanic hazard, independently of any consideration about magma ascent times.

## **Volcanism at the spreading ridge of the Marsili back-arc basins (Southern Tyrrhenian Sea, Italy) as highlighted from a new high resolution Digital bathymetric model**

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*Keywords:* marsili, back-arc spreading ridges, submarine volcanism.

The mechanisms of growth and formation of back-arc spreading ridges are comparatively less known with respect to those of Mid-Ocean Ridges because geophysical, geochemical, and morphological data are scarce and of low density. Here we present a high-resolution (5 m resolution) bathymetry of the Marsili Seamount (MS; 1 Ma-3 ka), which represents the inflated spreading ridge of the 2 Ma old Marsili back-arc basin formed on a 10 to 12 km thick oceanic crust and associated to the subduction of the Ionian Sea below the Calabrian Arc and Tyrrhenian Sea (Italy). MS is a 70 x 20 km extended, NNW-SSE elongated volcanic complex rising 3200 m from the seafloor of the Southern Tyrrhenian bathyal plain. MS last erupted 2-3 ka BP, and it is now characterized by shallow seismicity and hydrothermal activity.

The here-presented new digital bathymetric model has a 5 m grid cell size resolution and covers the MS bathymetry from 1670 m b.s.l. to its top at 491 m b.s.l.. The new model allowed us to: (a) identify the detailed features of volcanological, morphological and geological features and (b) better understand how volcanoes, overlapping and/or segmented spreading centres, and faults interact and control the growth and evolution of back-arc basins ridges. The morphometric and morphological analyses of the bathymetry led us to recognize landforms due to volcanic, tectonic, hydrothermal and gravity processes. We relate the morphology of MS, which resembles that of fast-spreading ridges, to the progressive addition of a subduction-related component to a pure spreading mantle source.

Our results emphasize the importance of high-resolution bathymetry data in deciphering the geodynamic evolution of back-arc basins. The results may also help to individuate sites of hydrothermalism and identify areas where landslides or flank/sector collapses occurred in the past and, eventually, could develop in the future.

## **Application of photogrammetry processing to understand the structure of the Fremrinamar Fissure Swarm, Northern Volcanic Zone, Iceland**

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*Keywords:* Fremrinamar Fissure Swarm, rift zone, photogrammetry processing.

We present a study focused on the characterization of the Fremrinamar Fissure Swarm (FFS), one of the seven volcanic systems of the Northern Volcanic Zone, a tectonically and volcanically active area that accommodates the plate spreading in Northern Iceland. The FFS has a length of 130 km and a width between 8 to 9 km. Given its dimension, it was necessary to combine field surveys with remote-sensing methodologies to obtain a clear and comprehensive depiction of the main structures that characterize the area.

We performed photogrammetry processing through Agisoft Metashape (v. 1.7.1), using 983 historical aerial photos, freely available from the National Land Survey of Iceland. These images were acquired in three different years (1983, 1990, 1991), and have the same overlap value (60%) and the same flight elevation (5486 m a.s.l). We obtained three Digital Surface Models (DSMs) and three orthomosaics with a maximum resolution of 2.07 and 0.52 m/pixel respectively. For both photo alignment and dense cloud processing, we tested different quality parameters, identifying a medium one as the best compromise between good-quality results and relatively short processing times. The geometry of the rift zone was depicted in a GIS environment at a 1:50,000 scale. Normal fault scarps were distinguished from extension fractures and classified into E- and W-dipping through orthomosaics and shaded DSMs. Eruptive fissures were identified by the nearby presence of volcanic deposits or through the morphometric analysis of eruptive centers. Length and azimuth values were determined, followed by the extrapolation of the X and Y coordinates of the structures' mean points. For normal fault scarps with a total length > 2 km, slip profiles were collected to evaluate the overall along-axis rift propagation of the FFS. Field surveys were performed on key areas to validate the classification obtained from the remote-sensing analysis and to verify length and azimuth values.

We identified 146 eruptive fissures, 1128 extension fractures, and 766 normal fault scarps. The entire dataset of structures shows an overall strike of N-S to NNE-SSW. The highest length values (up to 14.2 km) were generally associated with normal faults. Slip profiles of 74 normal fault scarps showed that they generally tend to propagate northward. We interpreted this as the effect of lateral propagation of dykes towards the North from the magma chamber below the Fremrinamar central volcano located in the southernmost part of the FFS. This is supported by the increase in rift width north of the central volcano, the concentration of eruptive fissures around this area, and the northward decrease in the total number of structures.

## Experimental constraints on crystallization of alkaline basalt melt in presence of pre-existing phases

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*Keywords:* crystallization/dissolution experiments, open system crystallization, alkaline magma.

Time-series crystallization/dissolution experiments were conducted on a natural potassic basalt to study the evolution of a magmatic system towards new conditions of physical and chemical equilibrium induced by the incorporation of pre-existing crystals. Experiments were performed at the fixed cooling rate/heating of 100°C/hour, at atmospheric pressure, in air, at temperatures ranging between 1180 to 1240°C and dwell time up to 20 hours. The charges were seeded with homogeneous bytownitic plagioclases (An<sub>76-78</sub>). Crystallization experiments show that the initial nucleation behavior of the melt is influenced by the presence of plagioclase seeds by promoting the early formation of new plagioclases whereas they overgrow, dampening the clinopyroxene crystallization. Plagioclase microlites tend to be equant in habit already in the early stage of crystallization growing at a rate of 10<sup>-6</sup> cm·sec<sup>-1</sup> during the cooling step, and 10<sup>-7</sup> cm·sec<sup>-1</sup> to 10<sup>-8</sup> cm·sec<sup>-1</sup> as the dwell time increases. Seeds overgrown at similar rate. Depending on undercooling (DT = 5 - 45°C), the clinopyroxene appears after a lag time of at least 3 hours under isothermal experimental conditions, producing a significant impact on the composition of both the residual melt and newly plagioclases. For undercooling higher than 35°C the clinopyroxene delay causes a strong supersaturation of this phase in the basalt that results in a sharp decrease of the plagioclase microlite nucleation and a fast attainment of a high crystallinity during the first 3 hours at isothermal conditions. The coarsening and growing of clinopyroxene, along with the decreasing of crystallinity in the 15 hours experiments appear related to the achievement of a near-equilibrium conditions. Clinopyroxene growth rate is estimated to be in the order of 10<sup>-7</sup> cm·sec<sup>-1</sup> showing very limited variation for the investigated experimental DT and durations (3 - 15h). Finally, the variation of the melt composition due to plagioclase seed dissolution is already detectable in experiments lasting 3 hours for the investigated superheating of 5-15°C. The dissolution rates estimate from the long lasting experiments is in the order of 10<sup>-9</sup> cm·sec<sup>-1</sup> remaining virtually constant as the experimental dwell time increases from 10 to 20 hours. The two orders of magnitude lower of estimated values than those determined by other authors for this mineral in the same lava sample for similar temperatures and resting times probably reflect the difference in plagioclase seed composition closer in our experiments to that of plagioclase on equilibrium with the natural potassic basalt.

The set of our results suggests that in natural systems, the takeover of antecrysts by a magma can induce changes in its initial nucleation behavior on a short time scales, with remarkable petrological implications for the solidification paths and eruptive dynamics of potassic basaltic magmas.

## **Magma dynamics and surface phenomena interactions at Mt. Etna (Italy) from InSAR and GNSS observations**

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*Keywords:* Etna Volcano, ground deformation, remote sensing.

Deformation measurements of volcano edifices and the pattern analysis of their evolution in space and time are fundamental to understand and constrain the volcanic dynamic. Given the large data availability and the numerous volcanic, seismic, and gravitational phenomena, Mt. Etna is one of the more studied and fascinating volcanoes worldwide. More than 30 permanent GNSS stations measure his surface deformation, monitoring deformation phenomena related to shallow and deep magma dynamic or flank slidings. In addition, the free availability of satellite SAR images from Sentinel1 sensors, allows us to reconstruct the recent deformations related to the volcanic and seismic events. We processed and analyzed GNSS time series and InSAR dataset from January 2015 - March 2021 period. We observe a spectacular velocity modulation of the superfast seaward motion of the eastern flank, superimposed to the large scale inflation and deflation displacement pattern. Rare flank motion reversal indicates that short-term contraction of the volcano occasionally overcomes the gravity-controlled sliding of the eastern flank. Oppositely, fast dike intrusion guided the acceleration of the sliding flank, potentially evolving into sudden collapses, fault creep, and seismic release. Thus, ground deformations are crucial for short term scenario determination and forecasting of the quantity of magma accumulating within the plumbing system.

## Timescale of emplacement and rheomorphism of the Green Tuff ignimbrite (Pantelleria, Italy)

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*Keywords:* ductile deformation timescales, welding, rheomorphism.

We present a multidisciplinary study based on Differential Scanning Calorimetry (DSC), paleomagnetic analysis, and numerical modeling to gain information on the timescales of syn- and post-depositional ductile deformation of the strongly welded and rheomorphic Green Tuff ignimbrite (GT; Pantelleria, Italy).

DSC measurements allow the determination of glass fictive temperatures ( $T_f$ ; i.e., the parameter accounting for the cooling dependence of glass structure and properties). Using a  $T_f$ -based geospeedometry procedure, we infer the cooling rate ( $q_c$ ) experienced by the glassy phases in different lithofacies within the GT formation. Glass shards from the basal pumice fall deposit record a fast  $q_c$  of  $\sim 10^\circ\text{C/s}$ . In contrast, the ignimbrite body returns slow  $q_c$  values depending on the stratigraphic position and lithofacies (basal/upper vitrophyres, *fiammae*-rich and rheomorphic layers), ranging from  $\sim 10^{-2}$  to  $\sim 10^{-6}^\circ\text{C/s}$ . Moreover, paleomagnetic analyses of the natural remanent magnetization of ignimbrite matrix and embedded lithic clasts indicate an emplacement temperature higher than 550-600°C.

By integrating calorimetric and paleomagnetic datasets, we constrain a conductive cooling model, describing the temperature-time-viscosity ( $T-t-\eta$ ) evolution of the ignimbrite from the eruptive temperature to below  $T_f$ . Outcomes suggest that the upper and basal vitrophyres form and deform over hours, highlighting the entire GT underwent intense syn- depositional ductile deformation (from macro- to the micro-scale). In addition, the central/upper body remains above  $T_f$  for a much greater timespan (>1 month), allowing for post-emplacement rheomorphic flow.



## Plagioclase textural and compositional parameterization: A tool for tracking magma dynamics at Stromboli

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*Keywords:* plagioclase, Stromboli, paroxysm.

The Present-day (<1.2 kyr) activity of Stromboli (Aeolian Islands, Southern Italy) is characterized by periodic and mildly explosive “Strombolian” eruptions alternating with episodic lava effusion and more violent eruptive events (i.e., major explosions and paroxysms). The plumbing system controlling the eruptive behavior is fed by a vertically-extended mush column in which the shallow magmatic reservoir (highly porphyritic or *Hp*-magma) is continuously refilled with mafic magmas (low porphyritic or *Lp*-magma) rising from depth. Currently, we are investigating the textural and compositional attributes of plagioclase phenocrysts and microlites from nineteen scoria clasts ejected during mild to violent explosions at Stromboli over a timespan of ~18 years, from 2003 to 2021. The morphological stability of large-sized, euhedral phenocrysts is superimposed on an internal textural heterogeneity due to growth-dissolution phenomena associated with the input rate of hot, H<sub>2</sub>O-rich recharge magmas rising from depth. As a result, the volumetric plagioclase proportion, dominant size, and number of phenocrysts per unit volume decrease from mild to violent explosions, responding to a more efficient magma mixing process via sustained injections of mafic magmas into the shallow reservoir. Crystallization of hybridized recharge basaltic melts is faithfully recorded by intracrystalline major-trace element and Sr-isotope variations in plagioclase phenocrysts, providing temporal and spatial constraints on crystal recycling and mush remobilization phenomena. On the other hand, the formation of anhedral plagioclase microlites is controlled by fast growth kinetics taking place in the uppermost part of the conduit during magma acceleration towards the surface. Under such highly dynamic crystallization conditions, the microlite number density closely depends on the increase of melt liquidus temperature via magma decompression and H<sub>2</sub>O exsolution. This mutualism allows to model the degassing rate and ascent velocity of magma under open-conduit flow regimes for the different eruptive styles, thereby supporting the idea that violent explosions at Stromboli are driven by sustained influxes of recharge magmas leading to strong acceleration, decompression, and H<sub>2</sub>O exsolution before magma discharge at the vent.

## The evolution of the long-lived Ollagüe volcano, Central Andean Volcanic Zone: Volcano construction from central to lateral activity and destruction by sector collapses

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*Keywords:* Andes, flank collapse.

Volcanic landscapes result from the interplay of alternate phases of construction and destruction. The construction of composite volcanoes may result from temporal and spatial vent-growth relations, while destruction processes such as sector collapse may profoundly influence the growth and evolution of large volcanoes. These modifications of the external morphology can largely and suddenly modify the mass distribution above shallow magma reservoirs, leading to shifts in the style, rate, composition, or distribution of post-collapse eruptions. The Ollagüe volcano is an active and mainly effusive center located along the Chile - Bolivia border in the Central Volcanic Zone of the Andes. It is a long-lived, 1,259 ka to present, and multiple-collapsed volcano, developed along an NW - striking extensional fault belonging to the Pastos Grandes - Lipez - Coranzuli regional fault system. In this contribution, we present a new evolutionary scheme for the volcano based on detailed field-based mapping, accompanied by morphological and morphometric analysis, petrochemical data, and a new large radiometric dataset. From a morphological and volcanological perspective, the volcano comprises the products of an old and eroded cone dominated by central activity on the northern and eastern flanks. The southern to northwestern portions of the edifice record the youngest activity, with growth-destructive cycles due to catastrophic flank collapses and a dynamic shift of the activity from central to lateral mid-flank vents and vice versa. Based on field observations and satellite-DEM based analysis, we identify at least three debris-avalanche events deposits with their classical hummocky morphology. In addition, we recognize two debris avalanche deposits (DADs) in the western flank of the volcanic edifice, each followed by a lateral blast explosion, challenging the proposed origin and unique debris-avalanche nature of the deposit emplaced in the Salar de Carcote Basin. Also, we characterize the morphology and quantify morphometrical parameters for hummocks from all the DADs, analyzing their spatial distribution around the volcano and their relationships with their lithofacies and internal structures. Spatially and petrographically, the Ollagüe lavas can be divided in two main groups. The first comprises andesitic lavas from the old cone and some post-collapse lateral flows with a modal composition of two pyroxenes with scarce amphibole and biotite. The second group corresponds to the northwestern lava flows, lateral parasitic domes, and youngest post-collapse domes, with their associated block and ash deposits. It is characterized by an assemblage dominated by amphibole and biotite with only minor pyroxene. In general, volcanic activity typically occurred following the main flank collapses in response to reorganizing shallow crustal magma reservoirs within the volcanic edifice.

## Crystal chemical textures record plumbing system dynamics as modulated by ice load - The Pleiades Volcanic Complex, Antarctica

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Keywords: plumbing system, volcano ice load, Antarctica.

The timing of volcanic eruptions in glaciated terrains is potentially modulated by climate-controlled variations in the glacio-lithostatic load, that modify the failure conditions around magma chambers. Thus, rising magmas will experience extended residence times in the crust during glacial periods, which allow them to crystallise, differentiate and accumulate volatiles over longer times to a greater extent at higher pressure.

In Antarctica, volcanic activity is occurring since the Miocene in several glaciated regions. In northern Victoria Land, volcanism occurs on both thick and attenuated cratonic lithosphere, linked to Cenozoic rifting processes. The Quaternary complex of The Pleiades sits on thick lithosphere and is made up of some 20 monogenetic, partly overlapping cinder cones, that erupted during the last 900 ka.

Erupted products define a complete mildly Na-alkaline differentiation trend. Mafic samples have OIB within-plate affinity and variable radiogenic isotopic ratios supporting the hypothesis of open-system evolution, with significant crustal assimilation during fractional crystallization. The occurrence of a complete fractionation trend coupled with large assimilation rate is unusual, if not unique, among alkaline monogenetic volcanic fields. Textures investigated by FE-SEM-BSE are commonly complex, therefore laser ablation ICP-MS spot analyses and mapping have been coupled with EMPA analyses. Olivine crystals are commonly unzoned and embayed, while the high- $F_0$  cores in mafic samples are invariably slightly embayed and rimmed with strong, continuous normal zoning. Clinopyroxene usually presents spongy cores, with scattered occurrences of low Mg# zones, often mantled by high-Mg and high-Cr bands. Alkali feldspar is usually reversely-zoned and often shows a coarse to fine sieve texture. Machine-learning thermobarometric estimates figure out a P-T crystallisation path of magma rising adiabatically from the crust-mantle interface up to the upper crust, then stalling in what is probably the main plumbing system where it starts to cool off.

The petrological observations coupled with the thermobarometric estimates suggest that these magmas experienced a long residence time in the upper crust, building up a complex plumbing system by magma refilling episodes. Then, the arrival in the system of a rather primitive and volatile-rich magma batch probably triggered the eruption(s).

The long time of residence, continuous differentiation and refilling of an unusually large plumbing system could have been modulated by the variability of the overlying ice load. Finally, it is likely that unloading of the ice cover would have facilitated the eruptions.

## **OH-defects and trace element content in magmatic quartz of the Sesia Magmatic System (Southern Alps, Italy): characterization by FTIR and LA-ICP-MS**

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*Keywords:* magmatic quartz, OH-defect, trace element.

Quartz is a major constituent of upper crustal, felsic igneous rock (e.g., granites) and can incorporate significant amounts of trace elements in its crystal lattice (Li<sup>+</sup>, Al<sup>3+</sup>, B<sup>3+</sup>, Ti<sup>4+</sup>, Ge<sup>4+</sup>, etc.) through a variety of isoivalent to Si<sup>4+</sup> and coupled substitutions (i.e., Si<sup>4+</sup> ↔ Al<sup>3+</sup> + H<sup>+</sup>). In this latter case, participation of hydrogen in the substitution mechanism can lead to the formation of hydroxyl dipoles (OH) with the oxygen anions from the quartz lattice (Potrafke et al., 2020). In magmatic quartz, incorporation of trace elements and OH-defects formation is controlled by melt physio-chemical parameters (temperature, pressure, composition, and water activity). Their relative abundance has been proposed as a sediment provenance tool in detrital studies (Stalder & Neuser, 2013), however literature still lacks detailed studies on OH-defects distribution at the scale of an entire magmatic system.

Here we present the results of a systematic study on the variation of OH-defects and trace element contents in magmatic quartz of a well-studied crustal section exposed in the SW Alps, which include the plumbing system of a large caldera (Sesia Magmatic System) (Sinigoi et al., 2010). Quartz grains were sampled across a floor-to-roof section of the Valle Mosso pluton (granitic intrusion) and within two rhyolitic units of the Sesia Caldera. In this study, a total of 120 quartz grains have been analysed using Fourier Transform InfraRed (FTIR) spectroscopy to investigate hydrous defects both qualitatively (defect species) and quantitatively (defect water content). LA-ICP-MS was then applied to the same crystals in order to determine trace element content.

Textural and geochemical evidence of the Valle Mosso pluton indicate that this intrusion constituted a single, zoned magma body, with a crystal-rich base and a thick (~3 km), high-silica cap (up to ~77 wt% SiO<sub>2</sub>) (Tavazzani et al., 2020). We observe a gradual increase of total defect water content with stratigraphic height, in parallel with the degree of differentiation in the intrusion. The amount of Li incorporated in the quartz lattice is strongly anti-correlated with the abundance of OH defects, however the cumulate, basal unit of the intrusion shows a stark decoupling of Li and OH defects, suggesting an additional process that controls the diffusion of hydrogen outside the crystal lattice.

Overall, the composite OH-defects and trace element stratigraphy preserved in rocks of the Sesia Magmatic System represents a primary magmatic signal, providing an additional tool to unravel the cryptic processes of crystal accumulation and melt segregation in upper crustal silicic bodies.

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**S43.**

**Progetto METIQ-mare: a new view of the Quaternary  
Geology of the Italian Seas**

*CONVENERS AND CHAIRPERSONS*

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## The METIQ Project – The North-Western Sicily offshore area

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*Keywords:* marine geomorphology, submarine canyon, Southern Tyrrhenian Sea.

In the framework of the geological national METIQ Project (Evolutionary Model of the Italian Territory in the Quaternary), a wide marine area offshore north-western Sicily has been analysed and mapped to highlight the Quaternary morphological, sedimentary and tectonic features. The study area has been investigated by means of data coming from previously published papers and from swath bathymetry, side-scan-sonar and seismic reflection surveys formerly recorded.

The investigated area shows a very variable physiographic setting, because it develops across the southern Tyrrhenian border encompassing continental shelf to continental slope sectors (Sulli et al., 2012) and where several intra-slope basins and seamounts are located. This area is separated from the southern Tyrrhenian bathyal plain by a prominent, east-west trending ridge (Elimi Chain) made up by both volcanic (Ustica, Anchise, Aceste) and structural relieves (Drepano Smt).

The overall morpho-structural setting (Agate et al., 1993) reflects the results of severe shortening recorded by the Sicilian (African) continental crust during the late Tertiary to Quaternary Sicilian-Maghrebian orogeny; episodes of tectonic subsidence also occurred during the Plio-Quaternary, resulting in the formation of the major bathymetric lows, up to a couple of thousand meters deep, that are currently recognizable across the continental slope. This articulated morpho-structural setting has strongly controlled the pathways of terrigenous sedimentary supply: sediments coming from Sicily mainland feed littoral to neritic depositional systems growing along the northern Sicily continental shelf, as well as intra-slope basins by means of a number of submarine canyons scouring the continental slope (Lo Iacono et al., 2014); also mass wasting deposits, coming from extensive slope failures affecting the submarine escarpments, feed the intraslope basin infilling; close to the island of Ustica, volcanoclastic sediments also accumulate in the basins. On the whole the analysed margin displays an immature setting characterized by narrow shelves and steep, uneven slopes, some of which currently affected by seismic activity (Agate et al., 2000).

A different setting can be envisaged in the most southern sector (Egadi Islands) where a wide sector of continental shelf develops, which account for extensive diffusion of seagrasses and coralligenous-platform habitats, that in turn promoted abundant, autochthonous, biogenic sediment deposition.

The analysis of morpho-sedimentary features occurring in this area allow to unravel relationships between tectonics, sedimentation, and sea level change in an underfed, tectonically active margin.

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## **The 1:500000 mapping of marine areas offshore of the Campania Region (central-eastern Tyrrhenian Sea, Southern Italy), in the frame of METIQ Cartographic Project**

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*Keywords:* seascape analysis, submarine thematic mapping, geodatabase, Quaternary.

Thematic mapping of the Quaternary geo-morphological features of the Campania continental margin (central-eastern Tyrrhenian Sea) covers an area of approximately 13000 km<sup>2</sup>, from the shoreline to the lower continental slope, down to about 2500 m water depth.

The area is delimited by major physiographic features, notably the Cuma Canyon to the North-Northwest, the Sirene Seamount to the Southwest and a series of intraslope reliefs north of the Palinuro volcanic ridge, to the Southeast. Mapping was realized by integrating information derived by Digital Elevation Models (DEM) analysis, previous background data (CARG and Magic cartographic Projects), available high-resolution, single-channel reflection seismic (Sparker and Sub-bottom) profiles and major structural lineaments documented in the literature. Cartographic elements provided by previous mapping were processed to achieve a spatial resolution appropriate to the working scale (1:200.000) of the METIQ project.

The cartographic work has been carried out in a GIS environment as a standard procedure to ensure rapid update of the geo database and permanent georeferencing of mapping targets. All data have been included into the METIQ database that has been populated according to a structure agreed upon by the working group. Each mapped feature has been associated to a unique code with relative descriptions in the tables of attributes.

Compared to the cartography developed within the MAGIC project, additional 7300 km<sup>2</sup> have been mapped beyond the -700 m bathymetric contour, along with additional 580 km<sup>2</sup> at water depths shallower than 50 m. Moreover, mapping criteria, purposes and scale of the survey have been selected according to the main scope of this cartographic project which is mainly focused on Quaternary geomorphological processes and sedimentary environments, rather than on geo-hazards.

With respect to MAGIC cartography, the METIQ mapping project provides a spectrum of additional information, including: i) a general outline of the continental margin; ii) Quaternary structural lineaments with inferred age of faulting; iii) submarine extension of the volcanic complexes; iv) patterns of active depocentres, v) erosional/gravity-driven features and vi) outline of the intraslope reliefs and basins.

It is worth noting that, despite the efforts to ensure consistency among all the cartographic elements, the new METIQ map is still based on a relatively inhomogeneous data base, with uneven distribution of multibeam surveys, often resulting in Digital Elevation Models of variable resolutions within the same bathymetric range and incomplete understanding of the nature and origin of some offshore structures.

## **How tectonics and lithology control the physical characteristics of slope parallel drainage systems**

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*Keywords:* Quaternary marine geology, slope processes, geological mapping.

In tectonically active marine margins the interchange between canyon-type processes, regulated mainly by vertical erosion and sediment bypass and those dominated by lateral erosion can take place in a single slope-parallel drainage system. In the absence of sudden gradient changes, the factors controlling these shifts are the effects on the drainage path of active faults and volcanic activity and the lithological makeup of the substrate on which the drainage system develops. Tectonics and volcanic activity and related deposits obviously also provide the external morphological setting of the slope.

During the course of the METIQ project we examined a small size canyon system that develops north of Alicudi and Filicudi Islands on the north Sicily continental slope. This slope region consists of two relatively flat-lying benches at about 1500 m depth and between 2000 and 2600m depth. These are separated by the volcanic structures of the islands and the submarine Eolo seamount. The canyon system develops for 30 km parallel to the slope before turning perpendicular to the gradient for 8 km and reaching the Tyrrhenian abyssal plain. Apart from this latter segment, there is a constant gradient throughout the canyon system. The external and inherent controlling factors concerning the origin and the different configurations of the drainage system are discussed as well as the possible implications this small system can offer on overall regional slope dynamics.

## Mapping the Quaternary in the Tyrrhenian Sea: a renewed “exploration” and its scientific and applied significance

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*Keywords:* marine cartography, geohazards, georesources.

Within the framework of the METIQ project, our unit mapped the deepest parts of the Northern and South-western Tyrrhenian Sea, and the Eastern Sardinian and North-eastern Sicilian margins. Quaternary elements develop in extremely different physiography settings, which are the response to deep processes occurring in different geodynamic and tectonic contexts, from active to passive margins, from deforming and quiescent rifts, to ocean-like back-arc basins. Large areas of the external continental shelf lack any Holocene deposit, and thus a series of submerged coastal systems record the pace and the outcomes of the last sea-level transgression. Canyons span a range of morphologies, which illustrate general rules for their evolution, from inception and erosion to infill and deposition. At the base of slope, canyons often join leveed-channels, whose planform and architecture varies depending mainly on the tectonic history of the margins. Both canyons and channels have internal elements related to the processes of sediment feeding and routing to the deep-sea. Fans have different dimensions, shape and relative importance of smaller morphologic constituents. Landslides are a major feature in all the sectors of the mapped area. Mapping has shown the variety of sediment collapses mechanisms, comprehensive of the complete removal of thin, surficial extensive layers, glacial-like, slow downslope movements, and large margin collapses with multiple failure episodes. Pockmark fields are present in many of the seamounts of the northern Tyrrhenian Sea and on the continental slope of Sardinia and Sicily. Their distribution is sometimes controlled by active tectonics, while in others, a possible relationship with the distribution of surficial sedimentary units is apparent. Particularly in the Northern Tyrrhenian area, contour currents shape some portions of the continental slope and the infill of intraslope basins; moreover, they appear to influence the degree of sedimentary cover on seamount top. A reappraisal of Quaternary and active tectonics shows various belts indicating a recent spatial focussing of extensional tectonics within the extended Tyrrhenian Sea. Various new volcanic buildings have been highlighted, particularly in the Sardinia margin and in the northern Tyrrhenian Sea, contributing to the enlargement of the extent of the magmatic provinces of the Tyrrhenian-Apenninic region. In general, our mapping stands out as a reminder of the importance of a basic description and understanding of the physical character of the submarine territory. Our results indicate that, with the METIQ map we have set a foundation for future investigations and for any study addressing scientific questions on the interrelated aspects of the sea. In addition, in view of new and maybe still unpredicted uses of the sea, the METIQ map is a required document for the achievement of primary societal needs, connected with geohazard, georesources, pollution, energy, climate change.

## **METIQ: a dynamic evolutionary model of Italy during The Quaternary**

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*Keywords:* Quaternary mapping, landscape evolution, geohazard.

The METIQ project (namely “Modello evolutivo del territorio Italian nel Quaternario”) is a scientific initiative involving the entire Italian community of Quaternary scientists from several academic and research institutes, under the coordination of AIQUA. METIQ aims at developing an evolutionary model of the Italian territory during the Quaternary. The base product will be a Quaternary Map of Italy at 1:500,000 scale, whose first preliminary version has been planned to be published for the 21<sup>o</sup> INQUA Congress. This map results from a careful review of available geological maps, that have been frequently published at different scale and with different purposes. Seven territorial groups (six for on-shore territory and one focused on off-shore areas) have classified mapped deposits by a METIQ legend ad hoc defined, through a strong harmonization effort. Additional layers on the map will provide information on Quaternary active faults and MIS 5.5 Thyrrenian records along the Italian coast. Beyond the map, the main product of the METIQ project will be a webGIS to access to other numerous other informative layers integrating the Quaternary base map, focused on info about active geohazards (from earthquakes, volcanic eruptions, landslides), Quaternary geosites, paleoclimatic data, etc.

## Mapping of Quaternary lineaments in the Pelagic Islands area (MetiQ project)

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Keywords: Pelagic Islands, Quaternary activity, multibeam data.

In the framework of the MetiQ project, a map of main Quaternary geological and morphological features in the seabed in the area offshore the Pelagic Islands (Sicily Channel) has been created. The database includes recently acquired (2015-2017) multibeam bathymetric data, seismo-acoustic profiles, ROV transects and superficial sampling, locally integrated by data from literature and from the EmodNet dataset. From a physiographic point of view, Lampedusa (the largest island of the Pelagic, with a surface area of 20 Km<sup>2</sup>) and the small islet of Lampione lie on the Tunisian continental shelf, that is a relatively shallow-water area (depth within 100/200 m). Lampedusa and Lampione are entirely made of sedimentary rocks (mainly biolites and calcarenites); the seabed around the islands is covered by biogenic sediment (rodolithes and maerl facies) and by *P. oceanica* meadows (Innangi et al., 2019). An insular shelf is present in shallow water, overlaid by terraced depositional bodies. Linosa Island, on the contrary, is the emerging tip (area of about 5.4 km<sup>2</sup>) of a much wider volcanic edifice, lying on the western shoulder of the Linosa graben. This main tectonic feature is related to the rifting regime of the Sicily Channel and is mapped here as “intraslope basin with hemipelagic deposition”. The submarine extension of Linosa shows an articulated morphology, punctuated by several volcanic vents, mostly aligned in a NW-SE direction; overall they show a relatively fresh appearance, suggesting a Quaternary activity (Romagnoli et al., 2020). To the NW and the SE of the island, insular shelves are present down to about -100/120 m, partly covered by prograding terraced depositional bodies, both on the inner part and at the edge of the insular shelf. The NE and E submarine flanks of Linosa are, instead, quite steep (14-25°) and affected by active gullies and canyon heads from shallow water to the submarine base of the volcanic edifice. A wide area with pockmarks depression is also mapped to the south of Linosa (Tonielli et al., 2019). In the area between Lampedusa and Linosa, the presence of active tectonic lineaments dislocating the seabed is witnessed by recent data, and the mapping of these features is also supported by previous literature (Torelli et al., 1995).

Innangi S., Di Martino G., Romagnoli C. & Tonielli R. (2019) - Seabed classification around Lampione islet, Pelagic Islands Marine Protected area, Sicily Channel, Mediterranean Sea. *Journal of Maps*, 15(2), 153-164. <https://doi.org/10.1080/17445647.2019.1567401>.

Romagnoli C., Belvisi V., Innangi S., Di Martino G. & Tonielli R. (2020) - New insights on the evolution of the Linosa volcano (Sicily Channel) from the study of its submarine portions. *Marine Geology*, 419, 106060. <https://doi.org/10.1016/j.margeo.2019.106060>.

Torelli L., Grasso M., Mazzoldi G., Peis D. & Gori D. (1995) - Cretaceous to Neogene structural evolution of the Lampedusa shelf (Pelagian Sea, Central Mediterranean). *Terra Nova*, 7(2), 200-212.

Tonielli R., Innangi S., Di Martino G. & Romagnoli C. (2019) - New bathymetry of the Linosa volcanic complex from multibeam systems (Sicily Channel, Mediterranean Sea). *Journal of Maps*, 15(2), 611-618. <https://doi.org/10.1080/17445647.2019.1642807>.

## **The METIQ project – the Evolutionary Model of the Italian Territory in the Quaternary in the Central sector of the Ionian Sea**

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*Keywords:* Central Ionian Sea, METIQ, Quaternary.

Within the METIQ (Evolutionary Model of the Italian Territory in the Quaternary) project we compiled the first Quaternary map of the Ionian Sea, by integrating information from the literature and analysing swath bathymetry and seismic data of different resolution. The effort provides critical new knowledge into the link between the morphological features observed on the seabed and the deeper structures and routing systems, which provide important insights into the mechanisms that led to the formation and evolution of these seabed morphologies.

Specifically, we identify widespread Quaternary morphologies along the continental margins of the offshore sector of the Ionian Sea, which are the seabed expression of the complex geodynamic evolution that affects this area. The subduction of the African plate underneath the European plate led to the development of the Calabrian accretionary prism, a 200-300 square km wide portion of the seabed, extending from the coastal areas to a water depth of about 3500 to 4000 m. The tectonic deformation has profoundly influenced and shaped the seafloor, often developing composite morphologies that are the evidence of still active geological processes. We imaged different morphologies such as submarine channels, gullies, canyons, landslide scars, mud volcanoes and complex mass wasting features, that dissect and shape the continental shelf and slopes of the Ionian seabed.

We assigned the seabed features in the study area to several morpho-structural domains: i) the Crotono-Spartivento basin incised by multiple submarine canyon systems and pierced by active mud volcanoes; ii) the inner accretionary prism characterised by elongated morphologies resulting from deformation induced thrusts, and iii) the outermost accretionary prism, which shows a distinct seafloor morphology, characterised by the presence of several smaller scale elongated depressions, also known as “cobblestone topography”. The distribution, erosive potential, and activity, of the various geomorphic elements represent a potential laboratory for geohazards, and moreover, some of these features may pose a serious threat to coastal infrastructures and communities. Their inception and the mechanisms that drive their evolution, are still a matter of controversial discussions for the entire marine research community.

Our cartographic effort and results allowed to gain a new knowledge into the link between the morphological features observed on the seabed and the deeper structures and routing systems, giving important insights into the possible mechanisms that led to the formation of the seabed morphologies we observe today. As such, they represent a step forward toward the characterisation of geohazard evaluation in the Italian offshore.



## The METIQ project – Sicilian Channel

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*Keywords:* Sicily Channel, METIQ, Quaternary.

As part of the METIQ project (Evolutionary Model of the Italian Territory in the Quaternary), we have produced an updated map of the topography of the seabed of the Sicilian Channel, integrating information from the literature and the analysis of available swath bathymetric and seismic data with variable penetration. The distribution and coverage of the high-resolution geophysical data is quite uneven in this sector of the Mediterranean, but an attempt has been made to provide a comprehensive and homogeneous picture of the main Quaternary morphological elements characterizing the area. Sectors where data coverage is denser include the entire Adventure Plateau and the Egadi Islands, the Capo Granitola-Sciacca offshore sector of the Sicilian coast, and the Graham and Terrible banks.

Fluid migration features such as pockmarks, mud volcanoes and fluid vents are present in several sectors of the Sicilian Channel, due to an intense tectonic activity observed particularly around the Graham Bank and in the offshore sector of the Capo Granitola-Sciacca coastal area (Civile et al., 2021). The active lineaments of the Capo Granitola-Sciacca fault zone control the occurrence and distribution of several volcanic phenomena near the coast (Lodolo et al., 2019).

Erosional features such as landslide scars, gully incisions, submarine canyon headwalls and extensive erosive areas have been recognized and analyzed both in the northern part of the Sicilian Channel around the Egadi Islands and off the coast of Agrigento, and along the Malta escarpment, where complex submarine canyon systems severely incise the continental slope.

The effects of post-LGM sea-level rise were largely documented in the study area by the presence of prograding wedges, palaeo-coastal line configurations, ravinement surfaces and sand ridges, which provide evidence of the succession of marine transgression phases that have left a distinct footprint, particularly on the Adventure Plateau (Lodolo et al., 2020).

The obtained results provide a valuable basis for new studies focusing on still poorly mapped areas, to analyze specific and detailed Quaternary features and point to the need for future efforts to implement the state of the art in marine Quaternary research.

Civile D., Brancolini G., Lodolo E., Forlin E., Accaino F., Zecchin M. & Brancatelli G. (2021) - Morphostructural setting and tectonic evolution of the Central Part of the Sicilian Channel (Central Mediterranean). *Lithosphere*, 2021, 1-24.

Lodolo E., Galassi G., Spada G., Zecchin M., Civile D. & Bressoux M. (2020) - Post-LGM coastline evolution of the NW Sicilian Channel: comparing high-resolution geophysical data with Glacial Isostatic Adjustment modelling. *Plosone*, 15, e0228087.

Lodolo E., Civile D., Zecchin M., Zampa L.S. & Accaino F. (2019) - A series of volcanic edifices discovered a few kilometers off the coast of SW Sicily. *Marine Geology*, 416, 105999.

## **METIQ-mare Project in the Gulf of Genoa (Ligurian Sea): an updated map with the integration of new CARG marine survey**

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*Keywords:* seafloor mapping, Ligurian sea, geo-hazards.

We present a new map and evolutive model of the main quaternary geological features in the Gulf of Genoa (Ligurian Sea, Italy) realized on the basis of an exhaustive review of available data collected during past projects (e.g., Malisar, Magic, Emodnet...) and integration of recent data acquired in the framework of the CARG Project (213-230 “Genova Sheet”). The new data set consists of high-resolution Multibeam bathymetry (cell size of 1 m.) and a dense grid of seismic lines (Sub-Bottom Profiler and Sparker 1 kJ) acquired during a marine Survey in 2022-23.

From the geological point of view, the Gulf of Genoa is located in the complex area known as the “collisional or Ligurian knot” (Laubscher et al., 1992), at the junction between the Alpine and Apennine margins and at the northern propagation of the Ligurian-Provençal basin. In this area, in addition to the tectonic complexity, intense seafloor erosion and widespread retrogressive sediment failures occur along the steep flanks and heads of canyons (e.g., the Polcevera and Bisagno canyons).

During the map compilation for the METIQ-mare we have made a detailed reconstruction both of the Quaternary evolution of the canyon heads (e.g., paleo-canyon axis within the shelf area) and of the morpho-dynamics processes active in the canyon heads areas (e.g., geo-hazard related seabed features) of the Gulf of Genoa.

The evidence of active retrogressive erosion at the canyon heads is confirmed in distinctive areas where seabed pockmarks or subcircular reliefs (i.e., fluid vents related features), possibly linked to tectonic structures, are frequently observed. These findings highlight the correlation between fluid escapes, seabed instability and erosive phenomena; therefore, mapping these features is of paramount importance either for the geodynamic and morphotectonic modelling as well as for geohazard marine evaluations.

Laubscher H., Biella G.C., Cassinis R., Gelati R., Lozej A., Scarascia S. & Tabacco I. (1992) - The collisional knot in Liguria. *Geol. Rundsch*, 81, 275-289.

## **Morphotectonic processes in the southern Ionian sea: deciphering links between plate convergence, shallow structural deformation and sediment dynamics**

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*Keywords:* Southern Ionian Sea, morphotectonics, plate convergence.

Plate convergence along the irregular Africa/Eurasia plate boundary has produced a wide range of morpho-structural domains that are intimately related to slab dynamics, active tectonics and deep fragmentation of the continental margin along transtensional faults.

A combined dataset of multi-beam bathymetry and seismic reflection data at different resolution allowed mapping first order morphological, sedimentary and tectonic features in the southern Ionian Sea, where African plate sediments are scraped off from the downgoing plate and piled up in the accretionary wedge. Main morpho-structural domains include the outer Calabrian Arc accretionary wedge, broad regions of relatively flat seafloor related to sedimentary basins, numerous submarine canyons, areas dominated by sediment waves, the deeply incised Malta-Hyblean Escarpment, and the flay-lying abyssal plain bounding the subduction system to the South. The extent and geometry of the different domains show a close link with geodynamic and tectonic processes and their boundaries are often located along deeply rooted tectonic features that control the structural evolution of the continental margin. Both reverse and transtensional tectonic features are present and some of them may be considered as seismogenic faults capable of producing strong ground shaking, submarine landslides and tsunamis.

The analyzed dataset provides new insights into the interactions between sedimentary processes and active tectonics. Large sedimentary basins develop along major fault systems, and are filled by sedimentary sequences whose depositional geometries provide interesting constraints on fault kinematics and tectonic activity. Other sedimentary basins are present within the outer accretionary wedge, where the cobblestone topography is marked by small scale depressions and intervening salt-cored structural highs. Basin depocenters are filled with pelagic sediment alternating with turbidites and megaturbidites representing high-energy and instantaneous events triggered by seismic activity, at least during the Holocene.

## The Quaternary Italian map at 1:500.000 scale: a synthesis of the geological knowledge

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Keywords: METIQ, cartography, Quaternary.

The main result of the METIQ project (Modello Evolutivo del Territorio Italiano nel Quaternario) is an Italian map at the 1:500.000 scale, a thematic viewer and OGC web services.

The work involved the collection and harmonization of geological datasets produced by different working groups skilled on the basis of spatial and thematic expertise, such as tectonics, volcanism, offshore geology, and paleo sea levels.

Regarding the onland dataset, the starting point has been the polygonal extraction of the geological map of Italy at the scale 1:100.000 (Pantaloni et al., 2021, 2023), based on a query relative to the Quaternary as lower age.

Each working group used in addition different cartographic publications to integrate the initial information (e.g., CARG project geological sheets, Toscana, Emilia Romagna, Marche and Umbria geological map *continuum* at 1:250,000 scale and cartography at a regional scale), to enrich or improve the result. Cartographic and implementation database rules was shared by a guideline that was continuously updated to ensure a homogeneous compilation.

The guidelines concerned the use of geoprocessing tools to clip or merge polygons and lines below the threshold of 2,5 mm, the Plio-Quaternary boundaries and the resolution of the spatial data inhomogeneity relating to the coverage of geomorphological features. In order to obtain a harmonized geodatabase, the mandatory fields were compiled using a set of specific domains, relative to lithology, genesis and lower and upper age.

In the offshore mapping, polygons, lines and points were used to describe the geological and sedimentological features, and the physiographic characteristics of the seabed.

In particular, in the offshore mapping the polygons were used for physiographic environment, geomorphological and sedimentary features, the cartographic overprint were used for biological elements representation, lines and point were used to explain geomorphological and hydrothermal aspects.

Furthermore, the underwater biosphere was represented in relation to the geological environment.

To achieve a harmonized geodatabase, the mandatory fields were compiled using codelist related to lithology, genesis, and lower and upper age INSPIRE compliant (INSPIRE Data Specification on Geology – Technical Guidelines).

In order to ensure both the scientific dialogue between working groups and the monitoring the delivery status of the datasets, an online viewer was published and was made available. Finally, the map was cartographically set-up to be usable and easily readable.

The cartographic set-up followed the international standards where available (i.e., ICS for the age colour code) and those defined in the CARG project guidelines (Battaglini et al., 2009).

This activity has made it possible to synthesize the Quaternary geological knowledge both for the onland and for the offshore part of the Italian territory, offering a tool for understanding the recent evolution of the peninsula.

Battaglini L., Carta R., D'Angelo S., Delogu D., Falcetti S., Pantaloni M., Papasodaro F. & Tacchia D. (2009) - Aggiornamento ed integrazioni delle linee guida della Carta Geologica d'Italia alla scala 1:50.000. Quaderni serie III, volume 12, Fascicolo I, Servizio Geologico d'Italia, ISPRA.

European Commission Joint Research Centre (2013) - INSPIRE Data Specification on Geology – Technical Guidelines, INSPIRE Data Specification for the spatial data theme Geology. <https://inspire.ec.europa.eu/id/document/tg/ge>.

Pantaloni M., Congi M.P., Campo V., Primerano., Ventura R., & Monti G.M. (2023) - The geological map of Italy 1:100,000 scale INSPIRE harmonised [Data set]. 30th International Cartographic Conference (ICC 2021), Florence, Italy. Zenodo. <https://doi.org/10.5281/zenodo.7599556>.

Pantaloni M., Campo V., Congi M.P., Monti G.M., Primerano P. & Ventura R. (2021) - The INSPIRE harmonisation: the Geological Map of Italy at 1:100,000 scale. Proc. Int. Cartogr. Assoc., 4, 85. <https://doi.org/10.5194/ica-proc-4-85-2021>.

## The Southern Apulian margin mapped within the framework of the METIQ project: first results and knowledge gaps

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*Keywords:* submarine geomorphology, Apulian plateau, morphotectonic.

Within the framework of the METIQ project, published results from seafloor mapping data (i.e., multibeam bathymetry, side-scan sonar imagery, and high-resolution seismic reflection profiles), video footage acquired by underwater cameras, as well as dating and biostratigraphic and sedimentological analysis on sediment samples, were used to provide a first Quaternary map of the southern Apulian margin (Mediterranean Sea). The Apulian offshore, represents a Mediterranean margin where Quaternary dynamics have undoubtedly created a unique geological context, where complex interactions between tectonic, sedimentary and oceanographic processes have promoted a relevant occurrence of biogenic submarine landforms, which dominate the margin in both shallow and deep waters. The southern Apulian continental shelf is indeed home to numerous and diverse algal reefs (i.e. coralligenous bioconstructions), likely supported by low Holocene sedimentation rate and regional uplift. Deeper areas, largely dominated by mass-wasting deposits, host, on the other hand, one of the most know Cold-Water Coral (CWC) province of the Mediterranean Sea (i.e. the Santa Maria di Leuca CWC province). In this work, we elucidate the extensively studied and well-documented sedimentary processes that shaped the margin during late Quaternary (and interactions with distribution and growth of biogenic landforms as reported in Savini et al., 2016, Savini et al., 2014, Savini & Corselli, 2010, Malinverno et al., 2010), while addressing the significant knowledge gaps in geodynamic and tectonic activity. We aim to initiate critical discussions by addressing the substantial uncertainties surrounding the role of tectonic activity in controlling the recent evolution of sedimentary environments on the margin.

Malinverno E., Taviani M., Rosso A., Violanti D., Villa I., Savini A., Vertino A., Remia A. & Corselli C. (2010) - Stratigraphy and sedimentology within the Santa Maria di Leuca DWC Province. *Deep-Sea Research, II*, 57(5-6), 345-359.

Savini A., Marchese F., Verdicchio G. & Vertino A. (2016) - Submarine slide topography and the distribution of vulnerable marine ecosystems: a case study in the Ionian Sea (eastern Mediterranean). In: Lamarche G., Mountjoy J., Bull S., Hubble T., Krastel S., Lane E., Micallef A., Moscardelli L., Mueller C., Pecher I. & Woelz S. (eds): *Submarine mass movements and their consequences, Advances in Natural and Technological Hazards Research*, Springer, Dordrecht, 41, 163-170.

Savini A., Vertino A., Marchese F., Beuck L. & Freiwald A. (2014) - Mapping Cold-Water Coral Habitats at Different Scales within the northern Ionian Sea (central Mediterranean): an assessment of coral coverage and associated vulnerability. *PLoS ONE*, 9(1), e87108. <https://doi.org/10.1371/journal.pone.0087108>.

Savini A. & Corselli C. (2010) - High resolution bathymetry and acoustic geophysical data from Santa Maria di Leuca Cold Water Coral province (Northern Ionian sea–Apulian continental slope). *Deep-Sea Research II*, 57 (5-6) 326-344.

**S44.**

**Open Poster Session**

*CONVENERS AND CHAIRPERSONS*

*Piergiulio Cappelletti (Università degli Studi di Napoli Federico II)*



## Crystal chemistry and mineralogy of phillipsite and analcime from Surtsey (Iceland)

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Keywords: ICDP, SUSTAIN, Surtsey.

Investigations on zeolites from pyroclastic rocks of Surtsey island (SW Iceland) were carried out in this work throughout petrographic studies, X-ray powder diffraction analyses, and SEM-EDS analyses performed at the Department of Earth, Environmental and Resources Sciences (DiSTAR) of the University of Naples Federico II.

Emplacement of pyroclastic and volcanoclastic deposits during episodes of active volcanism can be followed by syn- and post- depositional minerogenetic processes, resulting in the formation of secondary minerals: zeolites, as well as clay minerals, are notably among the most common authigenic minerals in pyroclastic and volcanoclastic deposits (Chipera & Apps, 2001) and their formation affected also the very young volcanic island of Surtsey (SW Iceland) since its formation (1963-1967) (Weisenberger et al., 2019). Therefore, the island and its peculiar geological environment represents one of the most suitable sites to investigate the formation of these secondary mineralizations, which in this case form as mineral precipitation in vesicles of basaltic pyroclasts, in both subaerial and submarine Surtsey deposits.

This work reports preliminary crystal-chemical and mineralogical results on phillipsite and analcime from drill cores retrieved in 1979 and 2017, in the frame of the Surtsey Underwater Volcanic System for Thermophiles, Alteration processes, and Innovative concretes (SUSTAIN) drilling project. Zeolites formation and their abundance is investigated as function of temperature, depth (above or below water table), fluid composition and activity of alkaline and alkaline-earth cations in the investigated environment.

Investigations on zeolites of Surtsey tuff deposits are still in progress: the systematic analyses of the 50-year-old tuff from one of the most well-monitored volcanic sites on Earth provide a reference framework to evaluate mineralogical evolution in other young Surtseyan volcanoes.

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## Reconstructing dinosaur foot motion from cross-section tracks: the case study of the Lama Balice dinosaur tracksite (upper Albian, Apulia, southern Italy)

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**Keywords:** dinosaurs, cross-section footprints, Apulia carbonate platform.

The Lama Balice dinosaur tracksite, few kilometres west of Bari (Apulia, southern Italy), is characterised by a diverse ichnoassemblage, with hundreds of footprints attributable to theropods, sauropods and ankylosaurs. The track-bearing succession, cropping out in Mazzitelli and Robles quarries, belongs to the upper Albian portion of the Calcare di Bari Fm (Spalluto & Caffau, 2010). Dinosaur tracks occur mainly on two exposed surfaces, and they were recorded and documented applying traditional methods, supported by close-range photogrammetry. The obtained results suggest an ichnological affinity of the theropod and sauropod tracks with the ichnoassemblages from the Upper Jurassic to Lower Cretaceous of Morocco and Algeria (Belvedere et al., 2010; Bessedik et al., 2019). The extraordinary richness of the ichnoassemblage is also represented by the occurrence, at different stratigraphic levels of the successions outcropping in both quarries, of numerous footprints exposed in cross-section. Several authors studied this kind of tracks, trying to simulate them in cohesive substrates (both performing *in vivo* experiments, simulations and digitization), with the aim of reconstruct foot motions of dinosaurs and other extinct animals (e.g., Falkingham et al., 2020). Dinosaur tracks from Lama Balice represent a unique opportunity to validate and test the previous laboratory hypotheses. They could indeed play a key role in understanding dinosaur foot motions and the interaction between autopods and substrate, highlighting the different degrees and geometries of deformation in both surface and deeper stratigraphic layers.

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## ***In vivo* reconstruction and body mass estimate in the anancine gomphotheriid *Anancus arvernensis* (Croizet and Jobert 1828)**

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**Keywords:** body mass estimate, regression formulas, digital sculpture.

Body mass (BM) is a critical characteristic of both extant and extinct organisms, influencing many biological factors such as metabolism, fecundity, life span, biomechanics, general ecology, trophic requirements and diets, reproduction dependence on the external environment, home range, and growth rate. For this reason, an accurate estimation of BM in extinct tetrapods can be of great importance, even for macroevolutionary studies. In this contribution, we estimate the possible living body mass (BM) of the anancine gomphotheriid *Anancus arvernensis* starting from two articulated skeletons and applying a recently proposed volumetric method based on hyper-realistic *in-vivo* 3D reconstructions. The obtained results were then compared with the classical regression formulas based on measurements of long bones and shoulder height proposed in the literature. The results indicate that the performance of regression formulas varies considerably in different clades, and plausible estimates are obtained only considering the mean values of all the formulas based on the individual bones. Differently, values obtained from single bones led to an underestimation or overestimation of up to 300% (BM ranging from 54 kg to 26 tons). The application of the new volumetric method based on the *in-vivo* reconstruction of *Anancus arvernensis* indicates a BM between 5.2 and 6 tons, a value comparable to that of an extant adult male African elephant. The present study demonstrates that estimating the body mass (BM) of terrestrial tetrapods from individual or fragmented bones may result in highly unlikely and misleading conclusions. Thus, the volumetric estimate of BM based on *vivo* 3D is always recommended in the presence of adequately complete mounted skeletons.

## **The base metal sulfide and Ni-Co arsenide-bearing veins of Valsassina (Lombardy, Italy): a possible “five element vein-type” system?**

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*Keywords:* five-element veins, Ni-Co-Fe arsenides, sulfides.

Valsassina (Lombardy, Northern Italy) represented a historically important mining district exploited since the Middle Ages for Fe, Pb, Cu, Ag and, in more recent times, barite extraction. This area is located in the Lombard southern Alps and it is characterized by the presence of metamorphic basement, by a major late-Variscan intrusive complex and by Carboniferous-Permian volcano-sedimentary cover units. These rocks host a pervasive system of poorly studied mineralized veins, in the past considered as directly related to the hydrothermal circuit of the Val Biandino intrusive complex.

Such veins are characterized by base metal (Pb, Zn, Cu, Fe) to complex polymetallic assemblages. None of these vein systems has been previously studied in detail, either for their geological setting, or for their mineralogical and geochemical features.

We investigated various vein deposits in terms of ore textures, mineral chemistry of sulfides and sulfosalts (EMPA-WDS and LA-ICP-MS analyses), stable isotopes (C and O) of carbonate gangue minerals, with the aim of obtaining clues about the conditions of deposition of these ore deposits.

Two different vein families can be recognized in Valsassina: NNW-SSE veins characterized by a complex polymetallic sulfide-sulfosalt assemblage, also with Ni-Co-Fe arsenides and other Ag-Bi-bearing minerals, and NE-SW veins with a simpler, base metal sulfide assemblage. In all the veins, gangue consists of variable amounts/fractions of quartz, siderite, dolomite and baryte.

The Ni-Co-bearing NNW-SSE veins show some distinctive features of the “five-element vein” type deposits, with the Ni-Co-Fe arsenide ore stage pre-dating a sulfide-tetrahedrite-dominated ore stage. LA-ICP-MS data on pyrite and sphalerite and stable isotopes (C and O) of the carbonate gangue minerals do not show clear differences between the two veins families, which are likely genetically linked. The isotopic compositions of the Valsassina vein carbonates are closely comparable with the signature of several major Five-element ore districts. Hence the mineralizing fluids could have been saline and mineral deposition might have been controlled by some reducing agents, either in the fluids (e.g., interaction with hydrocarbon components) or in the host rocks. In absence of fluid inclusion analyses, preliminary temperature estimates for the Valsassina vein systems were based on the sphalerite composition, applying the GIMFis geothermometer of Frenzel et al. (2016). The estimated temperatures for the sulfide-tetrahedrite-dominated ore stage range between 100 and 250°C.

The crosscutting relationships observed for all the veins with the host rocks, along with the results of recent and on-going studies on the pre-Alpine structural evolution of this sector of the Southern Alps, suggest a possible late Permian age, making these vein systems comparable with other late-post Variscan, polyphase hydrothermal events affecting large sectors of the Southern Alpine domain.

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# PhD Day 2023

## *CONVENERS AND CHAIRPERSONS*

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## **Petrographic and microstructural characterization of the lithospheric mantle exposed in the Wadi Tayin Massif, Oman ophiolite (Oman Drilling Project, CM Sites)**

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*Keywords:* Oman ophiolite, Oman Drilling Project, oceanic lithosphere.

The Oman ophiolite is the world's largest fossil oceanic lithosphere forming at a fastspreading ridge. It exposes a complete lithospheric sequence including mantle peridotites at the bottom overlain by the crustal section composed of gabbros, sheeted dikes and lavas. The absence of vegetation cover provides direct access at several kilometers of the lithospheric mantle and the observation of the magmatic structures in 3-Dimensions. Despite the importance of the Oman ophiolite, some aspects of its geodynamic evolution remain poorly understood, such as the large-scale tectonic settings in which the ophiolite formed and evolved.

The Oman ophiolite is composed by several massifs aligned long the Oman coast. Spatial organization of intrusives and extrusives indicates an increased arc signature in the northern massifs (Godard et al., 2003). On the other hand, the southern massifs (Samail and Wadi Tayin Massifs) best preserve the oceanic accretion of the ophiolite sequence at a ridge environment. The letters were recently sampled during the Oman Drilling Project (OmanDP) with the aim of understanding the full spectrum of processes that shape and modify the oceanic crust (GT Sites), the crust-mantle transition zone (CM sites) and the lithospheric mantle (BA Sites) of the Oman ophiolite.

My research project focus on the petrological and structural characterization of the diffuse reactive percolation and impregnation processes recorded within the Oman lithospheric mantle at different level from spinel- to plagioclase-facies conditions. Our study is based on (i) drilling-core samples collected by a Team of the University of Genova during the corecharacterization phases of the OmanDP (Holes CM1A and CM2B; Kelemen et al., 2021) on board the Chikyu drilling vessel in the 2018, and on (ii) field-samples collected by the same Team in January 2020 from the upper mantle section of Wadi Tayin Massifs nearby the drill sites. All rock samples are mainly composed by mantle harzburgite characterized by pyroxenerich layers, several impregnation-related structures with a mineral association of Plg + Cpx ± Opx, and gabbroic dikelets. Preliminary geochemical investigations have revealed a change in the chemistry between the impregnation structures (An = 94 mol%) and the gabbroic intrusions (An = 77 mol%), thus pointing to parental melts with different magmatic affinities and/or degree of evolution.

Our aim is to shed light on the complex and still debated geodynamic context of the Oman ophiolite combining multi-scale petrographic descriptions, in-situ geochemical analysis (major and trace elements), and detailed microstructural investigations. Understanding the evolution of the mantle peridotites is fundamental to constrain the tectonic setting and oceanic history of the Oman ophiolite sequence. Achieving this goal is equally important for understanding the dynamics that control the accretion of the oceanic lithosphere in modern oceanic ridges.

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## Transmission-based muography for mining prospecting and engineering geological applications

Beni T.<sup>1-2\*</sup>, Borselli D.<sup>2-3-4</sup>, Bonechi L.<sup>2</sup>, Bongi M.<sup>2-4</sup>, Brocchini D.<sup>5</sup>, Ciaranfi R.<sup>2</sup>, Cimmino L.<sup>6-7</sup>, Ciulli V.<sup>2-4</sup>, D'Alessandro R.<sup>2-4</sup>, Dini A.<sup>8</sup>, Vezzoni S.<sup>8</sup>, Frosin C.<sup>2-4</sup>, Gigli G.<sup>1</sup>, Gonzi S.<sup>2-4</sup>, Guideri S.<sup>5</sup>, Lombardi L.<sup>1</sup>, Nocentini M.<sup>1</sup>, Saracino G.<sup>6-7</sup> & Casagli N.<sup>1</sup>

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Keywords: muography, ore body, mineral deposit prospecting.

Transmission-based muography (TM) is an imaging technique that involves measuring and analyzing the attenuation of cosmic ray muon flux within an object of interest (target). Muons are low-interacting particles that, owing to their high energy and mass, may travel through hundreds of meters of rock before stopping, which is why they are used in radiography investigations. These particles are continuously generated in the Earth's upper atmosphere through the decay of pions and kaons resulting from the collision between primary cosmic rays and the oxygen and nitrogen nuclei of the atmosphere. TM has found successful applications in various fields such as geology, archaeology, engineering geology, and civil engineering. Another form of muography, scattering-based muography (SM), is commonly used for imaging smaller targets like nuclear waste casks or truck containers (Bonechi et al., 2020).

This study focuses on validating and verifying the reliability of TM using the MIMA detector (Muon Imaging for Mining and Archaeology) for mining exploration and preliminary assessment of Cu-Fe-Pb-Zn(-Ag) skarn ore deposits (Beni et al., 2023). It demonstrates how muographic surveys can complement traditional geophysical techniques like gravimetry, seismic surveys, and magnetic surveys. The measurements were conducted at the Temperino mine within the San Silvestro Archaeological and Mining Park in Campiglia Marittima, Italy (Baccani et al., 2019; Borselli et al., 2022)2019; Borselli et al., 2022. Considering the potential reevaluation of local mineral resources, including those of historical mining districts, the results of this study demonstrate the usefulness of TM as a complementary tool to other well-established geophysical techniques for mining/mineral exploration.

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## The DC methods: new prospectives and future applications

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*Keywords:* electrical resistivity tomography, direct current, monitoring, low-cost resistivimeter.

The DC (Direct Current) method has undergone evolution in both the acquisition method and data interpretation. The DC method has evolved over the years: from 1D investigation methodologies (vertical and horizontal electrical surveys, SEV and Profile) to 2D prospecting techniques, and further to current 3D and 4D or TL (time lapse) approaches. The modern approach to DC monitoring takes advantage of the combined development of fast acquisition instruments and advanced algorithms for the full 3D processing of resistivity measurements, in most cases acquired over non-conventional surface geometries. The continuous advancements in computer technology, as well as the techniques and software for fast data inversion, have made it possible to perform interpretation on commonly available computers. Multidimensional geoelectrical surveys are now widely used in environmental, engineering, hydrological, and mining applications. In the environmental, the use of geophysical monitoring has become essential to assess natural phenomena, enabling a more precise and accurate description of the case study. Anyway, there are several topics where the DC method is not well-known. In example, in civil engineering there are some potential applications for DC methods, especially for monitoring phenomena such as rebar corrosion or differential settlements. However, geoelectrical commercial devices are not yet ready due to their high cost and poor adaptability. The main limitations of commercial instruments do not lie in the quality of their measurements but in the cost of the devices and their poor adaptability to specific scientific issues. The main limitations of these commercial tools do not lie in the quality of their measurements or their robustness in the field; instead, they pertain to: i) the cost of the devices; and ii) their low adaptability to specific scientific issues (Clement et al., 2020). The purpose of my PhD research, in fact, is to give a contribute to improve a low-cost DC apparatus in order to have an efficient tool through new cheap technologies and devices that should be useful for monitoring applications and, above all, adaptable to the surrounding environment. Actually, I'm working on a development of a low-cost resistivimeter, following the OhmPI project, which is an open source and open hardware multichannel system for monitoring applications. Time-lapse electrical imaging has been used for diverse scientific and engineering problems to monitor changes in the subsurface associated with fluid injections, fluid flow, solute transport, phase changes, and other physical and chemical processes (Johnson et al., 2022). The burgeoning applications of time-lapse electrical imaging underscore its potential to provide valuable, qualitative insight to support development of conceptual models of subsurface frameworks and processes (Johnson et al., 2022). Taking in account these main elements, the main aim of the DC method is to underline the wide applicability of the geoelectrical method in various sectors and how monitoring different phenomena is becoming increasingly essential. There are several applicable fields: engineering infrastructure, contamination phenomena, salt intrusion, salinization, agricultural context, dams, levees, etc. In detail, my PhD research activities are addressed to unconventional applications in engineering and agricultural topic, such as rebar corrosion, condition foundation, levees, saline wedge, resin injections, etc.

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## Study of seismic waves attenuation in the Southern Italy

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*Keywords:* seismic attenuation, earthquakes, Southern Apennines.

In recent decades, seismic attenuation has become a crucial research topic in the field of seismology as it allows investigating and mapping the physical state of the lithosphere, in relation to the presence of fluids, heat flux and discontinuities. Southern Italy, and in particular the Southern Apennines, is an excellent natural laboratory for the study of seismic attenuation due to its significant seismic activity. For my doctorate study, I selected two areas of Southern Apennines: the first one is the Gargano Promontory (Apulia region), pertaining to the foreland domain, where OTRIONS and INGV seismic networks have been recording thousand of earthquakes since 2013; the second area is the High Agri Valley (Basilicata), located in the axial zone of the Apenninic chain, where INGV and ENI seismic networks have been operating since 2000. In addition to them, the seismic stations of the HAVO (former INSIEME seismic network) provide a continuous acquisition of natural and induced seismicity of the area since 2016. The research work aims to apply already validated methods to estimate general and local seismic attenuation in these areas, through the analysis of the recorded seismic events with a good signal-to-noise ratio. The ultimate step consists of the imaging analysis by applying heuristic and deterministic approaches. Finally, by performing a multidisciplinary geological-geophysical comparison, the results of the studies have been interpreted to improve the state of knowledge on the structural and geodynamic setting of the examined areas.

**Mercury and metalloid background and baseline in soils, waters and stream sediments:  
a geochemical approach in the eastern portion of the Mt. Amiata district  
(Southern Tuscany, Central Italy)**

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*Keywords:* Mt.Amiata, heavy metals, geochemical baseline.

Heavy metals (HMs) are critical components in waters and soils and play a key role for human health since they are either essential or toxic. Their distribution in environmental matrices is rather heterogeneous since they are affected by different processes (e.g. original concentrations of the bed-rock, water-rock interaction). Background (BG) concentrations of HMs that may impact human health are thus useful references to establish whether they are related to the possible presence of anthropogenic activity or are geogenically derived. However, the term geochemical baseline (GB) is more useful. It represents those conditions where the anthropic pressure is (was) already occurring, such as in the Hg district of the Mt. Amiata (MA) volcanic complex (Tuscany, central Italy) where HgS-rich ore deposits have been cultivated for a century to produce liquid mercury. Here, the mineralization (Hg and SbAs-sulfide ore deposits) was likely due to shallow hydrothermal systems associated with the emplacement of granitoid rocks at mid and upper crustal levels in southern Tuscany during the Plio-Pleistocene. The PhD project is focused on a rectangular area (~120 km<sup>2</sup>) that covers the eastern portion of MA and includes the main Hg-already abandoned mines such as Abbadia San Salvatore (AAS) and other six of the most important sites of exploitation and production of Hg. To respond to the EU and Italian regulations, it is of paramount importance to define BG-GB values in the selected area, the target elements being Hg, As and Sb (HAS). However, the analytical spectrum includes other parameters useful to understand their possible source(s), e.g. mineralogical composition and HMs, usually associated with HAS. Previous studies showed that the main Hg source in the riverine network waters is possibly caused by the interaction of meteoric waters with the MA Hg-mines, while recent investigations showed high contents of chalcophile elements in soil even far away from the mining areas. Thus, it becomes important to establish the HAS concentrations in the environmental matrices to understand the real source of contamination and quantify environmental pollution. The main aims of this study are: 1) analyzing the HAS concentrations and other associated metals in top- and sub-soils (10-50 and 50-150 cm, respectively), and stream sediments to estimate the BG-GB; 2) determining the GB values in the AAS groundwater system; 3) using a statistical and geostatistical approach, such as robust PCA, combined with a geochemical mapping to understand the spatial distribution of the investigated metals; 4) defining at what extent the mining activity has affected the environmental compartments; 5) investigating speciation, bioavailability and relation with organic matter of HAS in both the pedological cover and stream sediments. Hg speciation will be carried out by thermal desorption techniques; 6) suggesting possible remediation actions to reduce the exposure to HMs.

## A comparison between forward modelling and independent thermobarometry: preliminary results for Grt-bearing metapelites from the Lesser Himalayan Sequence

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*Keywords:* phase diagram modelling, P-T metamorphic conditions.

Tectonic models of collisional orogens mostly derive from the study of metamorphic rocks nowadays exposed at the surface within orogenic belts. The understanding of geodynamic and geochemical processes occurring at depth within collisional belts relies on our ability to accurately estimate pressure ( $P$ ) and temperature ( $T$ ) conditions registered by metamorphic rocks. Four major groups of techniques are nowadays available for petrological investigations (e.g., Lanari & Duesterhoeft, 2019): (i) conventional thermobarometry, (ii) multi-equilibrium thermobarometry, and (iii) forward thermodynamic modelling, which are now routinely applied, and (iv) “less-conventional” thermobarometric approaches (e.g. trace element thermometry, spectroscopic thermobarometry). Of the three routinely applied methods, forward thermodynamic modelling allows the prediction of equilibrium mineral assemblages by minimizing the total Gibbs free energy of a system for a specific bulk composition. This approach thus uses mineral assemblages, compositions and modes together to constrain  $P$ – $T$  conditions, which is particularly robust for well-equilibrated samples. In fact, the forward modelling approach has some limitations which may influence the reliability of the  $P$ – $T$  results (e.g., the choice of an appropriate reactive bulk composition; the possibility that kinetic factors prevent the achievement of equilibrium; the uncertainties inherently associated with different databases and solution model packages; Spear et al., 2016). Alternatively,  $P$ – $T$  conditions may be determined using empirically calibrated thermobarometers (e.g., trace element thermometry, elastic geobarometry), or multi-equilibrium thermobarometry requiring few phases to be in equilibrium (e.g., white mica and quartz).

Here we present a preliminary comparison of thermobarometric estimates obtained through forward thermodynamic modelling and independent thermobarometric approaches on garnet-bearing metapelites from different sectors of the Lesser Himalayan Sequence (LHS). Since the LHS is characterized by a structural upward increase in metamorphic conditions, the analysis of samples from different structural levels can also help in identifying specific advantages and disadvantages of each methodology at different metamorphic grades.

Lanari P. & Duesterhoeft E. (2019) - Modeling metamorphic rocks using equilibrium thermodynamics and internally consistent databases: Past achievements, problems and perspectives, *Journal of Petrology*, 60, 19-56.

Spear F.S., Pattison D.R.M. & Cheney J.T. (2016) - The metamorphism of metamorphic petrology, in: *The Web of Geological Sciences: Advances, Impacts, and Interactions II*, edited by Bickford, M.E., Geological Society of America Special Papers, 523.

## **Tephrochronologic study on Hasandağ pyroclastic deposits (Central Anatolian Volcanic Province) in order to reconstruct its recent explosive volcanic history**

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*Keywords:* Hasandağ Stratovolcano, pyroclastic deposits, tephrostratigraphy, tephrochronology, physical volcanology.

The Central Anatolian Volcanic Province (CAVP) is a significant region of postcollisional volcanic activity in Turkey. The most notable product of volcanic eruptions within this area is the extensive Cappadocian Ignimbrites, encompassing an impressive expanse of about 20000 square kilometers. The CAVP has witnessed eruptive activity in both basaltic monogenetic volcanic fields and large felsic polygenetic complexes, which include Acıgöl caldera, Erciyes, and Hasandağ stratovolcanoes (the most active, and dangerous composite volcanoes in the CAVP) since the early Quaternary period. Hasandağ volcano has produced large explosive eruptions during the last million years and several caldera collapses. The lack of information about young explosive eruption products and the related tephra layers is a significant limitation in the investigation of the Hasandağ volcanic history. This knowledge gap hinders our understanding of recent volcanic activity and its potential volcanic hazards. The fumarolic and seismic activity recently increases around Hasandağ volcano (e.g., Diker et al. 2018; Ulusoy et al. 2021). Therefore, further studies on the volcanic history, magnitude, distribution, and impacts of its explosive eruptions are necessary. For this reason, the main goal of my Ph.D. project is to reconstruct the recent explosive volcanic history of the Hasandağ Volcanic Complex. The specific objectives of this Ph.D. are: 1) Identify and characterize Hasandağ proximal pyroclastic deposits using stratigraphic correlations, volcanic glass geochemistry and morphology, granulometry, and geochronology analyses (U-Th and Ar-Ar); 2) Elaboration of a new geological map of the Hasandağ, including the newly differentiated pyroclastic deposits; 3) A volcanic glass geochemistry (major and trace elements) and geochronological databases of the Hasandağ pyroclastic deposits will be generated and published to use for future tephrochronological correlations; 4) Interpretation of eruption dynamics and estimation of the physical parameters of one of the most important explosive eruptions by detailed physical volcanology studies. All this Ph.D. research will allow the completion of the reconstruction of the explosive volcanic history of Hasandağ Volcano. The physical parameterization of volcanic eruptions can play a crucial role in volcanic hazard assessment. The glass chemistry analysis in pyroclastic deposits can contribute to the complete tephrostratigraphic framework of Hasandağ volcano and allow data for paleoenvironmental reconstructions and archaeological studies.



## The Jurassic Paleogeographic evolution of a carbonate succession in the Sciacca area (Southwestern Sicily)

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Keywords: platform drowning, Jurassic, condensed section.

The sedimentological-stratigraphic study of the Mesozoic carbonates outcropping in the Sciacca area (southwestern Sicily) provided new data on the paleogeographic evolution of the southern sector of the western Tethys margin during the Jurassic. The study area belongs to the so called “Saccense” carbonate platform that was one of the paleogeographic domains that developed along the Western Tethys.

We analysed three sections at Mt San Calogero (A and B) and Rocca Porcaria (C). The microfacies analysis allowed to distinguish two units separated by an unconformity: i) a shallow water peritidal limestone unit and ii) a condensed pelagic unit. A complex network of neptunian dykes, sills and syn-sedimentary faults has been observed along the studied successions.

The shallow water unit consists of parallel-bedded peritidal limestone organized in shallowing upward cycles. Wackestone/packstone with abundant benthic foraminifera (*Siphovalvulina* sp. and *Lituosepta* sp.), calcareous algae (*Paleodasycladus mediterraneus*, *Thaumatoporella parvovesiculifera* and *Cayeuxia* sp.), small bivalves and gasteropods characterize the latter. This microfacies association allowed to date the unit to Sinemurian – Pliensbachian age, differently from Ruggieri (1959) who indicated an Upper Triassic age.

An interval of non-deposition, represented by Fe-Mn oxide crust, occurs between the two units only along the section B.

The condensed pelagic unit consists of pinkish to reddish packstone/grainstone with abundant thin-shelled bivalvs (*Bositra* sp.), often chaotically arranged, planktonic (*Protoglobigerina* sp.) and benthic foraminifera, passing upward to ammonites-rich nodular limestone.

The *Bositra* packstone was attributed to late Bajocian–early Oxfordian p.p. thanks to a correlation with closer sections (Contrada Monzealese and Contrada Diesi). The nodular limestone of section A was ascribed to the middle Oxfordian by the association of *Gregoriceras riasi*, *Gregoriceras fouquei* and *Sowerbicerias* sp..

A level of wackestone/packstone with tangential micritic ooids and planktonic foraminifera occurs only at section A at the top of *Bositra* packstone, followed by nodular ammonitic limestone.

The drowning of the carbonate platform, testified by the uncoformity between the shallow water peritidal limestones and the condensed pelagic unit, reflects paleoenvironmental and paleogeographic variations related to the opening of Alpine Tethys. Moreover, the microfacies differences observed along the three sections reflect the influence of tectonics on sedimentation processes during the Middle – Late Jurassic interval.

Ruggieri G. (1959) - Osservazioni preliminari sulla stratigrafia della regione di Sciacca. Rivista Mineraria Siciliana, 58-59, 189-195.

## **The influence of tectonic confinement on lateral and vertical turbidite facies distribution (Firenzuola turbidite system, Marnoso-arenacea Formation, Italy)**

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*Keywords:* Marnoso-arenacea Formation, foredeep turbidites, facies analysis, tectonic confinement, depositional lobes.

This work focuses on the serravallian foredeep turbidites of the Marnoso-arenacea Formation (MAF), known in the literature as the Firenzuola system or Unit V. This Unit records progressive closure of the MAF inner basin and consequent depocenter shift toward the outer basin due to the coeval growth of two regional tectonic structures parallel and perpendicular to paleocurrents, which are the Mt. Castellaccio thrust and the Verghereto high. Unit V depositions is also controlled by the Casaglia mass transport complex (MTC), a 500m thick transversal unit.

The main goal is to provide a high-resolution stratigraphic framework of Unit V, thanks to bed-by-bed correlations and a detailed facies analysis. Grain size was also analyzed using a laser diffraction granulometer for characterizing facies and sedimentary structures.

As shown in previous works, Unit V can be subdivided into two sub-units, Unit Va and Unit Vb, separated by the Bedetta MTC, found for the first time in the study area. This MTC testifies a further basin narrowing phase and an increase in basin confinement that favour flow deceleration and possible hydraulic jumps. This is testified, in Unit Vb, by the drastic increase in the sandstonemudstone ratio, mud-draped scours and massive to crudely laminated coarse-grained sandstones characterized by widespread occurrence of mudstone clasts, flame structures and traction bypass facies. In fact, while Unit Va is dominated by contained reflected beds that tend to be controlled by the morphological barrier created by Casaglia MTC, Unit Vb is dominated by facies recording high deceleration rates of basal high-density supercritical flows and the bypass of low-density turbulent flows. These processes influence the lateral and vertical facies variations of depositional lobes, as well as their geometries.

This work has allowed a paleogeographic reconstruction of this portion of the basin, which can be particularly suitable for stratigraphic modeling and analogs for laboratory experiments. A subdivision of Unit Vb in depositional lobes is also provided, in order to better understand lobe and interlobe geometries, architectural hierarchy and depositional mechanisms.

## New studies and characterizations of mineral deposits and mining dumps in Sardinia

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*Keywords:* critical raw materials, Sardinia, mines.

Since 2010 the European Union established a list of materials of great importance to the economy and industry – the Critical Raw Materials (CRMs) – for which there are supply risks due to geological and geopolitical factors (European Commission, 2023). Accordingly, the European Union focused on substituting the most problematic CRMs in the industrial cycles, on their recycling, and on new reassessments of mineral resources in European districts. Sardinia is historically the most important Italian mining region, still hosting CRMs ore deposits (e.g., fluor spar, feldspar, etc.) of continental relevance. In this region, the last century's mining activities particularly involved the exploitation of base metal (Pb and Zn) and Ag ores, producing millions of cubic meters of waste materials. Among the CRMs enlisted in 2023 by EU, Sardinia hosts: Bauxite (Nurra district), Antimony (Gerrei district), Baryte (Sulcis-Iglesiente and Sarrabus districts), Bismuth-Cobalt-Gallium-Germanium-Nickel (Montevecchio district), Feldspar (Orani district), Fluorspar (Gerrei and Sarrabus districts), HafniumManganese-Scandium-Vanadium (W Sardinia – Sulcis), LREE-Tungsten (Sulcis) and Copper (Central Sardinia). Are these CRMs deposits of economic relevance?

Starting from the bibliography and the data present in the previous metallogenic maps of Sardinia (1978 and 2008), it will be necessary to study, characterize and update the marginal deposits that have not yet been exploited or partially explored, aiming to discover new deposits and, also, to reevaluate the CRMs content in waste and residues deriving from previous mining activities. It will be necessary to carry out field activities, during which mineralisation and mining wastes will be sampled and analysed in the laboratory.

The laboratory activities will consist of X-Ray Diffraction (XRD) analyses to detect their mineralogical composition, X-Ray Fluorescence (XRF) to investigate the trace elements and Scanning Electron Microscope (SEM) analyses to study their chemical composition and their morphology. Some samples will be analysed by inductively coupled plasma optical emission spectroscopy (ICP-OES) analyses and inductively coupled plasma mass spectroscopy (ICP-MS) to define their whole chemical composition, particularly the presence of the CRMs.

In conclusion, all these data will be synthesised in a database which will be an important reference for the possible retreatment of the mining dumps and for the eventual reopening of some mines. The database will also allow an update of the mining knowledge about Sardinia, now holding on to the second version of the Metallogenic Map of Sardinia (Tocco et al., 2008). The novelty of this study is the investigation of mining dumps as resources not considered in the two previous metallogenic maps of Sardinia. At last, the purpose of the project is the publication of a new metallogenic map of Sardinia in a digital format and viewable through a Geographic Information System (GIS).

European Commission (2023) - Study on the Critical Raw Materials for the EU. Fifth list. Final report.

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Tocco S., Marcello A., Mazzella A., Naitza S., Pretti S., Valera P. & Valera R. (2008) - Carta Metallogenica e delle Georisorse della Sardegna in scala 250.000.

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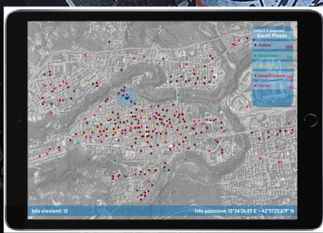
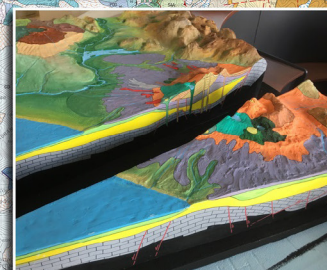
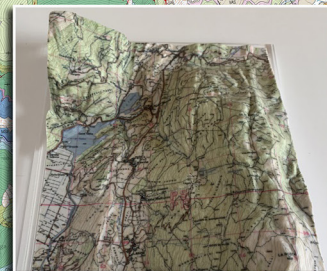
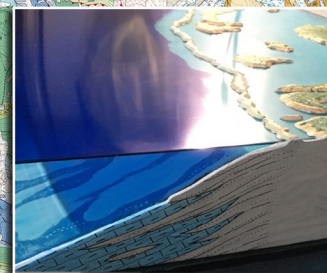
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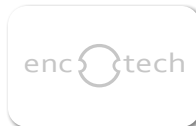
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