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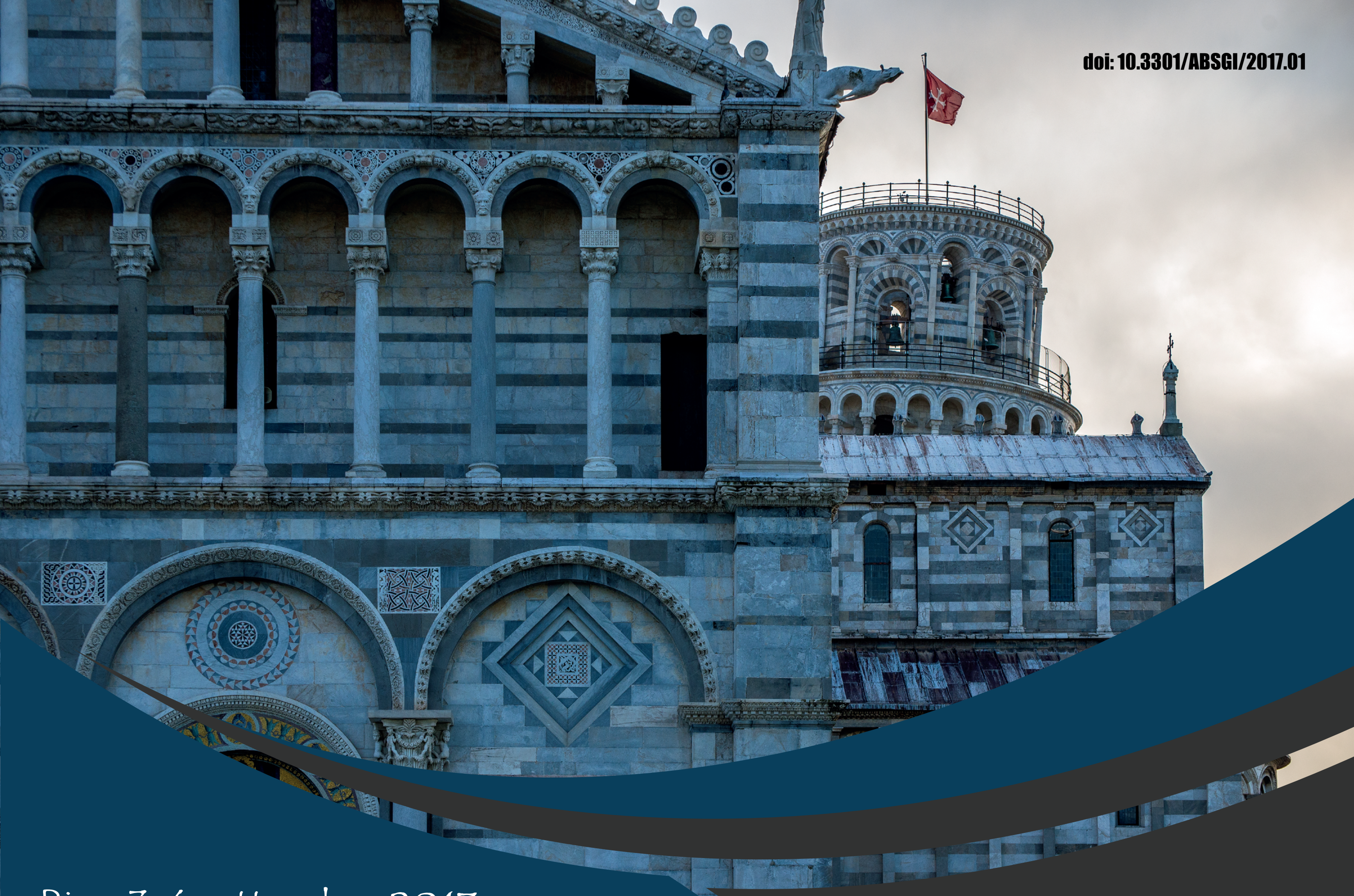

Pisa, 3-6 settembre 2017

ABSTRACT BOOK

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Geosciences: a tool in a changing world

Associazione Italiana di Vulcanologia

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Cristian Biagioni, Bernardo Carmina, Yuri Galanti, Marco Pasero, Fabio Massimo Petti.

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Plenary lectures

The 2016-2017 seismic sequence of Amatrice and Norcia

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Keywords: earthquake, Amatrice, Norcia.

1) Source complexity inferred from rupture models and seismicity evolution

The seismic sequence that struck the sector of the Central and Northern Apennines (Italy) comprised between the towns of Amatrice, Accumoli, Norcia and Visso consists of a series of moderate-to-large magnitude earthquakes ($5.0 < M_w < 6.6$) occurred within a few months activating a nearly 70 km long normal fault system oriented in the Apennines direction. The seismicity is relatively shallow (depths < 10 km) and the largest shocks nucleated at a depth of nearly 8 km. The main shocks and most of the aftershocks show NNW–SSE striking focal mechanisms in agreement with the current NE-SW extensional tectonic setting of Central and Northern Apennines.

The sequence began on August 24th with a M_w 6.0 earthquake, which struck the region between Amatrice, Accumoli and Norcia and caused 299 fatalities and extensive damages in the urban and rural surrounding areas. On October 26th 2016, another M_w 5.9 main shock occurred near Visso and Ussita at the northern edge of the aftershock zone that followed the August 24th event extending the activated seismogenic area toward the NW. Four days after the second main shock and more than two months since the beginning of the sequence, on October 30th 2016, a third larger earthquake (M_w 6.5) occurred near Norcia, roughly midway between Accumoli and Visso, severely damaging the already afflicted towns and villages in this sector of the Apennines. On January 2017 four moderate-magnitude ($5.0 < M_L < 5.5$) earthquakes occurred in the southern part of the activated seismogenic volume near Montereale and Campotosto. All the main shocks nucleated at the base of a SW dipping normal fault system, segmented by the presence of crosscutting compressional structures.

Field observations, GNSS and InSAR data and seismic waveforms reveal the heterogeneity of the rupture process during individual earthquakes and the complexity of the activated fault system. The August 24th M_w 6.0 earthquake ruptured a nearly 20 km long normal fault with a quite heterogeneous slip distribution characterized by two shallow slip patches located up-dip and NW from the hypocenter. For this earthquake fault dimensions and peak slip values are relatively large for a moderate-magnitude event. The October 26th M_w 5.9 main shock consists of a double event rupturing contiguous patches on the fault segment (SW dipping) of the normal fault system. The rupture history during the largest main shock of the sequence (M_w 6.5), occurred on October 30th 2016, reveals an extraordinary complexity: the coseismic rupture propagated on a normal fault and on a blind fault inherited from compressional tectonics.

Geodetic and seismological observations corroborate the interpretation of a seismic sequence characterized by complex multi-fault coseismic ruptures and heterogeneous distribution of slip on individual segments. These earthquakes raise serious concerns on our understanding of fault segmentation and seismicity evolution during sequences of normal faulting earthquakes.

2) Origin of the seismicity in the Apennines

The geodynamics of the Apennines is controlled by the "easterly" retreat of the Adriatic-Ionian subduction zone. This mechanism provides contractional tectonics in the frontal thin-skinned accretionary prism and contemporaneous thick-skinned backarc extension along the Apennines and Tyrrhenian Sea. Local transfer zones of differential slab retreat, salients and recesses in the accretionary prism, transfer zones within the dilatational backarc basin are rather characterized by strike-slip tectonics. This scenario is shaped by different geotherms that generate variable depth of the brittle-ductile transition (BDT), hence controlling the volumes that can be activated during the seismic cycles. The largest extensional earthquakes occur where the BDT is deeper along the Apennines belt. This happens where the topography is higher and the lithostatic load (sigma 1) is therefore greater, increasing the differential stress. Vice-versa, the most energetic contractional earthquakes generate where the topography is low, since the lower the lithostatic load (sigma 3), the larger the differential stress. All earthquakes are associated to the propagation of elastic waves. However, they are fueled by different types of energy. In contractional and strike-slip settings, the earthquakes dissipate elastic energy accumulated within a volume above the creeping layer of the crust. In extensional settings, earthquakes are rather the result of gravitational collapse of the brittle upper crustal prisms. Since the evolution and energy accumulation of earthquake preparation and nucleation between normal fault and thrust-related earthquakes are different, we need to distinguish the different processes, *i.e.*, graviquakes and elastoquakes. Graviquakes have the maximum depth of the seismogenic zone about one third with respect to the length of the volume affected by the collapse. The dimension of the volume dictates the length of the fault system that allows the crustal volume to fall and deform into a sag basin. InSAR data of the 2016 Amatrice-Norcia sequence show that the subsided area during the coseismic stage is about 10 times larger than the uplifted volume (180-230 Mm^3 *vs.* 15-20 Mm^3). This supports the notion that extensional earthquakes are due to the closure at depth of dilated crustal volumes throughout microfractures in the brittle upper crust during the interseismic stage. Gravitational energy is hundreds of times larger with respect to the earthquake energy, confirming that it is far than enough to generate the earthquake, plus folding, fracturing and shearing rocks. This may also explain why aftershocks last longer along normal faults, since the crust will continue to move in favour of gravity until the equilibrium will be reached, whereas along thrusts, the aftershocks are inhibited because the volume has to move against gravity. Seismic precursors, if any, may then have different sign and this can be one of the reasons why they have not yet been recognized.

Petrochronology – deciphering the temporal archive in rocks

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Keywords: petrochronology.

Not long ago, rocks had an age – even an "absolute" age – as detemined by geochronological methods based on one or more radioactive decay clocks (*e.g.*, U-Pb, Th-Pb, Nd-Sm). Recent advances have lead to a paradigm shift: as ever smaller sample volumes have become datable with increasing precision, results often showed *not one age* but *a range of dates*. Interpreting such results demands an integrative approach that combines petrogenetic analysis with local chronometry.

Petrochronology is this ambition of deciphering and dating detailed stages in a rock's evolution (Engi et al., 2017). In essence, this involves four steps: (1) investigation of petrographic textures and mineral assemblages with the aim of establishing a relative chronology; (2) microchemical analysis of coexisting minerals by EPMA (electron microprobe) and LA-ICP-MS (for trace elements); (3) petrological quantification of *P-T* conditions by thermodynamic (or kinetic) modeling; (4) micro-dating of individual growth zones in one or more datable minerals from the assemblages analyzed (in 1-3).

Sounds like a lot of work – what's the benefit? Whether we aim to understand the formation of magmas – their chemical and physical evolution with time – or to trace metamorphism in a subduction factory, the rock archive preserves evidence of how the tectonic engine has changed thermal and baric conditions. Insight into the duration and rates of geological processes demands a detailed temporal sequence of well delimited events. While numerical models help us sharpen the questions we address when studying select samples, in turn the relevance of such models can and must be tested by comparison to the rock record. It is particularly critical to compare the *rates* – of heating and cooling, (de)compression and strain – determine in sample-scale studies with those used in numerical models or obtained from these. It is a two-way test: petrochronological data can provide critical tests to our understanding of Earth dynamics; conversely, the significance of individual age data needs testing in the context of a tectonic model.

This lecture highlights the state of the art and outlines current limits, both technical and conceptual. The key in petrochronology is establishing context: we must aim to link age data obtained by LA-ICP-MS or ion probe (SIMS, SHRIMP) reliably to the minerals or assemblages used to quantify physical growth conditions. Petrology now uses sophisticated tools, *e.g.*, inclusion barometry, thermometry in chemical domains or using trace elements in accessory minerals. Diffusion has long been seen as essentially a limitation or obstacle to age dating, while its utility is only starting to be realized, notably for constraining the duration of processes (Kohn & Penniston-Dorland, 2017).

Select studies of applied petrochronology will be presented, covering a wide range of geological contexts.

Engi, M., Lanari, P., Kohn, M.J. (2017): Significant ages-An introduction to petrochronology: Rev. Mineral. Geochem., 83, 1-12.

Kohn, M.J. & Penniston-Dorland, S.C. (2017): Diffusion: obstacles and opportunities in petrochronology: Rev. Mineral. Geochem., 83, 103-152.

Session S1:

Cosmochemistry of planetary materials and planetary processes

Conveners:

Luigi Folco (Univ. di Pisa)

Cristian Carli (INAF, Roma)

Structure characterization of impact natural diamond from Popigai crater

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Keywords: impact, diamond, lonsdaleite, stacking disorder.

Impact cratering is one of the most frequent high-energetic and potentially catastrophic event occurring at the Earth surface and in the planetary system. For example, the energy released from an impact occurring on the Earth's surface as calculated even for a small impact crater appears to be 3 orders of magnitudes higher than the Hiroshima atomic bomb. These enormous energies and the very short duration can cause unique irreversible changes to rocks and minerals (*e.g.*, deformations, phase transformations) and are compatible with P and T conditions required to transform graphite into diamond (4.5 GPa at 1000°C) and are also enough to induce deformation in the newly formed diamonds.

Popigai impact diamond represents a shock-metamorphosed mineral found in the large ~100 km diameter Popigai crater in Siberia, Russia, dated at ~ 35.7 Ma. The impact reached the basement rocks (*e.g.*, depth > 5 km) containing graphite-bearing gneisses, producing peak pressures ~ 600 GPa. It is estimated that shocked graphite was transformed throughout a large central region, within ~ 13.6 km of ground zero, into "lonsdaleite"-bearing "impact diamond" (Masaitis, 1998). The Popigai impact diamond contains up to 50% diamond and 50% diamond-related materials with significant hexagonal characteristics, interpreted as "lonsdaleite".

High-resolution synchrotron X-ray diffraction data of Jones et al., (2016) collected for a laboratory-shocked (DC4) and a natural impact diamond from Popigai (POP20) showed that hexagonality can be achieved by shocking diamond as well as from graphite precursors. Their approach provides an "hexagonality index" (Salzmann et al., 2013) that can be used to characterize and distinguish among samples that have experienced different degrees of shock or static high pressure-high temperature treatments. To better understand the origin of Popigai diamond and if the stacking disorder could provide an entire record of the impact shock event, we have investigated by high-resolution X-ray diffraction the preserved traces of deformation (Salzmann et al., 2013) in other natural impact diamonds from Popigai impact crater. Therefore, the new quantitative analyses, performed by analyzing X-ray diffraction data with the DIFFaX software package, enabled us to better characterize and constrain the high pressure and high temperature conditions experienced by diamonds from Popigai impact crater.

Acknowledgements: This work has been supported the Barringer Crater Award to M. Murri, and by the MIUR-SIR Mile Deep (grant number RBSI140351) to M. Alvaro.

Jones, A.P., McMillan, P.F., Salzmann, C.G., Alvaro, M., Nestola, F., Prencipe, M., Dobson, D., Hazael, R., Moore, M. (2016): Structural characterization of natural diamond shocked to 60GPa; implications for earth and planetary systems. Lithos, 265, 214-221.

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Impact ejecta from the Australasian microtektite layer: implication for target parent rock and impact location

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Keywords: tektites, Australasian tektite/microtektite, strewn field, impact ejecta, shock metamorphism, impact.

The nature of the target rock hit by the km-sized impactor that generated the Australasian tektite/microtektite strewn field ~ 0.8 Ma ago is still poorly constrained, although most authors suggest a sedimentary source rock (*e.g.*, Mizera et al., 2016). Its identification is of crucial importance to address the outstanding issue of the yet unknown crater location of the largest tektite/microtektite strewn field so far discovered on Earth (~ 15% of Earth's surface). Many authors suggest, however, that it should be located somewhere in Indochina and that its diameter should exceed 30 km (Ma et al., 2004; Glass & Koeberl, 2006).

In order to better constrain the nature of the target rock, we focused on the petrographic and geochemical characterization of hundreds of impact ejecta particles (namely, rock fragments and partly glassy particles up to some hundreds of micrometers in size) from the Australasian microtektite layer in two deep-sea sediment cores in the Indochina area (ODP 1144A, and SO95-17957-2).

Data so far gathered by means of µ-Raman Spectroscopy, FE-SEM, EMPA and LA-ICP-MS confirm the occurrence of highly shocked target rock material in the microtektite layer consisting of unmelted to totally melted particles. Unmelted and partly melted particles show evidence of shock metamorphism including coesite, high-pressure TiO_2 polymorph with an α-PbO_2 structure (*i.e.*, TiO_2 II) and shocked quartz with PDFs. The glass in the partly melted to totally melted particles is vesicular with major element bulk composition similar to that of the Australasian tektites/microtektites, thereby documenting their petrogenetic association. The mineral assemblage include mainly fine-grained quartz plus less abundant K-feldspar, plagioclase, mica phase and as accessory garnet, rutile, zircon, ilmenite, titanite, and apatite. Remarkably, some partly to totally melted particles bear evidence for dust accretion (mainly SiO_2 grains) during ejection. Additional evidence for late accretion are high Fe-Ni microcrystals, on the external surface of some particles, which may carry a signature of projectile contamination.

This study documents the potential for the impact ejecta materials found in the Australasian tektite/microtektite layer to yield further insights not only on the nature of the target rock but also on the impact scenario.

Acknowledgements: MIUR-Programma Nazionale delle Ricerche in Antartide *grant PNRA16_00029*

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Reflectance and Raman spectroscopy of glassy igneous material with variable oxidation states

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Keywords: igneous glasses, reducing-oxidizing conditions, reflectance spectroscopy, Raman spectroscopy.

Silicate glasses with igneous compositions may represent an abundant component of planetary surface material via effusive volcanism or impact cratering processes. Several planetary surfaces are mapped with hyperspectrometers in the visible and near-infrared (VNIR) and the middle infrared (MidIR) from Earth-based, orbit remote sensed and *in situ* rover data. In VNIR, crystal field absorptions are useful to discriminate iron-bearing silicate components; while in MidIR vibrational absorptions are related to asymmetric and symmetric stretches varying with the crystal lattice. Moreover, future Mars rover missions will carry aboard Raman spectrometers, which will permit identification of molecular vibrations related to inelastic scattering of the sample.

So far, few studies investigated the spectral properties of systematic glasses compositions and at different oxygen fugacity. For these reasons studying glasses represents an important effort to document and to interpret spectral features of planetary crusts where glasses are present, but may be difficult to map.

We consider samples from Carli et al. (2016), regarding VNIR spectroscopy of glassy igneous materials produced in Earth-like atmospheric conditions. Here, we expand on that effort by including glasses formed under reducing conditions. In this study, glasses were produced at -9.3 log fO_2 and 1400/1500°C at the University of Munich using a gas-mixing furnace. The major element composition, homogeneity, and the $Fe^{3+}/Fe_{tot.}$ ratio of products were analytically determined. Moreover, we extend the analysis to the MidIR and to Raman spectroscopy for all the samples.

Afterwards, powders were produced with sizes from 250-224 to 50-20 µm and measured in reflectance at IAPS-INAF, Rome. Reflectance spectra were acquired in the VNIR from 0.35 to 2.5 µm with a FieldSpec-Pro® mounted on a goniometer and in the MidIR from 5 to 14 µm with a Vertex-80 Bruker® FTIR. Spectra were obtained with 30° incident and 0° emission angles. Raman spectra were acquired using a m-Raman (HORIBA®; XploRa-Raman-System) equipped with a green laser focused through the 100× objective to a ~1 µm spot. The system was set with a 1200T grating and confocal hole of 300 µm and slit of 200 µm.

Reflectance spectra show the expected diagnostic bands in the VNIR correlated to the iron. Christiansen reflectance minimum in the MidIR shows a position related to the SiO_2 and an absorption at longer wavelength varying with the sample compositions. Moreover, Raman spectra show a clear variability between the different samples. These spectral characteristics will be discussed in this work and the comparison with spectra collected from samples synthesized at oxidizing and reducing condition will be investigated.

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Microscopic impactor debris at Kamil Crater (Egypt): the origin of the Fe-Ni-oxide microscopic spherules

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Keywords: Kamil crater, iron meteorite, Fe-Ni oxides, impact melt spheres, impact cratering, ablation.

Kamil is a small (Ø 45 m) impact crater in southwestern Egypt (22°01'06"N, 26°05'16"E) generated by the hypervelocity impact of a small iron meteorite (Gebel Kamil) on a sedimentary target (Cretaceous sandstones Gilf Kebir Formation) less than 5000 years ago. Due to its extraordinary state of preservation Kamil is considered a type structure for small-impact craters on Earth and thus a natural laboratory to investigate all the processes and products associated with the impact of small projectiles (Folco et al., 2011).

We focus here on the nature of the microscopic Fe-Ni oxide spherules abundantly found in the soil around crater whose origin is still uncertain. Folco et al.(2015) concluded that these Fe-Ni oxide spherules are i) the product of the melting of the iron projectile, having similar Ni/Fe (~ 0.3) and Ni/Co (~ 26) ratios to that of Gebel Kamil (D'Orazio et al., 2011); ii) likely impact melt debris being found together with other impact melt particles. These spherules are however similar to Fe-Ni oxide spherules found at the Sikhote Alin crater field (Russia) and interpreted as ablation spherules (Badyukov & Rajtala, 2012), *i.e.*, formed during the atmospheric flight of the Sikhote Alin iron meteorite through the melting of debris produced during its disintegration. Thus, whether the microscopic Fe-Ni oxide spherules formed through impact melting or ablation in the atmosphere is an open question.

We have selected 23 Fe-Ni oxide spheres in the 100-400 μm size range from four soil samples (S23, S24, S25, S26, downrange of the crater) collected during our 2010 geophysical expedition for a detailed mineralogical and geochemical investigation by FE-SEM, EPMA, μ-Raman and LA-ICP-MS analyses. SEM observations of the whole particles show that they are all spherical and characterized by a variety of quench textures, mainly dendritic. Minor amounts of target elements, *e.g.*, Si and Al, have been detected by EDS at the interstices between oxide dendrites. Target contamination is a key factor in discriminating ablation spheres from impact melt spheres, since the latter record the interaction projectile-target. The ongoing mineralogical and geochemical investigation of the interior of the Fe-Ni oxide spheres is expected to provide definitive proof on their origin as impact melt spheres and not ablation spheres as reported in literature for the Sikhote Alin impact event.

Acknowledgements: MIUR-PRIN2015 grant I20158W4JZ7

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Reflectance spectroscopy applied to terrestrial analogues of Martian water-related environments

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Keywords: Mars, reflectance spectroscopy, water-related environments.

Features related to mud, water and gas resurgences on Mars are primary objectives for climate change and astrobiology studies. Such environments have been recognized in numerous locations on the Martian surface (*e.g.*, Oehler & Allen, 2010; Pondrelli et al., 2011; Okubo, 2016) and many different interpretations have been suggested spanning between mud volcanism, ice-related phenomena and tsunami deposits and accordingly, to understand the processes that lie behind, various scenarios need to be addressed. Indeed, investigating the nature of the unconsolidated materials that have been mobilized could help us understand if the resurgences are related to i) sediments that could have been deposited and trapped during the Martian ancient past thanks to surficial sedimentary processes, hence hydrous alterations and possibly putative organic matter could be found, ii) or to serpentinisation, iii) or other hydrothermal alteration systems. We hence performed reflectance spectroscopy, from ultraviolet to far-infrared, at one fixed geometry (incidence 30°, emission 13°) on samples of basalt epithermal alterations, clay minerals, stromatolites and samples representative of wet sedimentary environments. We assigned the absorptions features to specific crystal field or molecular processes (Clark et al., 1999, and references therein) identifying diagnostic spectral parameters or indicator to provide new loads of information for present and future planetary exploration. In particular, considering the wavelength range from visible to near-infrared we retrieved parameters to be applied on hyperspectral images, as CRISM (onboard Mars Reconnaissance Orbiter) and OMEGA (onboard Mars EXpress), of Martian regions where mound fields, interpreted as sediment and water resurgences, have been detected in the lowlands (De Toffoli et al., 2017).

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The fractionation of rare earth elements (REE) in enstatite chondrites: implication for planetary formation in the Inner Solar System

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Keywords: enstatite chondrites, oldhamite, REE.

The solar system changes from a more reduced to a more oxidised chemistry with distance from the Sun (Baedecker & Wasson, 1975).

Most of the information on the genesis and evolution of the terrestrial planets in the inner solar system derives from geological studies of our own planet and the rare meteorites from Mars since samples from the two innermost planets Venus and Mercury are yet unavailable.

Enstatite chondrites (EC) are a relatively rare and unusual class of chondritic meteorites. They are made up of a highly reduced mineral assemblage consisting of FeO-free enstatite, variable amounts of metal and a complex assemblage of sulphides, phosphides and nitrides. This is indicative of formation in the innermost part of the solar nebula, possibly as near to the Sun as Mercury.

Rare earth elements (*REE*) are unique and valuable proxies for early solar system processes. *REE* have condensation temperatures between 1850 and 1400 K. At these conditions they are among the first elements that condensed ~4.6 Ga ago in the cooling solar nebula into refractory oxides and silicates, and so provide insights into the first stages of planet formation. Thermodynamic calculations predict that the *REE* abundances in meteorites are controlled by the relative *REE* volatilities, which depend on their oxidation state and are not smooth function of ionic size (Boynton, 1975).

EC contain oldhamite (CaS), which is recognized to be the major carrier of *REE* (Barrat et al., 2014). There are, however, few *in situ* studies of *REE* in EC.

Oldhamite and silicates (both enstatite and plagioclase) of 18 EC from the NHM-London, the Smithsonian NMNH, the meteorite collection of NASA and the MNA-Siena, have been analysed by LA-ICP-MS.

Preliminary results indicate that the *REE* distribution in oldhamite appears to be heterogeneous both between and within unequilibrated EC. For instance, data of 7 oldhamites in one unequilibrated EC (LAP 91020) show that *REE* are enriched 50 to 100 times with respect to CI, have variably fractionated *LREE*/*HREE* pattern and both positive and negative anomalies in Eu and Yb. It is unclear whether these patterns are related to nebular and/or planetary processes.

On the contrary, in equilibrated EC, oldhamite carries *REE* at concentrations ~150×CI and has deep Eu anomaly. Such pattern is likely the result of igneous processes.

Additional *REE* patterns, as well as the relationships between oldhamite and the other *REE*-rich phases will be discussed at the Meeting.

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Projectile identification in Australasian microtektites using Cr, Co and Ni ratios

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Keywords: tektites, microtektites, impact melting, impact cratering, Australasian.

Projectile identification is one of the challenges of large-scale impact cratering research due to the dilution of meteoritic material in impactites (typically < 1 wt%; Koeberl et al., 2012). The nature of the projectile that generated the Australasian tektite/microtektite strewn field, *i.e.*, the largest Cenozoic strewn field (~ 15% of Earth's surface), the youngest (~ 0.78 Myr old) on Earth, and the only one without a known impact crater so far (*e.g.*, Glass & Simonson, 2013), is an outstanding issue in large-scale impact cratering study.

We identify a chondritic impactor signature, most likely of an LL chondrite, in Australasian microtektites based on Co/Ni *vs*. Cr/Ni ratios in 77 Australasian microtektites (139 LA-ICP MS spot analyses from 47 microtektites studied in this work and 33 INAA bulk compositions of microtektites from literature) from within 3000 km from the hypothetical impact location in Indochina (~17°N, 107°E; Ma et al.2004).

Together with previous evidence from the ~ 35 Myr old Popigai and Chesapeake Bay ejecta (Glass & Simonson, 2013), our finding suggests that at least three of the five known Cenozoic distal impact ejecta layers were generated by the impacts of stony asteroids of chondritic composition, and most likely of ordinary chondritic composition. Tagle et al. (2007) pointed out that ordinary chondrite projectiles are responsible for a significant number of terrestrial impact craters. Our finding would thus strengthen previous hypothesis that this abundance could be related to the original position of their parent bodies close to the main resonance in the asteroid belt which generates a bias in the impactor population towards inner main belt objects.

The impactor signature found in Australasian microtektites documents mixing of target and projectile melts upon impact cratering, lending support to the impact cratering rather than to the low-altitude airburst scenarios discussed in the literature (Boslough & Crawford, 2008) as the process that formed the Australasian tektite/microtektites. Thus, the search for the Australasian tektite source crater needs to continue.

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Identification of mafic igneous rocks parentage by Handheld Energy Dispersive X-ray Fluorescence spectrometry

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Keywords: achondrites, classification, HH-EDXRF.

Forty-nine achondrites from Natural History Museum of London, Museo del Cielo e della Terra of San Giovanni in Persiceto, Museo Nazionale dell'Antartide of Siena, and the private collection of one of us were analysed with a handheld energy dispersive X-ray fluorescence (HH-EDXRF) spectrometer.

The studied achondrites include: 9 lunar meteorites, 17 Martian meteorites (SNCs), 5 angrites and 18 meteorites from asteroid 4 Vesta (HEDs).

The aim of our study is to demonstrate the effectiveness of HH-EDXRF for the preliminary classification of stony achondrites. The advantages of this technique include: i) portability of the instrument, ii) easy handling of the operating system, iii) minimal sample preparation, iv) rapid, non-destructive analyses with remarkable reproducibility and low detection limits for elements heavier than Na.

The instrument used in this study is a NITON XL3t GOLDD+ XRF spectrometer (50 kV, 200 µA, 2W). Analyses were carried out on smooth-flat surfaces and, if not available, on the most even surfaces. We have developed an analytical protocol for the accurate determination of elements of cosmochemical relevance, such as Mg, Al, Si, P, K, Ca, Ti, Mn and Fe.

Our results show that: (i) Fe and Mn are routinely obtained by HH-EDXRF allowing classification of differentiated stony meteorites based on bulk Fe/Mn ratios. (ii) The combination of Fe/Mn ratio with the concentration of other elements and/or element ratios can help to improve discrimination between different classes of achondrites where some overlap exists. We here demonstrate that Si and Ca/K against Fe/Mn can resolve the partial Fe/Mn overlap between lunar meteorites and angrites and between HEDs and SNCs, respectively. (iii) Fe/Mn values of achondritic meteorite fusion crust are indistinguishable from those of the interior. This implies that "rough and ready" Fe/Mn measurements of the fusion crusts of achondrites could be sufficient for preliminary screening and identification of their parentage.

Our study demonstrates that HH-EDXRF is a valuable and practical tool for curatorial purposes and is ideal both in the laboratory and in the field for first discrimination of achondritic meteorites.

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Kinetics and thermochemistry of carbonate mineral decomposition under conditions relevant to planetology and astrobiology

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Keywords: carbonates, decomposition kinetics, numerical models, spectroscopy.

In an astrochemical viewpoint, inorganic carbonates are often associated with the presence of organic matter and could be one of the key aspects of the Solar System complex chemistry (Flynn et al., 2003).

Carbonates are well known for their connection to organic molecules in cometary dust particles and are investigated in the context of planetology (Borg et al., 1999; Ehlmann et al., 2008; Busemann et al., 2009; Wray et al., 2016; De Sanctis et al., 2016). Recently, the role of carbonates as a cooling material in the context of the delivery of organic matter to biosphere from Space was pointed out (Bisceglia et al., 2017; Micca Longo et al., 2017).

Carbonate minerals decomposes into oxides and carbon dioxide (degassed), when moderately heated in vacuum. The kinetics of this process is still under investigation and its peculiarities have never been addressed in the space science field.

Here, we report on a research in progress aimed to establish decomposition kinetic models of carbonate materials of geochemical occurrence (aragonite, calcite, fossil materials).

Our models are based on simplified grain shapes, thermochemistry, Langmuir law of degassing, stoichiometry and empirical combination rules. In the experimental part, a set of carbonate samples is processed at different temperatures, between 900 and 1400 K. A transmittance spectrum of each powdered sample is taken before and after the processing, as well as an accurate measurement of its weight, both aimed to detect structural and chemical changes occurred in the sample.

Comparison suggests a lower decomposition rate than the one prescribed by thermochemical considerations. Possible explanations include the presence of water in the mineral sample, an activation energy, the diffusion of CO_2 in the porous material.

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Micro-imaging VIS-IR spectroscopy of Martian meteorites in support of the future MaMIss spectrometer measurements

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Keywords: hyperspectral microimaging, Martian meteorites, MaMIss, Mars anologues.

In the view of the future ExoMars 2020 mission, an activity of VIS-IR spectral investigations on terrestrial and extraterrestrial Mars Analogues is ongoing, in support of the Ma Miss *in situ* measurements. Ma_Miss is an imaging spectrometer that works in the range 0.4-2.2 µm with 20nm spectral sampling and that will observe the lateral wall of the borehole generated by ExoMars Rover's drill (Coradini et al., 2001). In this abstract, we describe some results about the spectral properties and characterization of mineral grains of the slabs of two Martian meteorites by means of the SPIM imaging spectrometer. SPIM works in the 0.22-5.05 µm spectral range, with a spatial resolution of 38x38 µm on the sample and represents the spare of the spectrometer on Dawn spacecraft (De Angelis et al., 2015). The meteorites investigated are North West Africa 8657 (NWA8657) and Dar Al Gani 489 (DAG489), basaltic shergottites. The average spectrum of the NWA8657 slab, in comparison with spectral measurements on other martian meteorites (Mcfadden & Cline, 2005) shows low reflectance values and 1 and 2 µm spectral absorptions indicating the strong presence of Ca-pyroxenes. The successive pixel by pixel analyses for the pyroxenes spectral speciation showed a great variability of clinopyroxenes in NWA8657. In fact, the 2 µm absorption at longer wavelength in some pixel does not always correspond to the 1 µm feature at longer wavelength. The average spectrum of DAG 489 is marked by a signature typical of low-Ca pyroxenes. Pixel by pixel analyses of DAG489 shows a more homogeneous composition of the pyroxenes characterized by the two major features centered at 0.98-0.99 and 1.98-2 µm. Further spectral absorptions related to sulfates, phosphates and carbonates were detected that are being validated by SEM-BSD to constrain the formation hystories of these two shergottites.

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Sedimentary rocks and processes in Margaritifer Chaos, Mars

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Keywords: Mars, phyllosilicates, CRISM, sedimentary processes.

The OMEGA and CRISM spectrometers revealed the presence of different hydrated minerals, including clay minerals, sulfates, carbonates and chlorides (Bibring et al.,2006), located in several areas of the Martian surface. The formation processes of clay minerals on Mars (Chevrier & Mathé, 2007; Ehlmann et al., 2013; Meunier et al., 2012; Bristow et al., 2015) is crucial to reconstruct the weather conditions and also the potential habitability of the planet.

On Earth, clay minerals mainly form through pedogenetic processes, or hydrothermal alteration or direct precipitation in water bodies.

Clay formation processes on Mars is thought to have been occurred early in its geological history, however reactivation of slope features (RSL) likely due to brine melting during the summer season has been extensively observed on recent data (Mushkin et al., 2010; McEwen et al., 2014). This may also indicate that chemical alteration of bedrock still occurs at places.

While we found the typical spectral adsorption bands of Al-rich clays, such as illite and montmorillonite belonging to the smectite group in Valles Marineris by using the CRISM hyperspectral data, a different clays assemblages was observed in Margaritifer Chaos, a complex fluvial system nearby Valles Marineris. The spectral signature of allophane (poorly crystalline clay), vermiculite, chlorite and other phyllosilicates belonging to the Fe/Mg smectite group, such as saponite and nontronite characterise the Margaritifer study area. This may suggest either a different alteration origin or an overlapping of different depositional processes. Polygons features are often associated to the clay signatures, suggesting the occurrences of desiccation processes.

On the contrary, large surrounding areas are dominated by basaltic composition with no evidence of diagnostic bands of clays or other phillosylicates, indicating the scale-dependency of these sedimentary events.

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Atmospheric entry model of mixed $Mg_xCa_{(1-x)}CO_3$ micrometeoroids

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Keywords: micrometeoroids, carbonates, atmospheric entry, decomposition kinetics.

Carbonates have been found in Mars meteorites (Borg et al., 1999), on the surface of Mars (Orofino et al., 2000), on the surface of Ceres (Rivkin et al., 2006), as well as in cometary dust (Busemann et al., 2009). Carbonates (dolomite) have been reported in a micrometeorite from the CONCORDIA collection (Duprat et al., 2007) and found in the form of mm-globules into Mars meteorites. Micrometeoroids, with a composition mainly based on carbonate minerals, have been the subject of recent studies (Micca Longo et al., 2017) as a possible delivery medium of organic matter to Earth. This concept complements previous studies on dolomite made in the STONE artificial meteor experiment (Brack et al., 2002) which considered macroscopic samples and LEO entry speed. In this context, decomposition kinetics and chemical self-cooling play an important role.

To address this issue, we generalize our previous atmospheric entry model in order to account for a mixed composition, including calcium and magnesium cations. The model is essentially an extension of that by Love and Brownlee (Love et al., 1991). Improvements include chemical decomposition, evaporation and consequent cooling. In the present extension to a solid mixture, we have included the stoichiometry of the material in its conversion from mixed carbonate to mixed oxide. Empirical relations are used to account for the energy transfer coefficient and the vapor pressure which are connected to the chemical composition.

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On the interior of carbon rich exoplanets: new insights from Si-C system at ultra-high pressure

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Keywords: C-rich exoplanets, Si-C, high pressure experiments.

More than 3200 exoplanets with different mass/radius ratio, therefore with a large diversity of sizes and compositions, have been discovered so far. Exoplanets with a mass between 1 and 10 times the mass of the Earth are defined as super-Earths and their mineralogical composition depends on that of the protoplanetary disk. The key variable in determining the chemical make up of such planets is the C/O ratio. Values of C/O ratio smaller than 0.8 correspond to an interior dominated by silicates (*e.g.*, terrestrial planets) whereas C/O ratio > 0.8 indicate interior enriched in carbon, resulting in a C-rich planet where Si may form carbides instead of silicates (Duffy et al., 2015). The recent detection of planet 55 Cancri e, with a particularly high C/O ratio, has increased the interest in carbon-rich planets. 55 Cancri e has been modelled as a layered structure of carbon, SiC and iron (Madhusudan et al., 2012). However, the accuracy of such type of models suffers the lack of experimental data on the behaviour of silicon-carbon compounds at extreme condition of pressure and temperature. Equations of state, determined from experimental data, only cover pressures up to 80 GPa (Nisr et al., 2017) and small amount of information are available about subsolidus relation, with only one theoretical study from Wilson & Militzer (2004) at pressures of multi-megabar. We performed high pressure and temperature experiments on SiC samples, combining laser heated diamond anvil cell and synchrotron X-ray diffraction. The obtained set of data provide information on the *P-T* region between 30-180 GPa and 300-3500 K. The results show evidences of coexistence of SiC with Si or C, depending on the starting composition, without the appearance of intermediate compounds. Moreover, between 65 and 80 GPa, SiC undergoes a phase transition with the zinc blend structure (B3), typical of ambient conditions, replaced by the rock salt structure (B1). This phase transition, also reported in previous literature work (*e.g.*, Yoshida et al., 1993), corresponds to a change in the coordination of the atoms, and is accompanied by a 20% volume reduction.

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Acfer 370: the "first" forsterite chondrite

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Keywords: Acfer 370, unequilibrated chondrite, forsterite chondrite.

The term forsterite (F) chondrites was used, for the first time, by Graham et al. (1977). These authors related four similar chondrites (Kakangari, Mount Morris, Pontlyfni and Winona along with some inclusions in the Cumberland Falls aubrite) to a new group of meteorites distinct from carbonaceous, enstatite and ordinary chondrites.

Soon after, further chemical and O-isotopes analyses allowed Davis et al. (1977) to establish a new meteorite group called Winonaites, whereas Kakangari was recognized as the type specimen of a separate grouplet. Nevertheless, the mineralogical and chemical characteristics of the inclusions in Cumberland Falls (CF) aubrite, as well as the inclusions in the Allan Hills A78113 (ALHA 78113) aubrite, were quite different from those of the winonaites and kakangari and, therefore, some authors decided to study systematically and completely such inclusions (Neal & Lipschutz, 1981; Verkouteren & Lipschutz, 1983; Lipschutz et al., 1988). Those clasts were provisionally named forsterite or F-chondrites, for the fact that the olivine found in these lithologies consisted of the pure magnesium-rich end-member of olivine.

Finally, Moggi Cecchi et al.(2009) studied and classified a new unequilibrated chondrite (Acfer 370) with similar textural (chondrule types PO, POP, PP, GOP-pk, RP, BO, C; mean size = 460 μm; abundance > 80% of the total volume), mineralogical (olivine Fa5.65; pyroxene Fs6.94-22.63) and isotopic ($\delta^{17}O = 2.67‰$; $\delta^{18}O = 4.17‰$; $\Delta^{17}O = 0.50‰$) characteristics to the chondritic inclusions of the Cumberland Falls and ALHA78113.

Therefore, Acfer 370 was recognized as the third member of the still unofficial Forsterite (F) chondrites group. However, differently from the Cumberland Falls and ALHA78113, it is a homogeneous meteorite and not a fragment or inclusion within an aubrite. Over the following years, other two meteorites with similar characteristics have been found, namely NWA 7135 (Irving et al., 2015) and El Médano 301 (Pourkhorsandi et al., 2016) meteorites.

In conclusion, the finding of Acfer 370 confirmed the existence of a new group of chondrites derived from a small and primitive chondritic asteroid of forsteritic composition that, at least in part, collided with the aubrite parent body short after their formation in the early solar system. The authors, consequently, recommend introducing the term F-chondrites in the official meteorite nomenclature.

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Oxygen isotopic analysis of Mineo (Sicily, Italy) pallasite

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Keywords: Mineo, pallasites, meteorites, ToF-SIMS.

Pallasites are stony-iron meteorites essentially composed of olivine [$(Mg,Fe)_2SiO_4$] with a metallic portion covering one-third of the total volume (Boesenberg et al., 2012) and principally consisting of Fe-Ni metal. The sample studied in the present work is a piece of the Mineo pallasite, named as the place where it fell in the South-Eastern part of Sicily (Italy) in 1826. The sole sample available in the world belongs to the Department of Physics and Geology at the University of Perugia. Preliminary chemical analysis allowed to locate Mineo meteorite in among the Main Group (MG) pallasites. A peculiar compositional variability of olivines was observed in terms of both iron (11-14 wt%) and trace elements. This observation is quite interesting because the composition of olivines is normally rather uniform within an individual pallasite (Buseck & Goldstein,1969; Boesenberg et al., 2012). The study of oxygen isotopes and trace elements is needed to definitely classify the Mineo meteorite.

The Mineo pallasite was sampled and the collected fragments were embedded in epoxy resin and polished up to 1 µm. The isotopic oxygen analysis was obtained by means of Time of Flight – Secondary Ion Mass Spectrometry (ToF-SIMS), which is a static technique used for surface analysis. Samples are bombarded with primary ions at typical energies of 10-30 k*e*V. The corresponding secondary ions are than accelerated into a flight tube and their mass is determined measuring their time of flight. Major advantages of this technique are: a) the high lateral resolution; b) only a limited destruction of the sample, *i.e.*, the erosion is very small due to the use of a pulsed beam; c) parallel detection of all secondary ions with one polarity in a single measurement; d) an adequate mass resolution for the separation of major mass interferences (Stephan, 2001). Five measurements were performed on Mineo fragments: 4 points in olivine and 1 in the metal phase. Oxygen isotopic ratios were used to calculate the $\delta^{18}O$ values. Four measurements have been done on a sample of the Brenham meteorite, used as internal standard. The ToF-SIMS analysis showed a variability of the oxygen isotopic composition in the Mineo olivines, on average $\delta^{18}O = 2.3\pm0.3$, in agreement with the previous findings on the chemical composition. Such a value lies in the lower part of the range of variation of MG pallasites and allows us to definitely classify Mineo among the MG pallasites.

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The role of very fine sizes in reflectance spectroscopy: new understanding for the interpretation of the finest fractions of regolith. Applications to the lunar regolith

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Keywords: Moon, reflectance spectroscopy, fine sizes, plagioclase.

Fine-grained particles dominate particle size distribution of many planetary surfaces. The electromagnetic radiation will interact differently for different sizes as the ratio of surface to volume scattering changes (Hapke, 1993). Fine particles also dominate the optical properties of the bulk soil, even if they constitute a minor mass fraction (Pieters et al., 1993).

On Mars, dust particles range between 1.2-2.5 µm (Erard et al. 1994); the interpretation of remotely acquired spectra will have to account for the fine nature of the dust. On the Moon, coarse sizes of the regolith are chemically and mineralogically very similar, while the <10 µm fractions are different and more feldspathic, probably due to simple comminution processes (Hörz et al., 1984). Despite the predominance of fine particles in planetary regolith, there have been few investigations of the effects of the finest sizes on reflectance spectra.

Here, we focused on a set of plagioclase-bearing mixtures analyzed at the <10 µm size, according to the more feldspathic nature of the very fine lunar soils.

Two mafic end-members, E1 (56 vol.% opx+44 vol.% cpx) and E3 (68 vol.% ol+28 vol.% opx+ 4 vol.% cpx), and two plagioclases, An80 with 0.36 (PL2) and 0.5 (PL3) wt.% FeO, respectively, were used to prepare mixtures and reflectance spectra (0.35-2.5µm; i=30°, e=0°) have been acquired. Quantitative analyses have been performed through the MGM algorithm (Sunshine et al., 1990).

We demonstrated how very reduced sizes imply higher albedo and decrease in the spectral contrast, with the plagioclase that becomes almost featureless. We also showed how in ol-bearing mixtures the complex absorption of olivine and plagioclase always shows the typical olivine value, differently from coarser mixtures. Furthermore, we evidenced how very fine plagioclase can be underestimated till 50% of abundance.

These results can have several implications for the lunar regolith: for example, remote sensed spectra with a well-defined and deep 1250 nm absorption reflect not only the crystallinity of the plagioclase but indicate also that the size cannot be too fine.

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Raman, SEM-EDS and cathodoluminescence mapping of an altered Ca-Al inclusion in the Ranazzo CR2 carbonaceous chondrite

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Keywords: Ca-Al inclusion, protoplanetary material, Raman fluorescence, carbonaceous chondrite, Renazzo.

The Ca-Al inclusion present in a sample of the CR2 Renazzo chondrite, preserved in the Mineralogical Museum of the university of Parma (Italy), was investigated by optical microscopy, scanning electron microscopy with energy dispersed X spectroscopy (SEM-EDS), cathodoluminescence (CL) and micro-Raman mapping. The use of separate techniques was necessary to unravel the mineralogy of this strongly altered inclusion. Optical microscopy shows clear Wark-Lovering rings, calcite alteration and, within the inclusion, poorly defined micrometer sized crystals. SEM-EDS point analyses proved partially ineffective, by strong spatial overlap, and EDS-mapping was necessary to determine the major phases. It was shown that Wark-Lovering rings are made of fassaitic pyroxene, $Ca(Mg_{0.78}Fe_{0.03}Cr_{0.03}Al_{0.16})(Al_{0.15}Si_{1.85})O_6$, with an internal ring made of almost pure anorthite. Within the internal part of the inclusion, gehlenite and spinel are found, surrounded by concentric rims of sodalite and forsterite. Calcite is present in cracks.

CL measurements reveal that anorthite is readily distinguishable by blue luminescence, induced by the presence of Ti; its presence was revealed by SEM-EDS in anorthite at the 0.1% concentration. Calcite is also distinguishable by a reddish luminescence induced by Mn impurities.

Raman spectroscopy proved extremely difficult due to the very strong fluorescence of almost all the investigated phases. Still it was possible to map the anorthite distribution, by the characteristic doublet at 485-505 cm^{-1}, as well as the distribution of calcite and pyroxene. Our investigation also aimed to test the feasibility of a mapping of laser induced fluorescence using a micro-Raman apparatus. Strong fluorescence for Cr^{3+} and Fe^{3+} was found in the fassaitic pyroxene, whereas in anorthite the fluorescence is due to Cr^{3+}, present in quantities below EDS detection, but clearly recognizable in the Raman spectra by its characteristic fluorescence.

The resulting analysis shows a picture of a B type CAI inclusion, made originally by gehlenite and spinel, which underwent subsequent alteration with formation of sodalite and forsterite in concentric rims (sodalite intenal, fassaite external). Anorthite, present only in rims at the border of the inclusions, and subsequently fassaite were formed in a secondary stage. The presence of sodalite and forsterite only in the inclusion and not in the bordering rims indicates that alteration occurred before the formation of anorthite-fassaite rims. Late calcite alteration is instead ubiquitous.

Session S2:

Antarctica: a privileged observatory to understand the dynamics of the planet Earth

Conveners:

Massimo Pompilio (INGV, Pisa)

Carlo Baroni (Univ. di Pisa)

Anna Maria Fioretti (CNR, Padova)

Emanuele Lodolo (OGS, Trieste)

ICE-VOLC Project: unravelling the dynamics of Antarctica volcanoes

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Keywords: volcanoes, Antarctica, geophysics, geochemistry, volcanology.

Melbourne and Rittmann volcanoes are located in the Victoria Land. Whilst Rittmann's last eruption dates probably to Pleistocene, Melbourne's most recent eruption between 1862 and 1922, testifying it is still active. At present, both volcanoes display fumarolic activity. Melbourne was discovered in 1841 by James Clark Ross, Rittmann during the 4th Italian Expedition (1988/1989). Our knowledge on both volcanoes is really little. The position of these volcanoes in the Antarctic region (characterised by absence of anthropic noise) and its proximity with the Italian Mario Zucchelli Station makes them ideal sites for studying volcano seismic sources, geothermal emissions, seismo-acoustic signals caused by cryosphere-hydrosphere-atmosphere dynamics, and volcanic gas impact on environment.

Hence, the main aim of the ICE-VOLC ("multiparametrIC Experiment at antarctica VOLCanoes: data from volcano and cryosphere-ocean-atmosphere dynamics") project is the study of Melbourne and Rittmann, by acquisition, analysis and integration of multiparametric geophysical, geochemical and thermal data. Complementary objectives include investigation of the relationship between seismo-acoustic activity recorded in Antarctica and cryosphere-hydrosphere-atmosphere dynamics, evaluation of the impact of volcanic gas in atmosphere. This project involves 26 researchers, technologists and technicians from University of Perugia and from Istituto Nazionale di Geofisica e Vulcanologia of Catania, Palermo, Pisa and Rome.

In this work, we show the preliminary results obtained after the first expedition in Antarctica, aiming to perform geochemical-thermal surveys in the volcano ice caves, as well as to collect ash samples and to install temporary seismic stations.

Towards a new geodynamic model of East Antarctica: intraplate strike-slip deformation corridor

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Keywords: East Antarctic craton, intraplate deformation belt, Cenozoic tectonics.

The East Antarctic Craton is characterized by major intracontinental basins and highlands buried under the 34M East Antarctic Ice Sheet. Their formation remains a major open question. Paleozoic to Cenozoic intraplate extensional tectonic activity has been proposed for their development and in this work the latter hypothesis is supported. This study presents the results of forward numerical models of a series of sections of the Aurora Trench (East Antarctica) derived from radio echo-sounding data that allowed to reconstruct the 3*D* shape of the Aurora Fault, a crustal listric normal fault characterized by a length exceeding 100 km. A similar extensional fault setting allows to replicate the asymmetric buried morphology of the magnetic basement at the Lake Vostok depression derived by the available gravity and magnetic profiles. Both the Aurora and Vostok listric faults reach their basal decollment at 34 km depth, possibly the base of the crust in this intracratonic environment. Integration of these results with the existing geologic interpretations of the tectonic origin of the Concordia Trench and of the Adventure Subglacial Trench by normal faulting allows to frame the Vostok, Aurora, Concordia and Adventure normal faults within an intraplate deformation belt. This intraplate corridor is about 800-km long and characterized by a left-lateral transpressional component. The westward projection of the proposed strike-slip deformation belt may develop in correspondence of an older tectonic lineament stretching from the Eastern flanks of the Gamburtsev Subglacial Mts to the Lambert rift and characterized by a poly-phased complex tectonic history. The possible Cenozoic reactivation of these structures is discussed. The corridor may represent the effect of far-field stresses induced by plate motions.

Interplay between ice dynamics, ocean water masses and the morphology of seabed

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Keywords: ice dynamics, numerical modeling, ice-ocean-bathymetry interactions, paleoclimate, future climate.

Marine sediment records from West and East Antarctic ice sheet (WAIS, EAIS) have shown that the ice sheet volume and extent have fluctuated substantially over the past millions of years. Antarctica started to grow about 33 million years ago, under climate conditions warmer than today and with an atmospheric CO_2 concentration almost twice as large as today. Because the range of climates under which Antarctica was able to maintain in the deep past is wide, it is crucial to understand the dynamical response of the ice sheet to different climate states. Over the last decade, the interest has focused increasingly on Antarctica while observations clearly show that the on-going climate changes induce a melting of the ice shelves and under the marine-terminating glaciers around Antarctica. The increase of melting is caused the strengthening of the westerly winds that push the warm Circumpolar Deep Water more systematically towards the Antarctic coasts. However, the melting of the ice shelves is not homogeneous around Antarctica, the West marine-based part being more exposed. The melting under the cavities contributes to the thinning of the ice shelves and the glacier fronts, reducing the buttressing effect that those floating areas exert on the grounding part of the Antarctic ice sheet. If the grounding line of the ice shelves or glaciers lies on a retrograde slope, the decrease in buttressing triggers the fast retreat of the grounding line, causing a rapid mass loss of the area of interest (*e.g.*, Larsen B, Antarctic Peninsula). This mechanism is called the Marine Ice Sheet Instability (MISI) and depends on the feedbacks between ice dynamics, ocean-induced basal melting and the morphology of the bedrock. This mechanism is thought to have caused the repeated collapses of the WAIS and part of the EAIS over the past 5 Millions of years at least, under different climate conditions.

In order to better constrain this dynamical mechanism, the numerical models need to be constrained by data that are used as forcing conditions to the models or as validation after simulation. Accurate reconstructions of the seabed morphology evolution as well as the ocean water masses and atmospheric conditions are needed to define the precise threshold of the MISI in the past. In turn, reconstructing the past evolution using both models and data is important to estimate the future tipping point of the Antarctic ice sheet, *i.e.*, the temperature threshold beyond which its mass loss will be irreversible under the projected climate states. Here we illustrate this mechanism by means of an ice sheet model forced by simulated Last Glacial Maximum and/or Eemian Interglacial/mid-Holocene climates. Conceptual simulations using idealised seabed bathymetries of the Ross Sea are used to test the relative importance of ice fluxes, ocean water masses and bathymetry in the advance and retreat processes of the ice sheet on the continental shelf. Results illustrate the importance of the synergy between geologists, geophysicists, oceanographers and ice sheet modellers in advancing the knowledge of Antarctic evolution.

^{3}He/^{4}He homogeneous mantle source below the Western Antarctic Ridge System: main evidences from volatiles in mantle xenoliths

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Keywords: CO_2 , noble gases, mantle xenoliths, Antarctica.

Mantle xenoliths from two localities in Northern Victoria Land (Greene Point, GP and Handler Ridge, HR) were investigated for noble gas (He, Ne, Ar) and CO_2 contents, in order to characterize the lithospheric mantle beneath the Western Antarctic Ridge System (WARS).

The majority of samples is anhydrous spinel-bearing lherzolite with rare secondary phases (secondary cpx and glass). Geochemical models evidence that this mantle domain represents a residuum after ~7 to 21% of partial melting in the spinel stability field, that was variably affected by metasomatizing melts with different compositions, acting in different times, from at least Jurassic to Cenozoic (Pelorosso et al., 2016).

He, Ar and CO_2 contents (varying between 1.52×10^{-14}-1.07×10^{-12}, 4.09×10^{-13} -3.47×10^{-11} and 2.60×10^{-8}-6.4×10^{-7}mol/g, respectively) are directly related in both HR and GP samples, except for some pyroxenes from GP that probably suffered a selective helium loss.

The ^{4}He/^{40}Ar* ratios, ranging between 0.004 and 0.39, are below the typical mantle values (^{4}He/^{40}Ar=1-5; *e.g.*, Marty, 2012), suggesting that the pristine signature could have been modified by partial melting processes in agreement with major and trace element geochemistry of minerals.

The ^{3}He/^{4}He values measured in the HR and GP xenoliths partially overlap, ranging between 6.76Ra and 19.79Ra in the HR samples and between 2.30Ra and 7.88Ra in the GP samples (where Ra is the ^{3}He/^{4}He ratio of air). The lowest and the highest values of ^{3}He/^{4}He are systematically measured in the He-poorer samples and are probably caused by post-eruptive input of cosmogenic ^{3}He and radiogenic ^{4}He, modifying the primary ^{3}He/^{4}He values, ranging between 6.76 and 7.45 Ra. This isotope signature reflects a SCLM, which suffered the influence of rising asthenospheric melts, featured by a MORB-type signature. In addition, the measured isotopic carbon values (δ^{13}C of -3.5‰, where $\delta^{13}C=[^{13}C/^{12}C_{sample} - {}^{13}C/^{12}C_{std}]/{}^{13}C/^{12}C_{std}\times10^3$) and $CO_2/^3He$ ratios ($7\times10^{+9}$- $6\times10^{+11}$), suggest that the mantle beneath WARS has a metasomatic memory of subduction-related fluids probably belonging to the fossil subduction occurred before 100 Ma.

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Joint Radio Echo Sounding and seismic observations in the David Glacier area, north Victoria Land

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Keywords: David Glacier, Radio Echo Sounding, seismicity, glacier dynamics.

Polar regions are geodynamic environments where it is possible the observation of interactions among lithosphere, cryosphere and hydrosphere connected in the global climate system.

Their complex interactions and their evolution can be studied and evaluated by integrated geophysical observations. We have collected Radio Echo Sounding (RES) measurements combined with continue passive seismic observations in the area of David Glacier (Victoria Land) in order to improve our knowledge about changes in basal conditions due to melting processes.

This work provides detailed maps of the bedrock morphologies, ice thickness and physical condition at ice/bedrock interface in the domain of the David Glacier. Moreover, the inferred 3*D* structural model of the ice and bedrock is integrated in the inversion algorithm in order to improve the accuracy of the seismicity location. In continuity with previous seismic monitoring experiments in the area, we analyse the seismicity induced by the glacier flow and we discuss the characteristic of seismic occurrences in terms of location, frequency and possible seasonal cycling.

The role of volatiles in the genesis of Cenozoic magmatism in Northern Victoria land: new data from primary olivine-hosted melt inclusions

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Keywords: mantle, primary magmas, volatiles, C-O-H, melting modeling, melt inclusion, Antarctica.

This study offers an innovative view of the petrogenetic processes responsible for the magmas erupted in the Western Antarctic Rift System (WARS) by studying the chemical composition and the volatiles content of basic lavas and olivine-hosted melt inclusions (MI). Lavas come from three localities: Shield Nunatak (Mt. Melbourne), Eldridge Bluff and Handler Ridge. They are olivine-phyric basanites (42.41-44.80 SiO_2 wt%; 3.11-6.19 Na_2O+K_2O wt%) and basalts (44.91-48.73 SiO_2 wt%; 2.81-4.55 $Na_2O + K_2O$ wt%) with minor clinopyroxene and plagioclase. Samples from Handler Ridge clearly differ by having the highest TiO_2 (3.55-3.65 wt%), Rb, Ba, Nb, La, Zr despite their more primitive features (60.83-44.87 Mg#, MgO/(MgO + FeO)%mol). Olivine-hosted melt inclusions (MI) were analyzed for major element and volatiles (H_2O, CO_2, S, F, and Cl) after *HT* (1300°C) and *HP* (6 kbar) homogenization. Despite a larger variability, MI are compositionally comparable to the host lavas and are characterized by two distinct trends (high-Fe-Ti-K and low-Fe-Ti-K). The H_2O content in MI ranges from 0.70 wt% to 2.64 wt% and CO_2 from 25 ppm to 341 ppm ($H_2O/CO_2 \sim 1$). At comparable H_2O contents few samples show an higher CO_2 values (1322 ppm to 3905 ppm) with a H_2O/CO_2 down to 0.8. F and Cl content varies from 1386 ppm to 10 ppm and from 1336 ppm to 38 ppm respectively. Concentration of volatiles show a good correlation with alkalies, especially with K_2O; Handler Ridge presents the highest total value of F and Cl (2675 ppm). Chondrite-normalized trace elements concentration in MI show a intraplate pattern with negative anomalies in Rb, K, Ti. Accordingly to the lava contents, MI from Handler Ridge have a significant higher concentration in Rb (12-45 ppm), Sr (700-834 ppm), Ba (433-554) and Nb (48.8-83.4 ppm) with respect to the other localities at comparable Mg#. Mantle melting mass balance calculations simulate the observed H_2O, CO_2 and Cl concentration by melting a spinel lherzolite from 3 to 7% of melting (F) with a 5% of modal amphibole with the same composition and modal proportion of mantle xenoliths from Baker Rocks, a locality near to Shield Nunatak. The model was not able to predict the F content which is less concentrated in natural sample. From the resulted partial melting percentage we calculated a total amount of CO_2 in mantle source of 273 ppm by assuming the highest 3900 ppm measured in MI as starting value. The estimated maximum content of H_2O and CO_2 in the primary melt is 2.6 wt% and 8800 ppm respectively. Obtained data were compared with those from mantle xenoliths from NVL with the aim to reconstruct the composition of the mantle source of the Cenozoic magmatism and to model the whole volatile budget from mantle to magmas starting from the measured volatile content in hydrous (amph) and NAM phases in mantle xenoliths. Preliminary results evidence that high-Fe-Ti-K basanites found in MI are very similar to the calculated metasomatic agent involved in the formation of the very peculiar Fe-rich lherzolites.

Tectonometamorphic evolution of metasediments of the Dessent Unit (northern Victoria Land, Antarctica): insights into the development of a *HT* suture zone

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Keywords: northern Victoria Land, Ross Orogen, high temperature mylonite, pseudosections.

Remnants of the Palaeozoic Ross orogen are present in northern Victoria Land (NVL, Antarctica) where three main fault-bounded litho-tectonic units occur (Palmeri et al., 2012, *cum bib.*): (i) Wilson Terrane (WT) composed of low to high grade metamorphic and Cambro-Ordovician igneous rocks, (ii) Bowers Terrane (BT) dominated by volcanic and sedimentary rocks which experienced low grade metamorphisms, and (iii) Robertson Bay Terrane (RBT) with very low grade turbidites.

WT and BT are tectonically juxtaposed by a shear belt involving also eclogites. The Dessent Unit (DU), made of amphibolite and metasediment (Capponi et al., 1988), marks this contact in the Mountaineer Range. In contrast to the amphibolites (e.*g*., Capponi et al., 1988; Palmeri et al., 2012), very few data are available for the metasediments (Capponi et al., 1988). We present a microstructural and petrological reappraisal of the DU metasediments (collected during Italiantartide expeditions). The main regional foliation in the DU is related to at least a second deformation event, since an older foliation is preserved within microlithons and intertectonic porphyroblasts. Evidences of upper amphibolitic to lower granulitic *HT* mylonitic shearing has been detected, later overprinted by a static growth of chlorite (and minor white mica). Pseudosections and multi-equilibrium thermobarometry indicate that most of the metasediments have equilibrated in the *P*-*T* range of 600-650°C and 6.5-8.5 kbar, followed by cooling and decompression, compatible with results from the DU amphibolites (Palmeri et al., 2012). Interestingly, relicts of a previous granulitic stage, already reported for some DU amphibolites (Scambelluri et al., 2003), have been also identified in one sample. In summary, our results demonstrate that metasediments shared a common history with the amphibolites, giving new constraints on the prograde path and the tectono-metamorphic evolution of the WT-BT suture zone, supporting starting of shearing at high *T* conditions. Trace element profiles through garnet show different intra samples trends, likely reflecting various developments of pairs of garnet and accessories phases.

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Extended magmatic differentiation in the Pleiades plumbing system induced by a thick ice cap during the last glacial maximum in the West Antarctic Rift System

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Keywords: West Antarctic Ryft System, Upper Pleistocene, Na-alkaline volcanism, ice-magma interaction.

The Pleiades volcanic complex is made up of at least a dozen monogenetic, partly overlapping scoria and spatter cones and an endogenous dome that crop out at the edge of the high Polar plateau close to the head of Mariner Glacier, in northern Victoria Land. On the basis of previously published and rather imprecise K–Ar ages (3±14 and 40±50 ka), the Pleiades complex was considered active. New ^{40}Ar-^{39}Ar laser step-heating experiments on alkali feldspar from two pristine samples of the most prominent edifices (*i.e.*, Atlas-Pleiones and Aleyone-Taygete) yielded late Pleistocene ages (within 20–35 ka) thus precluding the inclusion of this complex among active Antarctic volcanoes.

The erupted products vary in composition from hawaiite to trachyte, defining a complete Na-alkaline differentiation trend, without any Daly Gap. The samples are mildly alkaline, mostly weakly silica-undersaturated, whereas the most evolved samples exhibit both a peralkaline character and/or silica oversaturation.

Primordial Mantle-normalized multi-element patterns of mafic samples are characterized by humped patterns, typical of OIB magmas, low ^{87}Sr/^{86}Sr (~0.7037) and high ^{143}Nd/^{144}Nd (~0.51284) ratios, suggesting a within-plate affinity and derivation from a sub-lithospheric mantle source. Increasing Sr isotope ratios (up to 0.7052) and decreasing Nd isotope ratios (down to ~0.51277) along with increasing SiO_2 contents supports an open-system evolution, with a significant amount of crustal assimilation concomitant with fractional crystallization processes.

The erupted products are quite small in volume, we estimate approximately ~70 km^3 of trachytic magma. However, according to fractionation models, the accompanying volume of primitive magma may be 40 times larger, *i.e.*, about 2700 km^3. The large volume implied would correspond to a ~1300 m high stratovolcano, suggesting an unusually large magma plumbing system consistent with published suggestions that the exposed outcrops may be distributed along a caldera ring fracture of a much larger volcano, now almost completely covered by ice. According to our new ^{40}Ar-^{39}Ar ages, the volcano was active during the last glacial maximum, when the ice sheet may have been much thicker. A preceding thicker mantling ice cover would be capable of suppressing eruptions and ultimately lead to a high magma residence time in the subsurface. These conditions would also favour high rates of crustal assimilation and significant fractionation.

Polar region observations for the study of the magnetospheric dynamics and the contribution of Italian geomagnetic observatories in Antarctica

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Keywords: geomagnetism, geomagnetic observatories, magnetosphere.

The Earth's magnetic field shows temporal variations which go from seconds to hundreds of thousands of years. Variations with period from a few seconds to several days take most of their energy from the interaction with the solar wind. Antarctica is an excellent site for this kind of observations and the study of geomagnetic data sets from Antarctica gives important information about magnetospheric dynamics because local field lines reach extreme magnetospheric regions where the interactions with the solar wind occurs. Italian Antarctic research activities cover more than a quarter of a century providing very long data sets. This presentation describes Italian geomagnetic observatory activities and some important scientific results obtained studying these data sets, regarding mainly the daily variation and low frequency pulsations observed at these latitudes; the studies are based also on the comparison with data recorded at different sites in Antarctica, as well as with solar wind and interplanetary magnetic field data from satellite.

Petrological characterisation of northern Victoria Land lithospheric mantle, new insights from anhydrous and amphibole bearing mantle xenoliths

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Keywords: mantle xenoliths, refertilisation, metasomatism.

The petrological study of anhydrous (Greene Point, GP; Handler Ridge, HR) and amphibole-bearing (Harrow Peaks, HP; Baker Rocks, BR) xenoliths from four sites in northern Victoria Land (NVL), Antarctica, provide a general overview of the complex geochemical/geodynamic features that characterise the lithospheric mantle beneath a large area of the West Antarctic Rift System.

On the basis of mineral major and trace element modelling, this mantle domain represents a residuum after 10-20% of partial melting, largely modified by metasomatic melts acting in different times, from at least Jurassic to Cenozoic. The similarity between trace element contents of GP clinopyroxene and those from clinopyroxene of Ferrar tholeiites, as well as, the high modal orthopyroxene content (28%) at low Mg# value (88.54) in association with clinopyroxene with high *HREE* (Lu_N=17) content (*i.e.*, HP), allows to ascribe the first refertilisation event to the Jurassic Ferrar magmatism.

LREE–enriched clinopyroxene, recorded in all localities, suggest that silica–poor alkaline/carbonatite metasomatism heterogeneously affected the NVL lithospheric domain.

Using mineral geochemical models, the metasomatic agent was characterised and its action delimited in a time span of 10^2-10^3 years, just before xenolith's uprising.

At HP, clinopyroxene and amphibole are in disequilibrium between them and with the rest of the paragenesis. They can be considered as the main products of the reaction between olivine/orthopyroxene/spinel and silica poor CaO-MgO-enriched metasomatising agent.

Geothermobarometric calculations based on the Fe/Mg distribution among the peridotite phases at *P* of 15 kbar, reveal that the anhydrous suites have higher temperature (950-1050°C) than the amphibole-bearing population (850°C). Moreover, oxygen fugacity values calculated on the basis of the oxy-amphibole equilibrium reveal a strong disequilibrium of amphibole with the primary peridotitic paragenesis (*i.e.*, HP) (+7 QFM; Gentili et al., 2015) with respect to those obtained with anhydrous paragenesis (-2.78_-0.24 QFM). This discordance in the redox condition is not detected at Baker Rock (Bonadiman et al., 2014), where amphibole is clearly in equilibrium with the primary mineral assemblage.

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Provenance analysis of Ross Sea Drift in McMurdo Sound (Antarctica) during the Last Glacial Maximum: a petrographic approach

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Keywords: provenance analysis, last glacial maximum, Ross Sea Drift, McMurdo Sound.

During the Last Glacial Maximum (LGM) an extensive ice sheet grounded in the Ross Sea Embayment towards the continental shelf break, fed by the West Antarctic Ice Sheet but with an important contribution of the outlet glaciers from the East Antarctic Ice Sheet. The extension and timing of retreat to the current position after LGM are well constrained by terrestrial and marine geomorphological, geological and geophysical data. Indeed, once retreated, the Ross Sea Ice Sheet (RSIS) left drift sheets and moraines along the glaciated margin of the Ross Embayment, where a key area is represented by McMurdo Sound. In this region these glacial deposits are known as Ross Sea Drift and they have been studied in depth to reconstruct thickness, extent and chronology of the RSIS during the LGM. However, paleo ice-flows reconstructions in the region, also in the light of recent chronological data, are still under debate.

Herewith we present a provenance analysis of Ross Sea Drift deposits applying a petrographic approach. A total amount of 19 samples was collected in the Dry Valleys region in a coastal area comprised between the Wright Valley and the Royal Society Range (RSR) foothills, with four main sampling areas (Wright Valley, Taylor Valley, Miers-Marshall Valleys, and Walcott Bay). Deposits were classified following the lithological composition of cobble, granule, and coarse to very coarse sand-sized granulometric fractions, both with macroscopic and microscopic classification. Mineral chemistry of selected samples was also carried out in order to reveal different source rocks. Composition of clasts predominantly shows source rocks which crop out in the region between Mackay and Koettlitz glaciers, with volcanic lithics fragments of the McMurdo Volcanic Group being the most represented lithology in RSR samples, while granitoid rock fragments of the Granite Harbour Intrusive Complex are the most abundant in Taylor and Wright Valley samples. Lithological composition of Ross Sea Drift supports a glacial transport due to a grounded ice sheet from Ross Sea in Taylor Valley and RSR foothills during LGM and it is consistent with an expanded grounded Koettlitz Glacier lobe flowing northward, as recently supported by geomorphological and chronological studies.

A tuff cone erupted under frozen-bed ice (northern Victoria Land, Antarctica): linking glaciovolcanic and cosmogenic nuclide data for ice sheet reconstructions

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Keywords: glaciovolcanism, Mt. Melbourne volcanic field, paleoenvironmental evolution, ^{40}Ar-^{39}Ar dating, cosmogenic dating, polythermal ice.

In glaciated terrains, volcanic morphologies and lithofacies of the volcanic products are valuable indicators (proxies) for palaeo-ice type, thickness and extent. During the last 20 years, refinements to glaciovolcanic studies have enabled investigators to establish the presence of ice, its age (mainly by ^{40}Ar-^{39}Ar dating), ice thickness and surface elevation, and ice basal thermal regime. This is the largest range of critical parameters of past ice that can be obtained by any proxy methodology, and many of these attributes are quantifiable, which is another important feature of glaciovolcanic environmental investigations.

We describe the results of the first linked glaciovolcanic-cosmogenic nuclide study of a volcanic outcrop in northern Victoria Land, Antarctica, where the remains of a small volcanic centre are preserved on a thin bedrock ridge at Harrow Peaks. The outcrop is interpreted as a monogenetic tuff cone relict formed by a hydrovolcanic eruption of mafic magma at 642±20 ka, as dated by the ^{40}Ar-^{39}Ar method, corresponding to the peak of the Marine Isotope Stage MIS16. Although extensively dissected and strewn with glacial erratics, the outcrop shows no evidence for erosion by ice. From interpretation of the lithofacies and eruptive mechanisms, the weight of the evidence suggests that eruptions took place under a cold-based (frozen-bed) ice sheet. This is the first time that a tuff cone erupted under cold ice has been described. Indeed, because of the dominance of wet-based ice worldwide, practically all of the published studies relate to eruptions in that setting. Nevertheless, the distinction between wet-based and cold-based ice is important. Their physical properties are very different and their impact on landscape development and relative rates of global sea level change during climate variations are also different.

The most distinctive feature of the lithofacies is the dominance of massive lapilli tuff rich in fine ash matrix and abraded lapilli. The lack of stratification is probably due to repeated eruption through a conduit blasted through a thin ice cover probably just 50-100 m thick over the vent and accumulation mainly as crater (or ice conduit) infill. The remainder of the tuff cone edifice was probably deposited supraglacially and underwent destruction by ice advection and, particularly, collapse during a younger interglacial. ^{10}Be cosmogenic exposure dating of granitoid basement erratics indicates that the erratics are unrelated to the eruptive period. The ^{10}Be ages suggest that the volcanic outcrop was most recently exposed by ice decay at *ca.* 21 ka (MIS2) and the associated ice was thicker than at 642 ka and probably polythermal rather than cold-based, which is normally assumed for the period.

Session S3:

An entire rock entrapped inside a mineral grain.
What we can learn from it?

Conveners:

Matteo Alvaro (Univ. di Pavia)

Marco Scambelluri (Univ. di Genova)

Non-destructive, multi-method, internal analysis of multiple inclusions in a single diamond: first occurrence of mackinawite $(Fe,Ni)_{1+x}S$

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Keywords: diamond, sulfide inclusions, mackinawite, non-destructive analyses.

A single gem lithospheric diamond with 5 sulfide inclusions from the Udachnaya kimberlite (Siberia, Russia) has been analyzed non-destructively to track the growth conditions of the diamond. Sulfides are the most abundant mineral inclusions in many lithospheric diamonds and are the most favorable minerals to date diamonds by Re-Os isotope systematics. Our investigation used non-destructive, micro-techniques, combining X-ray tomography, X-ray fluorescence, X-ray powder diffraction and Raman spectroscopy. This approach allowed us to determine the spatial distribution of the inclusions, their chemical and mineralogical composition on the micro-scale and, finally, the paragenetic association, leaving the diamond host completely unaffected. The sample was also studied by X-ray diffraction topography to characterize the structural defects of the diamond and to obtain genetic information about its growth history. The X-ray topographic images show that the sample investigated exhibits plastic deformation. One set of {111} slip lamellae, corresponding to polysynthetic twinning, affects the entire sample. Chemical data on the inclusions still trapped within the diamond show they are monosulfide solid solutions of Fe, Ni and indicate a peridotitic paragenesis. Micro X-ray diffraction reveals that the inclusions mainly consist of a polycrystalline aggregate of pentlandite and pyrrothite. A thorough analysis of the Raman data suggests the presence of a further Fe,Ni sulfide, never reported so far in diamonds: mackinawite. The total absence of any oxides in the sulfide assemblage indicates that mackinawite is not simply a "late" alteration of pyrrhotite and pentlandite due to secondary oxidizing fluids entering diamond fractures after the diamond transport to the surface. Instead, it is likely formed as a low-temperature phase that grew in a closed system within the diamond host. It is possible that mackinawite is a more common phase in sulphide assemblages within diamonds than has previously been presumed, and that the percentage of mackinawite within a given sulfide assemblage could vary from diamond to diamond and from locality to locality.

Non-destructive *in situ* analysis of multiphase inclusions in a super-deep diamond

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Keywords: superdeep diamonds, Fe-periclase, polyphase inclusion, carbonates.

The investigation of multiphase inclusions trapped within super-deep diamonds provides extremely important petrogenetic information from depths into the lower mantle (*e.g.*, Palot et al., 2016, Smith et al., 2016). Methods commonly used to investigate these inclusions require cutting, crushing or ion/laser ablating the diamond host to expose inclusions for conventional and/or non-conventional geochemical analyses. These methods, however, can introduce significant artefacts and contaminations, especially on metallic inclusions or iron carbides. Non-destructive, *in situ* investigation of inclusions still trapped in their diamond host, is thus the only way to obtain, without ambiguities, information about diamond formation. With this aim, we studied a sample (JUc4) of inferred super-deep origin from São Luiz (Juina, Brazil) by using a multi-methodological approach. The inclusions still trapped within the diamond host were investigated by micro-computed X-ray tomography (mCXRT), micro X-ray fluorescence (mXRF), micro-Raman and Infrared (FTIR) spectroscopies. The structural defects were also investigated by X-ray topography (XRDT) (Agrosì et al., 2016). The diamond sample exhibits an irregular morphology, a light-brown colour and five optically opaque large inclusions from 100 to 300 μm in diameter. XRDT images show a clear plastic deformation. Micro-chemical maps, obtained by mXRF, show a high Fe content for all the inclusions; the identification of ferropericlase as a constituent was later confirmed by micro-destructive Laser Induced Breakdown Spectroscopy (μLIBS). One inclusion is different from the others because it exhibits a flask shape and a clear multiphase nature, as indicated by detailed mCXRT reconstruction. FTIR maps show a concentric zoning of N defects and this inclusion appears to be located near the center of diamond growth. Part of this inclusion consists of ferropericlase, as confirmed by non-destructive micro-X-Ray Diffraction. μ-Raman and FTIR investigations on this inclusion reveal also the presence of carbonates and pseudo-amorphous carbon. In particular, μ-Raman maps obtained reveal the typical large D and G bands corresponding to pseudo-amorphous graphite. The FTIR spectra show a doublet at 1430-1440 cm^{-1} corresponding to the presence of carbonates, suggesting a genesis of this diamond in a carbonate-rich system. No Raman or FTIR evidences for OH^- or CH_4 were observed.

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Synthesis of host-inclusion systems: preliminary data

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Keywords: geobarometry, inclusions, host, YAG.

Recent theoretical and methodological development on the determination of the remnant pressure on the inclusion, measured by X-ray diffractometry, birefringence analysis or Raman spectroscopy, provides an alternative and/or complementary method of barometry using elasticity theory (*e.g.*, Angel et al., 2014). A remnant pressure in an inclusion is developed because the inclusion and the host have different thermal expansion and compressibilities, and the inclusion does not expand in response to *P* and *T* as would a free crystal in air. Instead it is restricted to expand only as much as the host mineral allows, and this constriction in volume can result in inclusions exhibiting over-pressures when the pair is studied at room conditions (Angel et al., 2014).

Therefore, it is clear that the only validation for such elastic geobarometry methods and the theoretical approach has to come from experiments performed at controlled *P* and *T* conditions rather than from naturally occurring host-inclusion pairs.

To this aim we have performed preliminary test entrapping single crystals in host crystal at known *P* and *T* conditions. We use Yttrium Aluminium Garnet (YAG) as host and Si metallic, Ti metallic, diamond and ruby as inclusions.

The most common issues related to the host-inclusion synthesis quality are: i) a low degree of sintering; ii) a high number of fractures; iii) low chemical inertness of the inclusion. Therefore, at first we assessed the sintering quality by changing one variable at the time (*T*, *P* and setup of capsule). From the different experiments the best conditions of the experiment resulted to be: *T* = 1300°C, *P* = 3.0 GPa, with Pt capsule and two graphite disks at top and bottom of the capsule to reduce the fracturing (Tingle, 1988).

The assembly was made of two mirror-polished YAG rods (2.5 mm diameter) placed inside a platinum capsule (OD = 3.0 mm; ID = 2.8 mm) with YAG powder in between the two rods together with one single crystals of minerals as inclusions (immersed into the powder). The rods and the powder have been annealed at 3.0 GPa and 1300°C for 24 h in an end-loaded piston cylinder apparatus.

The preliminary analyses showed that YAG is not a reliable host because of its reactivity towards most of the inclusions, with formation of new mineral phases. However, the used protocol turned out to be successful in prompting a high degree of sintering and in reducing the number of decompression-related fractures.

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Geometry and size effects on Raman shifts in natural host-inclusion systems: an experimental validation

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Keywords: Raman spectroscopy, residual stresses, elastic geobarometry, *UH*P.

The study of inclusions by means of Raman spectroscopy provides information about the stress state of host-inclusion systems in terms of shifts of the Raman peaks that depend on the residual stresses still acting on the inclusion. These Raman shifts can be coupled with elastic geobarometry theory to allow *P*-*T* conditions attained during *UHP* metamorphism to be estimated (Angel et al., 2015). In this study we test the limitations of the commonly-used Raman approach to evaluate residual stresses preserved by non-spherical anisotropic inclusion in terms of shifts of the main Raman peaks. We investigated the changes in the Raman peaks for 20 zircon inclusions still entrapped in garnet megablasts from the *UHP* Dora Maira Massif. The selected inclusions were located in a fracture-free garnet host, with a radius at least three times larger than that of the inclusion. The proximity effect of the inclusion to the external host surface, in terms of residual stress, has been tested experimentally for the first time using a step-by-step polishing the host. After each polishing step immediate Raman measurements were carried out on the inclusion always at the same position within the inclusion. Our Raman measurements show that the stress acting on the inclusion is released when the inclusion approaches the surface. This approach confirms that for all analyzed inclusions the residual strain imposed is elastic. As predicted by numerical models (Mazzucchelli et al., 2017), we observed that both the shape and aspect ratio of the inclusions affect the Raman peak position. Rounded zircon grains exhibit the same Raman shifts throughout the entire volume, whereas elongated zircon grains show a stress gradients along corners and edges. These results allow us to develop a practical protocol to reliably determine residual stresses by considering all the above features and limitations.

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Halite recrystallization studies: potential key to understanding depositional histories of salt domes. An example from the Crotone Basin, Calabria, south Italy

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Keywords: halite crystals, fluid inclusions, Catanzaro trough.

The degree of recrystallization of halite crystals from a salt dome located in Verzino, Crotone Basin (Calabria, southern Italy) is investigated using petrographic and fluid inclusion (FIs) studies. The salt dome investigated formed during the Messinian (~ 6 Ma) and consists mainly of microcrystalline halite crystals. The samples of halite come from the base, middle and top of the saline body extruded into Pliocene clays. Each sample contains crystals with mosaic texture, sub-millimeter to millimeter in size and display prismatic habits and are oriented parallel to the water surface. Petrographic and FI analyses highlights the presence of relict primary crystallization features that survive the burying events. All samples show a low degree of deformation and display primary FIs located parallel to crystal growth zones with negative crystal shapes. FIs observed (5 to 60 mm in their longest dimension) are monophase liquid (L) (Type 1), two-phase (L+V) liquid-rich (Type 2) and multiphase solid-rich (L+V+S±O) with occasional organic matter trapped within (Type 3). Ultra Violet Light Microscopy (UV) has been used to determine the nature of this organic matter and confirm the occurrence of prokaryotes and eukaryotes. Their presence reflects the lack of deformation during burial. This study highlights the potential of this type of study for elucidating the depositional history of diapiric salt walls.

The palaeoenvironment of selenite-bearing evaporite formation in the Catanzaro Trough, Calabria, South Italy

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Keywords: giant selenite, fluid inclusions, evaporite, Messinian, Catanzaro trough.

Petrographic and fluid inclusion (FI) studies of giant selenite crystals from the Catanzaro Trough (Calabria, southern Italy) are used to investigate the palaeoclimate and palaeoenvironment pertaining during evolution of the deposit. The deposit, formed during the Messinian Salinity Crisis (~ 6 Ma), consists of twinned selenite crystals of centimetric to metric scale (Cianflone et al., 2012). Petrographic analyses reveal the presence of abundant primary FIs trapped along crystal growth zones. The majority are monophase liquid and show elongated and tabular morphologies (ranging in size from 10 to 100 mm). Selenite crystals show two growth zones, *i.e.*, *turbid* and *clear*. Turbid zones are rich in FIs, organic matter and solid clay mineral inclusions. The clear zones are devoid of all inclusion types encountered in the turbid zones. These alternating zones indicate possible variations in the temperature of crystallization that in turn lead to alternations in gypsum growth zone rates, *e.g.*, fast rate characterized by abundant FIs and organic matters, slow rate lack of inclusions. The nature of the trapped organic matter (both inside and outside the fluid inclusions) has been investigated using Ultra Violet light microscopy and Raman microspectroscopy. These techniques reveal the presence of several types of organic matter (xanthophyll, lutein, lycopene) located mainly along crystal growth zones and fractures *i.e.*, peloids and coccoliths as well as aluminium hydroxide. The peloids and coccoliths inclusions are marine in origin. The aluminium hydroxide is continental in origin (Bilonizhka et al., 2012) and may have been sourced from weathered metamorphic basement. Characteristics of the fluid inclusions observed in combination with the trapped organic matter, is used as a tool for palaeoclimatic reconstructions of the environment characterizing the selenite formation in the Miocene.

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A combined study of noble gases, trace elements and Sr-Nd isotopes for alkaline and tholeiitic lava from the Hyblean Plateau (Italy)

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Keywords: Plio-pleistocenic Hyblean lavas, fluid inclusions, noble gases, Hyblean mantle source.

Eight Plio-Pleistocenic lavas from the Hyblean Plateau, south-eastern Sicily (Italy), and varying in composition from tholeiites to nephelinites, were investigated for the noble gas, trace element and Sr-Nd isotope geochemistry. The noble gas content, extracted from fluid inclusions of olivine and orthopyroxene phenocrysts, was analysed for He, Ne and Ar and displayed ^{3}He/^{4}He ratios of about 7 Ra (where Ra is the atmospheric ^{3}He/^{4}He ratio of 1.38×10^{-6}), except for two lavas characterized by low He abundance and showing ^{3}He/^{4}He = 3.53 and 8.35 Ra, respectively. We suggest that a mantle source characterized by the average helium marker of about 7 Ra, comparable to that measured in local peridotitic xenoliths, generated the Plio-Pleistocenic lavas from the Hyblean Plateau. The deviation from the leading value (7 Ra) is attributed to secondary processes modifying the primordial marker of the gas-poorer samples.

The more depleted Sr-Nd isotopes of tholeiites (^{87}Sr/^{86}Sr = 0.702745-0.702842; ^{43}Nd/^{144}Nd = 0.513119-0.51162) with respect to basanites and nephelinites (^{87}Sr/^{86}Sr = 0.702937-0.703307; ^{43}Nd/^{144}Nd = 0.518928-0.513083) could be the consequence of the higher melting percentages associated to their origin as well as the wide compositional spectrum of the samples.

Trace element geochemistry evidenced that the mantle source feeding the Plio-Pleistocene volcanism is not perfectly coincident with that of the peridotite nodules outcropping at surface. Indeed, the Hyblean mantle xenoliths, widely studied in literature, suggest the action of a metasomatic carbonatitic component, modifying partially their trace element signature. The investigated lavas probably originate from mantle portions that maintained more primordial geochemical features, due to the milder metasomatic influence.

Trace element behaviour in deep subduction fluids: an example from the nature

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Keywords: subduction fluids, ultra-high-pressure metamorphism, LA-ICP-MS.

During subduction, dehydration reactions release fluids that are responsible for the mass transfer from the subducted crust to the overlying mantle wedge and, then, for the geochemical signatures observed in magmas derived by mantle partial melting. The chemical-physical features of these fluids depend on the bulk composition of the subducted lithology, on the dehydration reactions involved, and on the *P*-*T* conditions at which these reactions occur. The study of natural fluid inclusions trapped in ultra-high pressure (*UHP*) minerals is the direct way to characterize the fluids released during deep subduction.

The aim of this work is to study the processes involved in the building of the trace element signatures of *UHP* fluids released by terrigenous sediments along intermediate gradients. We performed *in situ* LA-ICP-MS analyses on primary multiphase solid inclusions (MSI) in kyanite core and rim of *UHP* Ky-quartzite from Sulu (China). This lithology was a former clay-rich sandstone that experienced subduction up to 700-860°C and 3.0-4.0 GPa during the Triassic.

The MSI mainly consist of an aqueous fluid and an aggregate of paragonite + muscovite + anhydrite + K-Na-hydrous sulphate. They are remnants of an alkali-alumino-silicate aqueous solution generated by internal dehydration reactions involving phengite and occurring during the *P*-*T* increase in the *UHP* prograde-to-peak metamorphic evolution.

The trace element patterns are relatively homogeneous and enriched in LILE and *REE* and depleted in HFSE with respect to the primordial mantle. The element contents and fractionations changes during *P*-*T* increase because of the progressive dissolution of minerals in presence or not of refractory minerals (*e.g.*, Phg, Aln, Grt).

With respect to hydrous melts obtained from experiments on pelitic system, the *UHP* alkali-alumino-silicate aqueous solution released by the Ky-quartzite from Sulu is more enriched in *REE* and have similar enrichments in U and Th. These features makes these solutions effective metasomatizing agents of the mantle wedge.

Partial melting of ultramafic granulites from Dronning Maud Land, Antarctica: melt inclusions and thermodynamic modelling

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Keywords: nanogranitoids, anatexis, Antarctica, granulites, thermodynamic modelling.

Crystallized melt inclusions (MI), or nanogranitoids, occur in garnet from ultramafic granulites hosted in orthogneisses of the Conradgebirge, in the Pan-African belt of the Dronning Maud Land. The granulites contain the peak assemblage Amp1+Grt+Cpx with rare relict Opx, and retrograde Pl+Spl+Opx+Amp2±Ol±Bt symplectites at contacts between Grt and Amp1. Garnet contains two generations of MI. Type1 MI are primary, isolated, < 10 µm in size, and generally with negative crystal shape. They contain Kml, Kok and Phl, with Qz and Zo as minor phases; glass was identified in one single inclusion. Type2 MI are up to 30 µm, pseudosecondary, and contain Amp, Felds, Zo, minor Mgs, Hl and Opx. A CO_2-rich fluid may be present in Type2 MI. MI were re-homogenized after heating for 24 h in a piston cylinder at 950°C, 15–24 kbar. The composition of Type1 MI is trachytic with *ca.* 68 wt.% SiO_2, 17–18 wt.% Al_2O_3, K/Na = 3.55 and $H_2O \approx 2.5$ wt.%; Type2 MI are dacitic with K/Na = 0.56 and $H_2O \approx 12$ wt.%. Thermodynamic modelling of the ultramafite composition in the NCKFMMnASHTO system shows that the peak assemblage Hbl+Grt+Cpx+melt±Bt±Rt, inferred from petrography, is stable at *ca.* 15 kbar and 850–900 °C, and that at these conditions the modelled melt composition is felsic, K-rich and quite similar to that analyzed in Type1 MI. The thermodynamic modelling, combined with the MI study, supports the interpretation that both melt and garnet are products of the anatexis of the ultramafic boudins at peak conditions, most likely through amphibole and biotite fluid-absent melting, and that the Type1 MI contain the anatectic melt that was present during garnet growth. The high-silica, K-rich melt composition of Type1 MI, unexpected in an ultramafic source rock, can be explained by the participation of biotite and amphibole as reactants in the melting reaction, and by low melting degrees.

Fluid inclusion analysis of gypsum from Lesina Marina (Apulia, Italy): A preliminary report

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Keywords: gypsum, Lesina Marina, fluid inclusions, mineral growth.

In the Lesina Marina area (northern Apulia) exotic Upper Triassic gypsum rocks belonging to the Burano Anhydrite Fm crop out along the Acquarotta Canal (Festa et al., 2016). Cotecchia & Canitano (1954) and Bigazzi et al. (1996) suggested that these rocks ascended from the deep Burano Anhydrite layer, dragging upwards Paleocenic hypabissal magmatic rocks and Upper Triassic limestones. Bigazzi et al. (1996) hypothesized, but not demonstrated, that gypsification of anhydrite occurred at very shallow depth. An useful contribution to better constrain the gypsification process could arise from the analysis of fluid inclusions entrapped within gypsum. As this kind of study is lacking for gypsum outcropping at Lesina Marina, a fluid inclusion and microstructural investigation has been started on samples from surface outcrops and boreholes to elucidate the mineral growth and evolution of this gypsum.

Three distinct types of gypsum are found: stromatolitic, amoeboid and clear selenitic. The first one is found in the lower stratigraphic layers; the latter two are strictly associated with each other in the upper stratigraphic layers. Every gypsum type is characterized by a peculiar fluid inclusion texture, and several fluid inclusion assemblages (FIAs), *i.e.*, groups of inclusions all trapped at the same time (Goldstein & Reynolds, 1994), have been observed. Monophase liquid, monophase vapour, biphase liquid-rich, biphase vapour-rich, multiphase solid, and hydrocarbon inclusions are all found. The petrographic analysis of fluid inclusion textures has been followed by preliminary microthermometric analysis on the different FIAs. Heating experiments allowed to determine the homogenization temperatures of biphase liquid-rich inclusions, and also to fix the upper temperature limit above which the gypsum is no more stable and dehydrates to anhydrite. The temperature range for the mineral growth of gypsum at Lesina Marina is consequently derived. The freezing-heating cycles allowed to gather some information on the composition and salinity of the entrapped fluids, circulating when these gypsum rocks formed.

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DiaMap: New applications for processing IR spectra of fluid-rich diamonds

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Keywords: diamond, fluid inclusions, infrared spectroscopy, chemical mapping.

High-density fluids (HDFs) encapsulated in micro-inclusions within diamonds provide key information on different C-O-H-bearing mantle fluids (Navon et al., 1988), as well as water and carbonate cycling in the Earth's deep interior. These fluids vary between four major compositional types: saline, silicic, and high-Mg and low-Mg carbonatitic. IR spectroscopy is the only method that provides the relative concentrations of water and secondary phases of the mineral assemblage in the microinclusions (*i.e.*, carbonates, silicates and apatite) that grew from trapped HDFs. Constraining the relative abundances of these phases provides information on the amount of water and carbonate in different HDF types, and was proven as a semi-quantitative method to determine carbonatitic to silicic compositions (Weiss et al., 2010). However this was accomplished by manual subtraction of diamond intrinsic absorption and nitrogen absorption, followed by deconvolution of the IR absorbance due to various phases in the micro-inclusions; a long and slow process to be conducted routinely in the study of fluid-rich diamonds.

The complete automation of deconvoluting fluid inclusion-rich diamond IR spectra is complex for the following reasons: (1) a "one size fits all" approach to baselining and subtracting the various components in the spectrum is almost impossible given the chemical variability observed; (2) automation offers little to no user refinement, and the need to discern the quality of the data output undermines the time saved by automating it. We therefore developed a semi-automated approach – DiaMap_Fluid – for fast subtraction and deconvolution processing of a fluid inclusion-rich diamond IR spectrum. This software allows for user refinement during each stage of spectral processing, making it a much faster user process, while also greatly enhancing precision in the data output from a single spectrum compared with manual processing by different individuals.

We have applied the DiaMap_Fluid program to 38 fluid inclusion-rich diamonds, from localities in Africa (Finsch, Kankan, DeBeers-Pool, Koingnass), Canada (Ekati) and Russia (Udachnaya, Aykhal). The samples have been studied by quantitative methods including electron microprobe and laser ablation ICP-MS (Weiss et al., 2008; 2010), allowing the FTIR data on the water (OH), carbonate and silicate components of the microinclusions to be compared with their bulk chemistry. The results provide the phase concentrations (in ppm by weight) in the diamonds, and show that on a ternary plot of carbonate – water – silicates + apatite, the four HDF end-members fall in fairly distinct groupings. This makes FTIR analyses using the DiaMap_Fluid software a very simple method for determining phase concentations and broadly discerning the chemistry of HDF in fluid-rich diamonds.

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A new framework for shock transformation of terrestrial minerals in the lithosphere during bolide impacts

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Keywords: shock transformation, impact crater.

Large bolide impacts were a transformational feature of the early Earth's surface, producing well-characterised impact craters, shock metamorphism and melting which must have influenced the development of the early lithosphere. This contribution will assess the depth and scope for shock transformation of silicates in the subsurface target region according to the size of the impact event in two size categories: (1) large impact events (100-300 km) capable of penetrating average continental crust (~ 30 km thick); and (2) giant lunar Mare-sized impact basins (~ > 300-2500 km) which would have penetrated both the crust and the Earth's mantle to depths of > 150-250 km where diamond is stable. The largest impact craters (1) preserved on Earth include the Vredefort and Sudbury craters, of which only the Sudbury impact crater preserves a thick within-crater ejecta sequence and record of post-cratering surface geological activity. Detailed investigation of the petrology and composition of the rocks at Sudbury (Ubide et al., 2017) has revealed that explosive submarine volcanism was initially fed by crustal melts, but that with time, volcanic activity was progressively fed by more Mg-rich magmas originating at deeper levels within the lithospheric mantle. This supports hypothetical models for volcanism triggered by impact cratering, both in principle and in the size range predicted (Jones et al., 2002; Jones, 2014). There are 17 Mare impact craters (2) on the Moon, and although none are preserved on Earth, we expect there to have been 23 times this number (~ 400) on Earth. We have calculated the effects of large to giant impacts on the terrestrial lithospheric target, taking a simple mineralogy for the mantle lithosphere dominated by olivine, and including the effects of shock transformation for olivine inclusions trapped within diamond. We show that shock pressures at the depth of diamond easily exceed conditions required to transform olivine to wadsleyite and ringwoodite, but the kinetics of the transformations are less well understood. Comparable to the 3-stage model for impact-melting (Jones 2014; Elkins Tanton et al., 2004) we consider 3 categories and time-scales of geological process capable of driving shock transformation in lithospheric mantle silicates. This has implications for geodynamic models, and for the future identification of dense relics in old lithospheric mineral assemblages.

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Multiphase solid inclusions as record of the redox budget of crust-derived fluid phases at the slab-mantle interface

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Keywords: subduction zone, ultrahigh pressure, oxygen fugacity.

The redox processes taking place in the portion of the mantle on top of the subducting slab are poorly investigated and the redox budget of crust-derived fluid phases is still poorly constrained. A case study of supra-subduction mantle affected by metasomatism from crust-derived fluid phases is the Maowu Ultramafic Complex (China) deriving from harzburgite precursors metasomatised at ~ 4 GPa, 750-800°C by a silica- and incompatible trace element-rich fluid phase. This metasomatism produced poikilitic orthopyroxene and inclusion-rich garnet porphyroblasts. Solid multiphase primary micro-inclusions in garnet display negative crystal shapes and infilling minerals (spinel, ±orthopyroxene, amphiboles, chlorite, ± talc, ± mica) occur with constant modal proportions, indicating that they derive from trapped solute-rich aqueous fluids. FT-IR hyper spectral imaging analyses and micro-Raman spectroscopy, together with X-ray microtomography performed on single inclusions, indicate that liquid water is still preserved at least in some inclusions.

To investigate the redox budget of these fluid phases, the Fe^{3+} concentration of the micron-sized precipitates of the multiphase inclusions has been measured for the first time using EELS on a TEM. Results indicate that spinel contains up to 12% of $Fe^{3+}/\Sigma Fe$, amphibole about 30%, while the ratio in inclusion phases such as chlorite and phlogopite may reach 70%. The Fe^{3+} fraction of the host garnet is equal to that measured in spinel as also confirmed by Flank Method EPMA measurements.

Forward modelling fO_2 calculations indicate that the garnet orthopyroxenites record $\Delta FMQ = -1.8 \div -1.5$, resulting apparently more reduced with respect to metasomatised supra-subduction garnet-peridotites. On the other hand, oxygen mass balance, performed both on the Maowu hybrid orthopyroxenite and on metasomatised supra-subduction garnet peridotites, indicate that the excess of oxygen (nO_2) is the same (10 mol m^{-3}). An oxygen mass balance of the crust-derived fluids also indicates that the fluid precipitates are more oxidised than the host rock, reaching up to 400 mol m^{-3} of nO_2. This suggests that even after their interaction with the metasomatic orthopyroxenites, the residual fluid phases could be potentially carrier of oxidised components when escaping the slab-mantle interface.

Elastic geobarometry: the strain and the stress distribution in the host-inclusion system revealed by Finite Element Modeling (FEM)

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Keywords: elastic geobarometry, host-Inclusion systems, Finite Element Modeling (FEM).

Ultra-high-pressure metamorphic (UHPM) rocks are the only rocks that can provide insights into the detailed processes of deep and ultra-deep subduction. Minerals trapped as inclusions within other host minerals develop residual pressure (P_{inc}) on exhumation as a result of the differences between the thermo-elastic properties of the host and the inclusion. If correctly interpreted, measurement of the P_{inc} allows good estimates of the entrapment pressure to be made by means of elastic geobarometry.

The solution for isotropic non-linear elasticity has been recently incorporated into the classic host-inclusion model available in the EoSFit7 suite of software (Angel et al., 2015 and references therein). However, this solution is only valid for simple ideal geometries (*e.g.*, small spherical inclusion located at the center of an infinite host).To extend the analysis beyond the existing geometrical assumptions we performed numerical calculations using Finite Element Modelling (FEM) that allows us to evaluate how the pressure (mean normal stress) in real host-inclusion systems deviates from that predicted by the ideal analytical model. To determine the effects of the geometry alone we performed calculations with isotropic elasticity. Moreover, the FEM simulations give the complete state of strain and stress inside and around inclusions with any shape and with any position inside the host. This allows the interpretation of the strain gradients developed within natural inclusions, as recently revealed by Raman measurements on inclusions entrapped in garnets from UHPM rocks.

Our results show that when a spherical inclusion is close the external surface of the host the residual pressure in the inclusion is partially released, and the strain and the stress within the inclusion becomes inhomogeneous. The pressure release is greater than 1% when the distance is smaller than two times the radius of the inclusion. Deviations produced by changes in the shape of the inclusions include two contributions. First, the effect of edges and corners is small, and introduces pressure deviations of less than 5%. Second, the aspect ratio of the inclusion gives rise to large deviations in P_{inc} with shifts in the calculated pressures of more than 10% for platy inclusions (*i.e.*, aspect ratio 1:5:5). The exact effect on P_{inc} is a complex function of both the values of the bulk and shear moduli of both host and inclusion, and the contrast in these values. Moreover, the presence of corners and edges affects the homogeneity of the stress and of the strain in the inclusion.

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Metamorphic history of UHPM rocks: What can tell us inclusions under pressure?

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Keywords: tourmaline, diamond, metamorphism, Kokchetav, inclusions.

Coesite and diamond inclusions have been used as an evidence of *UHP* host mineral crystallization. However recent findings of intergranular coesite (Liu et al., 2017) and diamond (Korsakov et al., 2004) raised the question about the simultaneous growth of the inclusion and host mineral. The inclusion study in the *UHP* rocks is a source of the unique information about the environmental conditions of the entrapment. Although thorough analysis of the inclusion-host-mineral system is prerequisite for correct reading of the metamorphic history.

Raman spectroscopy is a non-destructive tool for identification of micro scale inclusion compositions, allowing to estimate the value of residual pressure. Measurements of the residual stress in the inclusions can, in combination with the equations of state (EoS) of the two phases, be used to infer the pressures and temperatures of the encapsulation and consequently host-mineral crystallization.

Different types of inclusions in tourmaline along with its compositional zoning make this mineral an excellent example of the inclusion-host system. Tourmaline from Kokchetav *UHP* metamorphic rock has the following peculiarities: the significant amount of K in its structure (enough to separate out individual end-member maruyamaite (Lussier et al., 2016)) and microdiamond inclusions. The presence of the latter in the K-dominant zone of tourmaline was one of the main evidence of its crystallization in the diamond stability field (Shimizu & Ogasawara, 2005).

Tourmalines from Qz-Tour gneisses and Grt-Px rocks (Kumdy-Kol mining exploration gallery, Kokchetav massif, Northern Kazakhstan) were examined with particular attention to the diamond-bearing grains. Tourmaline was found to contain different types of inclusions, which can be divided into 2 groups: (i) fluid inclusions with a variation of chemical composition, that carry information about tourmaline-forming fluid; (ii) solid crystalline inclusions presented by abundant inclusions of the minerals from present mineral association of the host rock (quartz, K-feldspar, mica, graphite) and diamond inclusions.

Formation of the tourmaline and its inclusions are not necessary simultaneous processes. The main purpose of our study is to recover the *P-T* conditions of tourmaline crystallization and find its place in the Kokchetav metamorphic history.

Acknowledgements: This study was supported by a grant from the Russian Science Foundation (RSF 15-17-300-12).

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Super-deep diamonds, iron and hydrogen: what's going on in the deep Earth?

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Keywords: super-deep diamonds, hydrogen, iron, methane, ringwoodite.

It is well-known that diamonds are the only direct sampling of the deep Earth thanks to their capability to travel through our planet from more than 1000 km depth to its surface remaining nearly uncorrupted over time (some diamonds show crystallization ages close to 3.5 billion years) and space. Rarely, diamonds might bring to the surface fragments of deep Earth, which are represented by mineral inclusions typical of the Earth's mantle. In detail, recent discoveries showed that not only diamonds entrapped inclusions from the upper mantle (down to 410 km depth) (these are the typical lithospheric diamonds, representing about 94% of the diamond population), but also from the transition zone (between 410 and 660 km depth) and even from the lower mantle (below 660 km depth). These super-deep diamonds constitute a different diamond category representing only about 6% of the diamond population. Their study is providing totally new scenarios about the very deep Earth, reporting unexpected mineral inclusions like ringwoodite (Pearson et al., 2014), metallic iron and hydrogen plus methane fluid (Smith et al., 2016). A general overview of all the recent discoveries about super-deep diamonds will be provided.

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H_2O in mineral inclusions in diamonds: Constrains on the water content of cratonic lithosphere peridotites and diamond-forming melts

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Keywords: H_2O, volatiles, mantle, diamond, inclusions.

H_2O plays a major role in many geological and biological processes occurring at the Earth's surface including for instance volcanism, which impacts the composition of the atmosphere. H_2O is also recycled into the Earth's interior where is found as hydrogen defects in nominally anhydrous minerals of mantle peridotites (*e.g.*, Bell & Rossman, 1992). Even if present in very limited amounts, H_2O can significantly alter the physical and chemical properties of minerals (Bolfan-Casanova, 2005). Therefore, determining the H_2O content of the mantle is crucial to understand Earth's dynamics and evolution.

Mantle H_2O contents can be constrained by studying peridotite xenoliths found in kimberlitic rocks in cratons (*e.g.*, Doucet et al., 2014). However, xenoliths can react with magmas that deliver them to the surface or melts/fluids that infiltrate the cratons, affecting thus their original mantle signature. Alternatively, mineral inclusions trapped in diamonds can be investigated to infer the mantle pristine H_2O contents. Diamond inclusions are representative of the mantle conditions before they were included in the strong and chemically inert diamond, which shields them during their journey to the surface and prevent reactions with secondary melts/fluids to occur.

In this presentation we will discuss recent investigations of H_2O content of mineral inclusions in diamonds from the Siberian craton (*e.g.*, Novella et al., 2015; Taylor et al., 2016). Minerals in diamonds have considerably lower H_2O contents compared to those found in xenoliths from the same locality (Doucet et al., 2014), suggesting that H_2O contents of xenolith minerals may be affected by secondary processes such as metasomatism. We will evaluate the importance of studying H_2O contents in diamond inclusions to infer the H_2O content of cratonic lithosphere peridotites, with implications for the stability of cratons over geological times, and the volatile nature of diamond-forming melts.

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Organic inclusions in forearc serpentinites from the Mariana mud volcanoes: Message in a bottle from a deep biosphere?

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Keywords: deep biosphere, serpentinization, subduction zone, forearc, organic inclusions.

Serpentinization-fueled systems in the cool, hydrated forearc mantle of subduction zones may provide an environment that supports deep chemolithoautotrophic life. Here, we examine serpentinite clasts expelled from mud volcanoes above the Izu–Bonin–Mariana subduction zone forearc (Pacific Ocean) that encapsule complex organic matter and nanosized Ni–Fe alloys. Using time-of-flight secondary ion mass spectrometry and Raman spectroscopy, we determined that the organic matter consists of a mixture of aliphatic and aromatic compounds and functional groups such as amides (Plümper et al., 2017). Although an abiotic or subduction slab-derived fluid origin cannot be excluded, the similarities between the molecular signatures identified in the clasts and those of bacteria-derived biopolymers from other serpentinizing systems hint at the possibility of deep microbial life within the forearc. To test this hypothesis, we coupled the currently known temperature limit for life, 122°C, with a heat conduction model that predicts a potential depth limit for life within the forearc at ~ 10,000 m below the seafloor. This is deeper than the 122°C isotherm in known oceanic serpentinizing regions and an order of magnitude deeper than the downhole temperature at the serpentinized Atlantis Massif oceanic core complex, Mid-Atlantic Ridge. We suggest that the organic-rich inclusions within the serpentinites may be indicators for microbial life deep within or below the mud volcano. Thus, the hydrated forearc mantle may represent one of Earth's largest hidden microbial ecosystems. These types of protected ecosystems may have allowed the deep biosphere to thrive, despite violent phases during Earth's history such as the late heavy bombardment and global mass extinctions. Only if we keep exploring the windows into the deep subsurface, such as the organic inclusions within the serpentinite clasts presented here, will we be able to establish a full budget of Earth's deep carbon and the potential for a subsurface biosphere.

Plümper, O., King, H.E., Geisler, T., Pabst, S., Savov, I.P., Rost, D., Zack, T. (2017): Subduction zone forearc serpentinites as incubators for deep microbial life. Proc. Nat. Acad. Sci., 114, 4324-4329.

Fluid-related inclusions in Alpine high-pressure peridotite monitor subduction-zone dehydration of serpentinized mantle (Cima di Gagnone, Swiss Alps)

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Keywords: subduction, serpentinite, metasediment, fluid.

Serpentinites release at sub-arc depths volatiles and several fluid-mobile trace elements found in arc magmas. Constraining element uptake in these rocks and defining the trace element composition of fluids released upon serpentinite dehydration improves knowledge of mass transfer in subduction zones and to volcanic arcs. The eclogite-facies garnet metaperidotite and chlorite harzburgite bodies embedded in paragneiss of the subduction melange from Cima di Gagnone derive from serpentinized peridotite protoliths and are unique examples of ultramafic rocks that experienced subduction metasomatism and devolatilization. In these rocks, metamorphic olivine and garnet trap polyphase inclusions representing the fluid released during high-pressure breakdown of antigorite and chlorite. Combining major element mapping and laser-ablation ICP-MS bulk inclusion analysis, we characterize the mineral content of polyphase inclusions and quantify the fluid composition. Silicates, Cl-bearing phases, sulphides, carbonates, and oxides document post-entrapment mineral growth in the inclusions starting immediately after fluid entrapment.

Compositional data reveal the presence of two different fluid types. The first (type A) records a fluid enriched in fluid-mobile elements, with Cl, Cs, Pb, As, Sb concentrations up to 10^3 PM (primitive mantle), □10^2 PM Tl, Ba, while Rb, B, Sr, Li, U concentrations are of the order of 10 PM, and alkalis are □2 PM. The second fluid (type B) has considerably lower fluid-mobile element enrichments, but its enrichment patterns are comparable to type A fluid.

Our data reveal multiple fluid uptake in these peridotite, including selective element enrichment during seafloor alteration, followed by fluid–rock interaction along with subduction metamorphism in the plate interface melange. Here, infiltration of sediment-equilibrated fluid led to As, Sb, B, Pb enrichment of serpentinites. This trace element-enriched signature was then transferred to the fluid released upon serpentine dehydration (type A fluid). The type B fluid hosted by garnet may record the composition of the chlorite breakdown fluid released at even greater depth.

The Gagnone study-case demonstrates that serpentinized peridotites acquire water and fluid-mobile elements during ocean floor hydration and through exchange with sediment-equilibrated fluids in the early subduction stages. Subsequent antigorite devolatilization at subarc depths delivers aqueous fluids to the mantle wedge that can be prominently enriched in sediment-derived components, potentially triggering arc magmatism.

Study of polycrystalline inclusions in garnets from granulites of the Athabasca Granulite Terrane (Canada)

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Keywords: crustal anatexis, peritectic garnet, fluid inclusions, melt inclusions, nanogranite, CO_2, FIB-SEM.

In the last decade the study of fluid and melt inclusions has become a key tool to acquire unprecedented information in crustal anatectic rocks. In this work a detailed microstructural and microgeochemical study has been performed on polycrystalline inclusions trapped in peritectic garnets of felsic granulites from the Upper Deck domain, in the Athabasca Granulite Terrane (Canada). Inclusions have been characterized by SEM-EDS and FIB-SEM techniques, and by Laser Raman microspectroscopy. The inclusions are small (≤ 10 µm), they are primary in origin, and do not show evidence of decrepitation. FIB-SEM analyses permitted to recognise the main crystalline phases and their distribution. The polycrystalline assemblage is always made of ferroan magnesite, quartz and graphite, in association with minor amounts of corundum and Zn-spinel. Calcite and dolomite can be present, and pyrophyllite was found only in one inclusion. Quartz and corundum coexistence has been interpreted as the product of metastable growth within pores of extremely small size. Raman microspectroscopy revealed the presence of CO_2, with traces of CH_4 and N_2. A good negative correlation between the CO_2 density and the total amount of coexisting solid phases has been observed. The main minerals occur in relatively constant proportions in the investigated inclusions, suggesting the entrapment of a compositionally homogeneous fluid characterized by a high-carbon content. These carbon-rich inclusions coexist in the same cluster with nanogranite inclusions. Because nanogranites are interpreted to be droplet of anatectic melt formed and trapped during incongruent melting of crustal rocks, the investigated polycrystalline inclusions prove the presence of a carbon-rich fluid during melting of these rocks, possibly in a situation of melt/melt or melt/fluid immiscibility.

Evolution of platinum group minerals (PGM) from high to low temperatures: examples from ophiolitic chromitites

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Keywords: platinum group minerals, chromitite, ophiolite.

The podiform chromitites that occur in the mantle section of some ophiolites are enriched in platinum group elements (PGE = Os, Ir, Ru, Rh, Pt and Pd), especially in the most refractory Os, Ir and Ru, compared to their host peridotite. In accordance with this geochemical signature, the podiform chromitites contains platinum group minerals (PGM) that mainly consist of Os-Ir-Ru sulfides, alloys and sulfarsenides. Generally the PGM occur as small grains (less than 10 µm) included in chromite crystal or associated with the altered silicates of the matrix. Based of textural position, paragenesis and composition, the PGM can be divided in two groups: 1) primary: formed at high temperature, at the magmatic stage, and 2) secondary: formed or re-worked at relatively low temperature. The crystallization of primary PGM mainly depends on the proportion of Os, Ir and Ru, on the availability of sulfur and temperature prevailing during the chromite formation. Experimental data supported by a large number of natural observations indicate that laurite is in equilibrium with Os-Ir-(Ru) alloys at a temperature of 1300°C and relatively low sulfur fugacity. Laurite becomes progressively enriched in Os with decreasing temperature and increasing sulfur fugacity, up to the stability field of erlichmanite. Therefore, in the magmatic stage, the PGM crystallized in the following order of precipitation: Os-Ir-(Ru) alloys, RuS_2, OsS_2 and Ir-sulfides. The primary PGM can be modified and altered after their magmatic precipitation, during serpentinization and weathering at low temperature. In particular, the magmatic PGE sulfides can be altered *in situ* by progressive loss of S and addition of base metals and, possibly oxygen, leading to the formation of PGE alloys or oxides. Few ophiolitic chromitites are enriched also in the more chalcophile Rh, Pt and Pd. This enrichment is controlled by the formation, at magmatic stage, of an immiscible sulfide liquid that collected the PGE as cluster consisting of few PGE atoms. During a sequent stage, part of the PGE bonded with chalcogenides to crystallize specific minerals of Rh, Pt and Pd. These PGM are also very small in size and occur interstitial to the host chromite associated with base metals sulfides. Part of the PGE remains in the immiscible sulfide liquid and precipitated to form PGE-rich base metals sulfides. During alteration processes, sulfur can be removed from the magmatic PGM sulfides and PGE-rich base metals sulfides. This process generated secondary sulfides as well as PGE and Ni-Fe alloys that sometimes contain tiny blebs of PGE-rich phases that precipitated as low temperature exsolution products. Although the PGM associated with podiform chromitites are rare and occur as tiny grains, their mineralogical investigation can be used to evaluate the sulfur fugacity and temperature prevailing in the mantle during their precipitation. The alteration of PGM, generally, caused only re-distribution of PGE on a small scale.

Session S4:

New insights on the mineralogical, petrological and geochemical composition of the lithosphere and implications on its geodynamical evolution

Conveners:

Paola Comodi (Univ. di Perugia)
Costanza Bonadiman (Univ. di Ferrara)
Patrizia Fumagalli (Univ. di Milano)

Early evolution of mantle melts intruding the lowermost continental crust of the Ivrea-Verbano Zone (southern Alps): insights from the Monte Capio peridotite-pyroxenite lens

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Keywords: mineral trace composition, Nd-Sr isotopes, Ivrea-Verbano Zone, Mafic Complex, Mafic-ultramafic cumulates.

Magma chambers in the deep continental crust play a major role in modifying the compositions of ascending mantle-derived melts, through complex evolution processes involving fractional crystallization, crustal assimilation and melt-crystal mush reactions. To unravel the early magmatic evolution experienced by the mantle melts intruding the lowermost continental crust of the Ivrea-Verbano Zone, we carried out a petrological and geochemical study of the km-scale ultramafic lens exposed near Monte Capio. This lens spreads for a few km from Strona to Mastallone valleys, near the Insubric tectonic line, and has a maximum thickness of 400 m. The magmatic ultramafic lens shows intrusive relationships with respect to a basement made up of metasediments and metabasites recrystallized under granulite facies conditions.

The Monte Capio ultramafic lens consists of peridotites (mainly dunites to olivine-rich harzburgites) and orthopyroxene-rich pyroxenites that are locally olivine- or plagioclase-bearing. The ultramafic sequence includes minor to accessory amounts of pargasitic amphibole, Al-rich spinel and, in places, clinopyroxene. Hornblendite to hornblende-rich gabbronorite dykes crosscut the ultramafic sequence with diffuse to sharp planar boundaries towards the host rocks. Gabbronorites also occur along the contact between the ultramafic rocks and basement metasediments. Olivine has relatively low forsterite and NiO amounts. Pyroxenes and amphibole show wide variations in Mg/(Mg+Fe), which decreases from peridotites to pyroxenites and crosscutting dykes. The anorthite content of plagioclase varies from 89 mol% in the pyroxenites to 75 mol% in the gabbronorites. The dykes overall have similar Rare Earth Element (*REE*) signature, which may be reconciled with modern enriched MORB compositions. Conversely, amphibole and clinopyroxenes from the peridotites and the pyroxenites show substantial variations in the *REE* patterns. Amphibole separates and whole-rocks for the peridotites, pyroxenites and crosscutting dykes have lower initial $^{143}Nd/^{144}Nd$ and higher $^{87}Sr/^{86}Sr$ than MORB.

The Monte Capio ultramafic lens documents the intrusion of olivine- and spinel-saturated melts into the extending lowermost continental crust of the Ivrea-Verbano Zone. These melts had previously experienced an evolution mainly driven by fractionation of olivine and minor spinel. We attribute the formation of the exposed peridotite-pyroxenite sequence to a magmatic evolutionary process ruled by fractional crystallization, with orthopyroxene replacing olivine at the *liquidus*. The development of the peridotite-pyroxenite sequence at least locally also comprised the late-stage reactive migration of amphibole-saturated melts through ultramafic crystal mushes. Furthermore, some of the samples selected for the present study document a process of crustal contamination, presumably in response to interaction of the melts with host metasediments. The primary melts of the Monte Capio ultramafic lens may have formed by mantle sources that had experienced subduction-related metasomatism.

Subsolidus phase relations in a secondary-type pyroxenite: an experimental study from 0.7 to 1.5 GPa

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Keywords: pyroxenites, experimental petrology, piston cylinder experiments, garnet stability, plagioclase, spinel, *subsolidus* assemblage.

Pyroxenites are diffuse heterogeneity in the upper mantle and represent key lithologies in melting processes and mantle deformation. Mantle peridotites exposed in ultramafic massifs are often veined by pyroxenites that can be originated by deep magmatic infiltration. Although these pyroxenites experienced the same metamorphic evolution of the host peridotites, they are expected to develop sensibly different phase assemblages in response to the different bulk composition. Despite of several experimental studies focused on melting relations in pyroxenites, *subsolidus* phase relations are still poorly known. This study aims to provide new experimental constraints on phase stability and mineral chemistry for a natural pyroxenite having a "hybrid" bulk composition, *i.e.*, originated by interaction between a mantle peridotite and pyroxenite-derived melt, characterized by a relatively high X_{Mg} (0.83) and CaO (14.5 wt%), and low Na_2O (0.48 wt%) (Borghini et al., 2016). Piston cylinder experiments were conducted at pressure from 0.7 to 1.5 GPa, temperatures from 1100 to 1250°C using a nominally anhydrous glass seeded with 1% of a mixture of synthetic pure spinel (50%) and garnet (50%). Al-rich spinel, clinopyroxene, orthopyroxene and olivine are ubiquitous phases within the whole pressure range investigated. At 1100°C, plagioclase is stable up to 0.9 GPa; anorthite content [An = Ca/(Ca+Na)] decreases as a function of pressure from 0.70 at 0.7 GPa to 0.61 at 0.9 GPa. Plagioclase modal abundance results of up to 14 wt% at 0.7 GPa; this amount is more than the double of modal plagioclase experimentally determined at same *P*-*T* conditions in fertile lherzolite (5-6 wt%, Borghini et al., 2010). At intermediate pressure (1-1.4 GPa), modal spinel abundance is almost constant (4-5 wt%). A pyrope-rich garnet is stable at 1.5 GPa and its modal abundance increases with decreasing temperature from 5 to 10 wt% from 1230 to 1150°C. As expected, pyroxenes composition varies significantly across the plagioclase-out and garnet-in transitions and is not pressure-dependent in the spinel pyroxenite field. At 1100°C, the plagioclase-out curve occurs at comparable pressures in the pyroxenite and in fertile lherzolites. On the contrary, the garnet-in curve is located at significantly lower pressure than the conditions reported for mantle peridotites. Pseudosections calculated for the investigated pyroxenite bulk composition slightly underestimates the pressure of plagioclase-out boundary and overestimates pressure of garnet appearance.

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Cratonic and CO_2-rich metasomatism signatures recorded in Veneto Volcanic Province xenoliths

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Keywords: cratonic signature, CO_2-rich metasomatism, Veneto Volcanic Province.

The Veneto Volcanic Province (VVP), a Tertiary magmatic province in the northeastern Italy, is one of the most important volcanic events of the Adria Plate. It is composed of five volcanic districts: Val d'Adige, Marosticano, Mts. Lessini, Berici and Euganean Hills. Most of its volcanic products are relatively undifferentiated lavas, ranging from nephelinites to tholeiites, with the most alkaline lavas commonly carrying ultramafic xenoliths. This study reports a petrological characterization of a new find anhydrous spinel-bearing mantle peridotites from Monte Gloso (MG) in the Marosticano district, that reveals the unexpected sub-craton related features of the lithospheric mantle sector beneath this area, including evidence for its metasomatic modification and evolution. Marosticano peridotites are cpx-bearing harzburgites and lherzolites that tend towards high contents of residual components as observed for the on-craton peridotites. These findings are consistent with ancient Re-Os ages (3.4 Ga) for Val d'Adige xenoliths and suggest that portions of cratonic mantle underlie the VVP. Across all lithologies, Mg# values of olivine and orthopyroxene (91-93) equate approximately to the point of clinopyroxene consumption in the sp-stability field, suggesting that they are secondary in nature formed by a carbonatite/CO_2-rich silicate melt reacting with residual peridotites. This is manifested in the clinopyroxene geochemical features as: i) enrichment in Th, U, Rb and *LREE*, but depletion in both *HREE* and HFSE (*e.g.*, Ta, Zr and Hf); ii) high $(La/Yb)_N$ and low Ti/Eu ratios; iii) *REE* patterns similar to those of cpx equilibrated with a synthetic carbonatitic melt at 1100-1150°C and 1.5-2 GPa. Despite the common metasomatic fingerprints, two different clinopyroxene trace element profiles highlights are observed. Group-1 are characterised by the least steep *HREE* pattern and positive Eu anomaly and group-2 with pronounced convex-upward *REE* patterns. The coexistence of the two clinopyroxene groups in the same populations is explained by a variable evolved carbonatite/CO_2-rich silicate metasomatic melt permeating different peridotite wallrocks. This metasomatic melt could be responsible also for the observed T-fO_2 conditions of MG peridotites (T = 923-1117°C; $\Delta\log fO_2$ (FMQ) = -0.6 +1.1), which are anomalously high for a proper cratonic environment but similar to the off-craton VVP xenoliths. Calculated dissolved CO_2 mole fractions for the metasomatic agent are close to 1, indicating that CO_2 was the largest component of the metasomatic melt. Therefore, T-fO_2conditions of MG primarily reflect matrix/carbonatitic melt interaction rather than the original cratonic fO_2 conditions. These samples support numerous lines of independent evidence plate boundary processing infuses CO_2 into cratonic mantle.

Looking for potential fluid-mobile elements reservoirs in the lithosphere: preliminary results from experimental studies

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Keywords: fluid-mobile elements, element recycling, amphibole sponge in crust, hydrous partitioning experiments.

The recycling of volatile and incompatible elements through the entire Earth's history is one of the most important processes for the chemical evolution of the lithosphere. In particular, some fluid-mobile elements (FME: *e.g.*, Sb, As) were demonstrated to be good geochemical tracers able to unravel geological processes where fluid-mediated mass transfer occurs (*e.g.*, subduction plate-interface; Cannaò et al., 2016). Despite olivine and pyroxene represent the most abundant mineral phases in the lower crust and upper mantle, the development of amphibole from a precursor hydrous melt (Müntener & Ulmer, 2006) or by metasomatic processes replacing pyroxene (Smith, 2014) play an important role in the chemical evolution of the lithosphere. The partitioning behavior of FME between amphibole, clinopyroxene, olivine and melt is still poorly constrained. This hampers to model the transport of these elements in the mantle wedge and to constrain if these elements can be stored in the upper mantle or in the deep crust.

In order to better constrain the partitioning of As and Sb between amphibole, clinopyroxene and melt, we carried out hydrous partitioning experiments at *P*-*T* conditions of the lower continental crust considering an alkali-basalt as starting material. The experimental runs were conducted at fixed pressure of 1.4 GPa and temperature ranging from 1075 to 1015°C. Given the multiple oxidation state of As and Sb different buffer techniques (graphite and hematite-magnetite) were used. At all run conditions, Ti-pargasites and kaersutite either as individual crystals or replacing former pyroxenes crystallized in equilibrium with the melt.

Trace and FME were determined by LA-ICP-MS techniques in melt, pyroxenes and amphiboles. Preliminary results show that amphibole has better capability to incorporate As and Sb with respect to pyroxene and glass (${}^{amph/l}D_{As}$ up to 2.6 and ${}^{amph/l}D_{Sb}$ up to 1.3).

Our first results highlight the capability of amphibole to trap FME in the lower crust and upper mantle becoming thus an important potential reservoir for the cycling and re-cycling of these elements in the Earth system. Partitioning results were applied to amphiboles from natural rocks of the lower continental crust in collisional settings in order to better constrain the natural As and Sb fluxes.

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Experimental study of interconnectivity of hydrous-carbonatitic melts and grain boundary wetness in mantle peridotite

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Keywords: dihedral angle, H_2O-rich melts, HP-HT experiments.

The mobility and infiltration rates of carbonatitic melts, together with their influence on the annealing of mantle peridotites, are processes poorly constrained. Although natural carbonatitic magmas are complex chemical systems bearing H_2O as a major chemical component, previous work has been performed in anhydrous model systems.

The percolation of carbonatitic liquids and the interconnectivity of melt pockets are investigated by placing a cylindrical dunite rod against a liquid reservoir. As peridotitic matrix we used a synthetic dunite starting from natural San Carlos olivine powder. Sintering has been performed in a single stage piston-cylinder apparatus at 0.8 GPa and 1200°C *P*-*T* conditions. Natural carbonatitic magmas in equilibrium with a mantle assemblage are mainly dolomitic. The starting material composition $(Ca_{0.541}Mg_{0.389}Fe_{0.069})CO_3$ was prepared from a powder mixture of carbonates, using free water as hydrous source (5 wt.% and 30% of the starting material). Time resolved infiltration experiments were performed employing an end loaded piston-cylinder apparatus, at $T = 1200°C$ and $P = 2.5$ GPa. In order to account for the different roles of gravity, chemical diffusion and Ludwig-Soret diffusion we used two opposite capsule geometries.

Hydrous carbonatitic melt pockets (> 3 mm) were found along olivine grain boundaries. BSE images and calcium X-ray maps of elements allow quantifying θ (apparent dihedral angle) between the liquid and olivine. True dihedral angle was estimated by the median of frequency distribution of the apparent angles.

Experiments performed at 5 wt.% of water content result in dihedral angles evolving from ~ 31° for 3 hours duration, to ~ 40° for 300 hours run. The volume of liquid infiltrated in the peridotitic matrix was ~ 8.5%, ~ 10.5%, and ~ 2.3% for run duration of 3, 30, and 300 hours respectively. Experiments conducted with 30 wt.% of water content provide a dihedral angle values of almost 50° with a volume of liquid infiltrated ranging from ~ 4% to ~ 8.7%. Overall the data available consistently indicate that dihedral angles progressively increase with increasing water dissolved, from 25°-28° in anhydrous carbonatitic liquids (*e.g.*, Hunter & McKenzie, 1989) up to 50° at 30 wt.% H_2O; as expected, the volume of interstitial liquid decreases with increasing H_2O (18 vol% in anhydrous experiments, Hammouda & Laporte, 2000). Remarkably, fluids show the opposite behaviour, as CO_2-rich fluids are less wetting (~ 90°) than H_2O pure fluids (~ 65°).

A quantitative assessment of melt distribution was obtained by calculating the grain boundary wetness, a measure of the intergranular melt distribution, by EMPA X-ray maps combined with high resolution EBSD grain boundaries image.

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Hydrogen content in nominally anhydrous minerals from Finero peridotite (Italy)

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Keywords: nominally anhydrous minerals, peridotites, lithospheric mantle, low water content in olivine, hydrogen, trace elements.

Hydrogen is present as a trace element in nominally anhydrous minerals (NAMs) composing the Earth's mantle. Such hydrous point defects are thought to have important consequences on fundamental physical properties such as rheology, seismic attenuation or electrical conductivity (Keppler & Smith, 2006; Demouchy et al., 2016). Hydrogen in NAMs generally occurs as hydroxyl groups (OH) associated to vacancies. Although there is a vast literature on hydrogen distribution in NAMs from relatively dry mantle xenoliths (Demouchy et al., 2016) there is a remarkable lack of data on NAMs in water-rich environments which makes challenging to address the effect of hydrous melt or aqueous fluids on the water partitioning in NAMs. The present work is aimed to investigate and quantify the water in olivine and pyroxenes from an unique locality where upper mantle peridotites are strongly metasomatised by hydrous melts (Finero Complex, southern Alps, Italy). This mafic complex might represents a useful, but yet unexplored, key location to investigate the partitioning of hydrogen in NAMs and to link them to a multistage metasomatic event characterized by the enrichment in volatiles, LILE, *LREE* and in radiogenic Sr, Pb but with low HFSE concentrations. Water content in NAMs has been determined by means of infra-red spectroscopy (FTIR), which is the most sensitive technique for measuring trace OH contents in NAMs that provides information on the speciation and orientation of the OH group in the structure. These analyses were made on ten double polished thin sections and on crystals separated covering most representative lithologies and deformation textures from the Finero peridotite (*i.e.*, coarse grained lherzholite, harburgite, dunite and clinopyroxenite veins). The approach of Kovacs et al.(2008) using unpolarized IR light was followed to constrain water contents and compared with measurements using polarized light on randomly oriented grains (Asimow et al., 2006). Preliminary results show water contents in olivine around 2 ppm wt. (Bell et al., 2003, calibration) with minor variations depending on the lithology and texture. Water contents in orthopyroxene and clinopyroxene are also comparatively low (around 42 ppm wt., and 137 ppm wt., respectively). These values are surprisingly low considering the water-rich nature of the multistage metasomatising event that resulted in the extensive crystallization of amphibole and phologopite (up to 30 vol.%). Interestingly the low water content in olivine is correlated with very low Ti contents in olivine (between 5-10 ppm) measured by laser ablation mass spectroscopy (LA-ICP-MS) on the same samples. This might suggest that Ti partitioning in the melt or in the hydrous phases is controlling the storage capacity in olivine (Berry et al., 2005) despite the availability of volatiles in the system.

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Subduction-related metasomatism as evidenced in ultramafic xenoliths from North Island, New Zealand

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Keywords: subduction metasomatism, calc-alkaline and boninite magmas, New Zealand.

Peridotitic xenoliths from Okete-Alexandra (2.74–1.60 Ma) and Ngatutura Volcanic Provinces (1.83–1.54 Ma), both included in the Auckland Volcanic Field, North Island (NZ), have been geochemically characterized. Xenoliths are entrained in piroclastites in Te Toto Gorge (Okete beach), while they can be found in alkaline basaltic boulders and pebbles at Ngatutura Point beach. It is worth noting that in the Okete-Alexandra Volcanic Province both alkaline and calc-alkaline magmas were erupted, in some cases almost contemporaneously. These ultramafic fragments may therefore shed a light on the evolution of the lithospheric domain where this peculiar magmatic shifting occurred.

Okete collection is mainly composed by lherzolites with few harzburgites, characterized by medium to coarse-grained protogranular textures; rarer clinopyroxenites, dunites and ol-clinopyroxenites with cumulitic textures also occur. The great majority of Ngatutura (NG) samples are dunites, with scarce harzburgites, wehrlites and ol-clinopyroxenites. Most of dunites are characterized by medium to coarse-grained equigranular textures; one is cut by a series of intertwined orthopyroxene veins having a sharp contact with the host olivines, while another shows an ol-websteritic portion.

On the basis of geochemical characteristics of olivine coexisting with spinels, Okete lherzolites and harzburgites fall in the mantle field, at slightly different degrees of partial melting, while dunites, clinopyroxenites and all NG samples clearly show the geochemistry of the phases properly assigned to crystallization products.

The lithospheric section represented by Okete peridotites underwent partial melting (F%) between 5 and 15%, as confirmed by spinel, olivine compositions and clinopyroxene *HREE* contents. Samples showing the highest F% degree are characterized by orthopyroxenes and clinopyroxenes with the highest degree of LILE, *LREE* and *MREE* enrichment. A metasomatic event occurred after depletion, due to the interaction with a calc-alkaline melt similar in composition to arc lavas found in the Alexandra Volcanic Group.

In the case of Ngatutura, the ultramafic xenoliths are cumulitic in nature. From both orthopyroxenes and clinopyroxenes chemistry, we can infer that the magma crystallizing the dunites was very primitive (Mg# between 65 and 72) and silica-rich, but poor in the “fertile” elements (mainly Al and Ti), thus possibly generated by partial melting of depleted mantle lithologies. The calculated melt resembles boninites from New Caledonia and Cape Vogel, although no arc-related magmas have been found in Ngatutura Volcanic Field.

Metamorphic evolution of a metaperidotite from the Monviso meta-ophiolite complex, Italian western Alps

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Keywords: subduction, *H*P metamorphism, serpentine, veins.

In the western Alps, the Monviso meta-ophiolite complex of the Piemonte Zone is one of the best preserved relics of the oceanic lithosphere formed during the opening of the Mesozoic western Alpine Tethys.

In the Monviso meta-ophiolite, two main tectonometamorphic units were distinguished on the base of the eclogite-facies metamorphic peak experienced during the Alpine orogeny. In particular, the "Lago Superiore" tectonometamorphic Unit experienced an early *HP* peak at 550°C and 2.5-2.6 GPa, followed by a re-equilibration under progressively lower pressures at epidote-blueschist- (*ca*. 450°C, 1.0-1.5 GPa) and greenschist-facies (*ca*. 400°C, 0.5-1.0 GPa) conditions, respectively. This tectonometamorphic Unit is constituted by two tectonostratigraphic units: the "Lago Superiore", mainly consisting of serpentinized peridotite and metagabbro (both Mg-Al and Fe-Ti), and the "Basal Serpentinite", mainly consisting of serpentinite.

Within the Mg-Al "smaragditic" metagabbro of the "Lago Superiore" stratigraphic unit, a few m thick lens of metaperidotite has been recently discovered. The metaperidotite, which exhibits an evident mylonitic fabric, consists of variable amounts of both porphyroclastic and neoblastic olivine, porphyroclastic orthopyroxene locally with exsolutions of clinopyroxene, Ti-clinohumite usually in equilibrium with neoblastic olivine, and magnetite. Hydrous minerals are mainly represented by lizardite, both in mesh structures after olivine and in bastite after orthopyroxene, by chlorite, mainly in association with olivine and Ti-clinohumite, and by antigorite after chlorite and olivine. Veins consisting of diopside ± chlorite, chlorite, antigorite, brucite + magnetite, talc, and carbonate are also present. The microstructural relationships among minerals suggest that the metaperidotite experienced a very complex evolution recording both an ocean-floor serpentinization and a polyphase Alpine metamorphism.

Petrology and geochronology of the Loro Intrusive Complex (Ivrea-Verbano Zone)

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Keywords: mafic complex, Southern Alps, Ivrea Verbano, Permian, U-Th-Pb, diorite, hornblendite.

The Loro Intrusive Complex is located in Valle d'Ossola (southern Alps) and is part of the Ivrea-Verbano Zone. Literature data on this igneous complex are relatively scarce (Boriani, 1966) and a detailed geochemical and geochronological study is missing. Therefore, for its location between the northern and the southern Ivrea domains, this poorly studied igneous complex is important to correctly understand the structure and igneous evolution of the whole Ivrea-Verbano Zone.

The Loro Intrusive Complex crops out along the Canavese Line and is in contact with the "Scisti di Fobello e Rimella" to the west and with mafic and felsic granulites of the Kinzigite formation to the east. Within the whole complex slices of basement rocks including milonitic granulites, marbles and serpentinites are locally found. Diorites and hornblendites are the main lithologies of the Loro Intrusive Complex. Diorites are relatively fine-grained and consist of pargasitic amphibole (60 vol%) and plagioclase (40 vol%) with average An contents of 47 mol%. A strongly altered clinopyroxene (Mg# = 0.7) is locally found. Hornblendites consists of brown amphibole and accessory plagioclase. The chondrite normalized Rare Earth Element (*REE*) pattern of clinopyroxene is characterized by a marked light–(*L*)*REE* enrichment (22 times CI chondrite) relative to heavy (*H*)-*REE*, which are at about 5 times CI chondrite (Gd_N/Yb_N up to 3.8). The *REE* pattern of amphibole is enriched in *LREE* (40 times CI chondrite) and *HREE* are about 15 times CI chondrite ($Gd_N/Yb_N = 1.5$). Occasionally a positive Eu anomaly characterizes the *REE* pattern of amphibole.

U-Pb geochronology was carried out with laser ablation ICP-MS on zircons from diorites. Zircon grains have round shape, thus suggesting a xenocrystic origin. Under cathodoluminescence they are generally homogeneous and rarely show ghost zoning. Most of zircons gave discordant U-Pb dates, only few grains are concordant and allowed to calculate a concordant date at 278±3 Ma (2σ). This date is interpreted as the age of reset of the U-Pb system induced by the intrusion of the dioritic rocks.

Similarities between the Loro and the Finero intrusive complexes were already suggested by Boriani (1966). These new results demonstrate a close geochemical affinity between the two complexes; in particular, peculiar similarities in terms of trace element composition of minerals are observed (*e.g.*, the positive Eu anomaly in amphibole). The inferred age of intrusion suggests that the Loro intrusive complex belongs to the same mantle-derived magmatism that gave origin to the Mafic Complex of the southern section of the Ivrea-Verbano Zone and perfectly overlap the Permian high-temperature event recognized in the Kinzigite formation in the Finero section of the Ivrea-Verbano Zone.

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Trace metal distribution in spinels from ultramafic bedrocks with different degree of serpentinization: insight from the *HP-LT* Voltri Massif (Ligurian Alps)

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Keywords: ophiolites, ultramafic bedrock, spinel-group minerals, trace metals.

Ultramafic rocks have high concentrations of trace metals such as Cr, Ni, and Co, which have potential impact on environmental and human health once they are mobilized into soil, water or dust. Trace metals-bearing phases are represented mainly by spinels (magnetite, picotite, and hercynite) and secondly by silicates (*i.e.*, serpentine group minerals, olivine, pyroxenes and chlorite). Hence, the knowledge of the spinel-group minerals distribution related to the degree of serpentinization, metamorphic re-equilibration and deformations may have interesting implication both in petrological and environmental fields.

In this study we investigated the mineralogy and the mineral chemistry of spinel-groups minerals of ultramafic bedrock (*e.g.*, partially serpentinized peridotites, antigorite-bearing serpentinites and serpentine schists) from different soil profiles of the *HP-LT* Voltri Unit (Ligurian Alps). In particular we focused on variations of the spinels composition in relation to different textures, microstructures and various degree of serpentinization and metamorphic re-equilibration.

The mineralogy, petrography, and mineral chemistry were analysed by means of optical microscopy, X-ray powder diffraction (XRPD), scanning electron microscopy and microprobe analyses (SEM-EDS and WDS), and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS).

In most of the analysed lithotypes, the spinel-group minerals occur with particular textural and microstructural features that can be grouped in four classes: i) primary magmatic spinel-porphyroclasts, with the characteristic holly-leaf texture, scattered within partially serpentinized peridotite and massive serpentinite. Primary magmatic spinels (hercynite and picotite) are partially to completely replaced by ferrian chromite- and magnetite-pseudomorphs. ii) Magnetite crystals within microfractures in primary magmatic spinels. iii) Idiomorphic to sub-idiomorphic magnetite crystals in trails along the rims of the mesh textures and within bastites in massive serpentinites. iv) Aggregates of magnetite crystals deformed and re-oriented along the foliation in microboudins or microfolds in serpentine schists. v) Magnetite crystals within veins often associated to other infilling minerals (such as chrysotile, talc, and chlorite).

The results evidenced significant variation in trace metal concentrations in spinels during the metamorphic and deformative evolution of the studied ultramafic bedrocks. In particular Cr, Ni, and Co concentrations progressively decrease with the serpentinization of the rocks. Moreover, Ti and V concentrations increase significantly in ultramafites occurring close to tectonic contacts with other lithologies such as eclogites, metagabbros and chlorite-Ca amphibole schists.

These results evidenced that ultramafic bedrocks, even within the same metamorphic unit, could have substantial differences in the trace metal distribution, which directly reflect on the soil chemistry.

The Forsterite-Anorthite-CaTschermak-Enstatite (FACE) geobarometer: tracking the exhumation history of mantle rocks

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Keywords: plagioclase peridotites, geobarometer, mantle exhumation, oceanic lithosphere.

Plagioclase-bearing assemblages in mantle rocks witness mantle exhumation at shallow depth. We present new constraints on the stability of plagioclase as a function of different Na_2O/CaO bulk ratio and a new geobarometer for mantle rocks. Experiments have been performed in a single stage piston cylinder at 5-10 kbar, 1050-1150°C at nominally anhydrous conditions using seeded gels of peridotite compositions ($Na_2O/CaO = 0.08\text{-}0.13$; $X_{Cr} = Cr/(Cr+Al) = 0.07\text{-}0.10$) as starting materials. As expected, the increase of bulk Na_2O/CaO ratio extends the plagioclase stability to higher pressure; in the bulk composition with the highest Na_2O/CaO investigated, the plagioclase-spinel transition occurs at 1100°C between 9-10 kbar; whereas in the peridotite with the lowest Na_2O/CaO ratio it occurs between 7-8 kbar, at 1100°C. This study provides, together with previous experimental results, a consistent database, covering a wide range of *P*-*T* conditions (3-9 kbar, 1000-1150°C) and variable bulk compositions, to be used to define and calibrate a geobarometer for plagioclase-bearing mantle rocks. The pressure sensitive equilibrium:

$$\underset{\text{Forsterite}}{Mg_2SiO_4{}^{Ol}} + \underset{\text{Anorthite}}{CaAl_2Si_2O_8{}^{Pl}} = \underset{\text{Ca-Tschermak}}{CaAl_2SiO_6{}^{Cpx}} + \underset{\text{Enstatite}}{Mg_2Si_2O_6{}^{Opx}}$$

has been empirically calibrated by least squares regression analysis of experimental data combined with Monte Carlo simulation. Result of the fit gives the following equation:

$$P = 7.2\ (\pm 2.9) + 0.0078\ (\pm 0.0021)\ T + 0.0022\ (\pm 0.0001)\ T \ln K$$
$$R^2 = 0.93$$

where *P* is expressed in kbar, temperature in kelvin, K is the equilibrium constant $K = a_{Ca\text{-}Ts} * a_{en} / a_{an} * a_{fo}$, where $a_{Ca\text{-}Ts}$, a_{en}, a_{an}, a_{fo} are the activities of Ca-Tschermak in clinopyroxene, enstatite in orthopyroxene, anorthite in plagioclase and forsterite in olivine. The proposed geobarometer for plagioclase peridotites, coupled to detailed microstructural and mineral chemistry investigations, represents a valuable tool to track the exhumation of the lithospheric mantle at extensional environments.

The elastic behaviour of the 11.5 Å phase and its petrological implications in subduction environments

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Keywords: high-pressure, subduction.

We report the study of compressibility, thermal expansion and solubility of chromium of the 11.5 Å phase, $Mg_6Al(SiO_4)_2(OH)_7$ a new high pressure phase (Gemmi et al., 2016), suggested as a candidate water carrier in subduction environments. It incorporates a significant amount of water, *i.e.*, 13 wt%. The 11.5 Å phase is a product of the decomposition of chlorite. It has been synthesized at 6.5 GPa and 700°C using a Walker-type multi-anvil device, in the $MgO-Al_2O_3-SiO_2-H_2O$ (MASH) and Cr-MASH system. The compressibility and thermal expansion of the phase was obtained by synchrotron high-pressure and high-temperature X-ray powder diffraction. The bulk modulus, obtained fitting the data with a second order Birch-Murnaghan equation of state, is K_0 = 109.9(2) GPa. The thermal expansion coefficients, derived using the Holland-Powell equation of state results in $\alpha_0 = 4.9(8)x10^{-5}\ K^{-1}$ and $\alpha_1=-2.6(1)x10^{-4}\ K^{-1/2}$.

The *P-V* and *V-T* EoS were used to model the density of the phase along subduction geothermal gradient, together with chlorite and mantle anhydrous phase assemblage. The chlorite breakdown reaction and 11.5 Å phase formation at 6 GPa and 700°C results in a density increase of *ca.*. 20%, without taking into account the released fluid fraction. This density variation is comparable to the complete chlorite dehydration. Therefore, it may be difficult to detect the presence of 11.5 Å phase by geophysical methods.

In the Cr-bearing system we determined a maximum Cr_2O_3 content of 3.6 wt%; the Cr-11.5 Å phase is associated with phase A and CrO(OH), suggesting a limited solubility of Cr component in this hydrous phase.

Gemmi, M., Merlini, M., Palatinus, L., Fumagalli, P., Hanfland, M. (2016): Electron diffraction determination of 11.5 Å and HySo structures: candidate water carriers to the Upper Mantle. Am. Mineral., 101, 2645-2654.

Effect of the composition on the *HP* behaviour of emplectite-chalcostibite solid solution

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Keywords: sulfosalts, synchrotron, X-ray diffraction, single crystal.

Sulphosalts are mostly accessory minerals in several types of mineralization related to the penetration of low temperature fluids into tectonically opened fractures. Their crystal-chemistry allows consideration on the mobilization of elements and may be useful for the reconstruction of the physico-chemical condition of the ore genesis. Moreover some of them are examples of modular structures of variable complexity based on octahedral and higher-number coordinations, therefore they are interesting as low-pressure equivalents for the high-pressure silicate phases of the Earth's interior, which are based on the octahedrally coordinated silicon in combination with other cations with the same or higher coordination number.This paper is part of more complex studies which investigate the structural evolution with *P* of a series of Cu-Sb-Bi sulphosalts. In particular we present here the evolution of the equation-of-state along the emplectite ($CuBiS_2$)-chalcostibite ($CuSbS_2$) series, by comparing data collected on $CuBiS_2$ at different pressures up to 9.2 GPa with those collected on $CuSbS_2$ in about the same pressure range and with the same experimental set-up (Comodi et al*.*, 2017).

Synchrotron single-crystal X-ray diffraction data were collected at GSECARS-BM13 beam-line of the Advanced Photon Source Laboratory (Argonne, USA) compressing the samples in an ETH-type DAC, equipped with beryllium backing plates.

The volume-pressure data, collected up to 9.2 GPa where fitted by a third order Birch-Murnaghan Equation-Of-State, yielding V_0 = 348.9(4) Å^3, K_0 = 55(5) GPa, and K' = 5(2). The compressibilities of the lattice parameters, up to 9.2 GPa, were calculated by fitting the data to a second order Birch-Murnaghan EOS and the following values were found: K_{0a} = 46.0(9), a_0 = 6.141(5)A, K_{0b} = 61.1(9), b_o = 3.92(2) A, and K_{0c} = 70(4), c_0 = 14.51(2) A. Notwithstanding the similar compressibility of the cell volume of the two end members (K_0 = 50(3) GPa, and K' = 6.9(9) in chalcostibite; Comodi et al., 2017), relevant differences were observed in the evolution of the *b* and *c* lattice parameters with *P*. In particular, *c* is less compressible in emplectite whereas in chalcostibite *b* is the least compressible parameter.

High pressure structural refinements indicate that no phase transition occurs up to 9.2 GPa. The difference in the compressibilities can be associated to the different expression of the lone electron pair in the two semimetals. At pressures higher than 9.2 GPa the deterioration of the quality of the data prevented further refinements of the structure of emplectite. This can be related to a strong increase in the mosaicity of the crystal. In chalcostibite, a phase transition is observed at higher pressures (Comodi et al., 2017).

Comodi, P., Guidoni, F., Nazzareni, S., Balić Žunić, T., Zucchini, A., Paprapenka, V. (2017): A high pressure phase transition in chalcostibite, $CuSbS_2$. This meeting.

Volatile contents in peridotitic minerals from Handler Ridge (northern Victoria Land, Antarctica) through micro-FTIR analysis

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Keywords: mantle xenoliths, volatile contents.

Separates of peridotitic minerals (olivine, orthopyroxene and clinopyroxene) of lherzolite xenoliths from Handler Ridge (northern Victoria Land, Antarctica) were analyzed for OH contents, in order to determine the role of volatile circulation in this segment of the Antarctic lithospheric mantle. Mantle xenoliths in northern Victoria Land are carried by Cenozoic lavas, which are part of the magmatism connected to the opening of the West Antarctic Rift System. In this framework, the influence of percolating melts through the peridotitic matrix has been testified in the nearby area of Baker Rocks also by the presence of amphibole (Coltorti et al., 2004). In Handler Ridge, despite no amphibole were detected among the mineral paragenesis, presence of secondary clinopyroxene suggests that the chemistry of the residual peridotite was variable modified by metasomatizing melts (Pelorosso et al., 2017). Preliminary FTIR data showed the presence of H_2O-related absorption around 3500-3600 cm^{-1} in all three studied mineralogical phases: olivine, orthopyroxene and clinopyroxene. In detail, optically clear orthopyroxene crystal fragments were oriented by optical means, for quantitative polarized FTIR measurements. Polarized FTIR spectra showed two strong polarized peaks at 3569 and 3520 cm^{-1} parallel to n_g or **c**-axis and sometimes a third less intense peak at 3599 cm^{-1} parallel to n_α. According to Skogby (2006), H_2O content in these minerals can be quantified around 50 ppm. Moreover an orthopyroxene showed the presence of a peculiar unpolarised peak around 2348 cm^{-1}, where the anti-symmetric stretching vibration of CO_2 should occur. Further investigation are on the way in order to determine the origin of this absorption.

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Skogby, H. (2006): Water in natural mantle minerals I: Pyroxenes. Rev. Mineral. Geochem., 62, 155-167.

Amphibole as a proxy for the volatile content in the Archean mantle

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Keywords: magmatic amphibole, Archean mantle, volatile elements.

The amount of volatiles (F, Cl and H_2O) dissolved in primary melts of Archean age and, in turn, the volatile content of the Archean mantle are still not fully understood. Magmatic amphibole is hosted in several Precambrian (Archean to Paleoproterozoic) ultramafic complexes. Being capable to incorporate and fix significant amount of volatiles, amphibole may represent an archive to infer the volatile contents of the Archean mantle. We selected primary magmatic amphiboles from ultramafic rocks in the Agnew-Wiluna (Australia, 2.7 Ga), Abitibi (Canada, 2.7 Ga) and Pechenga (Russia, 1.98 Ga) greenstone belts. All amphibole crystals were characterized in terms of major- and trace-element composition by EMPA and LA-ICP-MS, and of volatile contents (H_2O, F, Cl) and isotope signature (D/H and $\delta^{18}O$) by SIMS, with two ion microprobes.

Olivine and clinopyroxene are the major minerals of the studied rocks. Pargasitic to kaersutitic amphibole is a minor-to-accessory phase (< 10 vol%) and occurs as oikocrysts or at the margins of intercumulus clinopyroxene crystals. Amphibole trace-element composition strongly resembles/reflects the geochemical affinity of the host rock. Noticeably, amphiboles of the Canadian and Russian Fe-picrites show high $(Nb/Y)_{PM}$ values in agreement with the alkaline affinity of the host rocks. Amphibole from the Australian and Canadian komatiites and tholeiites on the contrary show low $(Nb/Y)_{PM}$ ratios, comparable to those of orogenic sub-alkaline amphibole of Phanerozoic age. The H_2O contents in amphibole are generally lower than 1.25 wt.% thus revealing a significant oxo component. F and Cl contents are variable up to 6000 and 4400 ppm, respectively. *In situ* δD measurements display values ranging between -99‰ and -129‰, whereas the amphibole from Canadian tholeiites of Ghost Range shows lighter δD composition ranging between -197‰ and -236‰.

Textural and compositional features suggest an igneous origin for the studied amphiboles and thus their utility as a proxy for the volatile content of the Archean mantle. However, some their compositional features do not agree with a closed-system evolution. In particular, the analysed amphiboles are markedly enriched in Ni-Cr-V-Zr in comparison to the early formed clinopyroxene. A multi-phase history in the evolution of the primary melts, involving the assimilation/resorption of the early crystallising minerals, has to be supposed in order to account for their peculiar Ni-Cr-V-Zr composition. The δD values suggest a degassing evolution of the parental melt. The application of ${}^{amph/L}D$ has allowed us to calculate the volatile content of the equilibrium melt and, consequently, to model that of the parental liquid and the mantle source. Results will be discussed in terms of the current knowledge on the volatile content of the Archean mantle and in relation to values obtained from igneous amphiboles from Phanerozoic ultramafic rocks.

Session S5:

Non-ambient conditions experiments for unraveling geological systems through mineral physics

Conveners:

Fernando Cámara (Univ. Milano)

Paolo Lotti (Elettra Sincrotrone, Trieste)

Compressional features of orthorhombic perovskites

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Keywords: perovskite, high-pressure, phase transitions, transition metal ions (TMI).

ABO$_3$ perovskite oxides represent a system which offers potential developments in Materials Science (the excess physical properties, consequence of structural phase transitions, promote perovskites as high-tech ceramics) and Earth Sciences (*e.g.*, the orthorhombic (Mg,Fe)SiO$_3$ perovskite is the predominant phase of the Earth lower mantle). Cubic in its aristotype form (s.g. *Pm*-3*m*) – a framework of corner sharing BO$_6$ octahedra with twelve-fold coordinated A cations within the framework cavities – perovskites with a lower symmetry (usually orthorhombic, s.g. *Pbnm*) derive from the cubic structure through a combination of octahedral tilts and distortion of the BO$_6$ octahedra.

The evolution of orthorhombic perovskites with P has been interpreted as the combination of the relative compressibility of constituent AO$_{12}$ and BO$_6$ polyhedra with the octahedral tilts. Specifically, if A has a lower formal charge than B (*i.e.*, 2:4), the AO$_{12}$ site is more compressible than the BO$_6$ octahedron, and the volume reduction is associated to an increase of the octahedral tilting; if A and B have the same formal charge (*i.e.*, 3:3), the AO$_{12}$ site is stiffer than the BO$_6$ octahedron, then the volume reduction is partially compensated by a decrease of the octahedral tilting.

Albeit true for several perovskites, the description of above is incomplete and it was recently reviewed showing that besides to define dichotomous trends depending on the charge of A and B cations, the evolution of orthorhombic perovskites at *HP* is affected whether transition metal ions (*TMI*) are hosted at the octahedral site (Ardit, 2015).

An overview on the structural evolution of perovskites upon P will be presented. Two specific cases will be also analysed.

1. The structural modifications of YAl$_{0.25}$Cr$_{0.75}$O$_3$ at *HP* with a detailed inspection of a YM^{3+}O$_3$ isotype series to emphasize a possible limit case when absences of change in octahedral tilting are found, *i.e.*, the so called ″locked-tilt″ YAl$_{0.25}$Cr$_{0.75}$O$_3$ perovskite (Ardit et al., 2017).
2. The dualism between Cr^{3+} and Ga^{3+} hosted at the octahedral site of Nd(Ga,Cr)O$_3$ at *HP* to appraise whether a specific electronic configuration allows the crystal field stabilization energy (CFSE) at octahedral sites to act as vehicle of octahedral softening (Cr^{3+} with partially filled 3*d* orbitals) or it turns octahedral into rigid units when CFSE is absent (Ga^{3+} with full 3*d* orbitals).

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High temperature characterization of Y-zeolite loaded with chlorobenzene

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Keywords: Y zeolite, chlorobenzene, water pollution, high-temperature, adsorption/desorption.

Due to their widespread use in many industrial sectors, low solubility in water and their bioaccumulation tendency, Volatile Organic Compounds (VOCs) are hazardous organic chemicals commonly present in water. Among this class of pollutants, chlorobenzene (CB) is included as benzene (*i.e.*, BTEX species) halogenated compound. Therefore, due to its toxic effects on both human health and environmental systems, the removal of CB from water is a primary issue. Recently, it has been highlighted that organophylic and hydrophobic zeolites are efficient as sorbent materials and completely regenerable without showing remarkable changes in adsorption capacity and structural properties. Nowadays, these zeolites features, combined with their high thermal stability, are exploited in regeneration processes through thermal treatment in order to reuse regenerated zeolites in new adsorption processes (Rodeghero et al., 2016). Therefore, the aim of the project is to investigate the desorption process of chlorobenzene (purchased by Sigma Aldrich with a purity of 99.8%) Y (HSZ-390HUA code; 200 SiO_2/Al_2O_3 ratio) system to: 1) determine the desorption temperature of extraframework content; 2) characterize the structural modifications induced by high temperature treatment and 3) highlight the temperature effects on the interactions between organic molecules and framework oxygen atoms. With this purpose, Y-CB sample was prepared and characterized by chromatographic (*via* Headspace Solid Phase Microextraction-GC) and thermal (TG and DTA) analysis. Desorption process was constantly monitored, through synchrotron X-ray powder diffraction, at the high resolution Beamline ID22 (ESRF, Grenoble) from room temperature to 590°C with a heating rate of 8°C/min. Rietveld refinements showed that chlorobenzene molecules are desorbed at about 210°C. These results are in good agreement with thermal analysis, which suggest that all the extraframework (H_2O and CB molecules) content is completely released between 190 and 210°C. Hence, the detected desorption temperature reveals an acceleration of desorption kinetics compared to that reported on a patent previously published (Vignola et al., 2008). Moreover, structural refinements highlighted that both only slight memory effects in terms of structural deformations are registered in 12MR channel geometry after regeneration process and the reactivated zeolite regain the unit-cell parameters of the bare material almost perfectly. Furthermore, any significant crystallinity loss is observed. Based on these results, the High Silica Y zeolite is potentially reusable in a new adsorption/desorption cycle.

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The manganite → pyrolusite transformation

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Keywords: manganese oxides, manganite, pyrolusite, *HT* trasformation, X-ray powder diffraction, Raman, FTIR spectroscopy.

Natural manganese oxides (MnO_x) are very attractive cryptocrystalline nano-materials, characterized by special physical and chemical proprieties that play a key-role in the partitioning of arsenic and heavy metals between soils and aqueous systems (Oscarson et al., 1983). Recent studies show that Mn-oxides are significant environmental indicators (composition, *p*H, *E*h, biological activities of the system), provided the samples can be characterized without ambiguity (Bernardini, 2017). The structure of the different MnO_x phases is indeed strongly controlled by these features, therefore understanding the processes that drive the crystallization and growth of the different MnO_x phases may provide an important tool in environmental studies. This work is a first contribution aimed at defining the stability field of MnO_x phases to better understand the role that these minerals play in the environment. Pyrolusite [β-MnO_2] (tetragonal) is characterized by well-formed crystals, while secondary pyrolusite often derives from the oxidation of manganite [γ-MnOOH] (monoclinic), by loss of hydrogen from the structure (Champness, 1971). The manganite → pyrolusite transformation has been investigated by high temperature XRPD, FT-IR and Raman spectroscopy. The unit cell relationships are such that manganite a and c parameters are halved with respect to those of pyrolusite, while the b parameter of manganite contracts from 5.28 Å to 4.40 Å to become symmetry related to the a parameter of pyrolusite. This 15% contraction along b gives rise to the possibility that microscopic cracks paralleling the manganite (010) planes might separate newly made crystallites of pyrolusite (Rask & Buseck, 1986).

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How quasicrystals form in outer space?

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Keywords: quasicrystals, shock experiments, meteorite, Khatyrka.

Naturally quasicrystals (Bindi et al., 2009, 2015, 2016), crystal-like solids with supposedly impossible symmetries, are among the rarest structures known. Only three have ever been found, and all come from the same meteorite: the Khatyrka CV3 carbonaceous chondrite (MacPherson et al., 2013). To uncover the reasons for that scarcity, we have recently demonstrated by means of laboratory experiments that AlCuFe-quasicrystals could arise from collisions between asteroids with unusual chemical compositions (Asimow et al., 2016). These materials could indeed be produced by the sudden compression, flash heating and rapid cooling caused by asteroid collisions, provided the asteroids contain suitable starting materials. To test if also the AlNiFe-quasicrystal, the synthetic analogue of decagonite (the second natural quasicrystal), could be produced by shock experiments, we undertook another series of experiments, culminated in the successful synthesis of decagonal AlNiFe. The results strengthen the argument from shock textures and high-pressure phases in Khatyrka (*e.g.*, Lin et al., 2017) that its shock history was responsible for the formation of its unique quasicrystalline minerals. We also note that both the icosahedral and decagonal quasicrystals we obtained are in fact distinct in composition and cell parameters from all previously known natural or synthetic examples, which shows that shock synthesis is a useful method of finding and characterizing new quasicrystals that cannot be formed by conventional metallurgy.

Asimow, P.D., Lin, C., Bindi, L., Ma, C., Tschauner, O., Hollister, L.S., Steinhardt, P.J. (2016): Shock synthesis of quasicrystals with implications for their origin in asteroid collisions. Proc. Nat. Acad. Sci., 201600321.

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High-pressure behavior of dravite tourmaline

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Keywords: pressure, diamond-anvil cell, tourmaline, stability field, dravite.

Experimental and petrological data show that tourmalines are stable over a wide range of *P*-*T* conditions, ranging from the diagenetic field to *UHP* and *UHT* zones. This large stability is likely related to the great flexibility of the tourmaline structure to adjust in composition in response to changing chemical environments and *T*-*P* conditions (*e.g.*, Dutrow & Henry, 2011). However, a definitive stability field of tourmalines, in particular for high-pressure conditions, is not available. Relative to the maximum high pressure stability, it appears that tourmaline with dravite composition is considered the composition stable at the highest values of pressure and breaks down to produce different Mg–Al phases at pressures as high as 5–8 GPa (Krosse, 1995; Ota et al., 2008), although showing a complex dependence on temperature.

In this study, we focused on the high-pressure behavior of a natural dravite, ideally $NaMg_3Al_6(Si_6O_{18})(BO_3)_3(OH)_3(OH)$, by single-crystal X-ray diffraction within a diamond-anvil cell. The unit-cell parameters for the investigated sample are: a = 15.9623(3) Å, c = 7.1972(1) Å, V = 1588.13(3) Å^3. Our investigation was performed at room temperature in order to obtain the pressure-volume equation of state of such high-pressure tourmaline and explore its pressure stability field. This work is part of a wide research project focused on the determination of the *P*-*T* stability field of tourmalines. Preliminary results will be discussed.

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Pargasite at extreme conditions: a comprehensive *P*-*T* study

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Keywords: amphibole, pargasite, high pressure, high temperature, synchrotron X-ray diffraction, diamond anvil cell.

Pargasite is a Ca-amphibole associated to medium- or high-pressure/high-temperature conditions. The occurrence of hydroxyl groups into the amphibole's structure has proved to be a significant agent in the water cycle within the upper mantle (*e.g.*, Gill 1981). In order to better understand the water cycle in the upper and potentially lower mantle, it is of critical importance to determine the stability of all hydrous minerals subducted into the mantle. However, despite their geological importance, only a few *in situ* high-pressure (*HP*) and high-temperature (*HT*) studies have been performed in order to describe the *P*-*T* stability fields, the thermo-elastic behaviour and the *P*- or *T*-induced deformation mechanisms of amphiboles at the atomic scale. The compressibility of tremolite, pargasite and glaucophane were investigated by Comodi et al. (1991) on the basis of *in situ* single-crystal X-ray diffraction experiments with a diamond anvil cell (DAC) up about 4 GPa. However, as pointed out in Welch et al. (2007), there is a need to extend the compressibility measurement to *P* higher than 10 GPa, in order to improve the accuracy of the refined isothermal bulk modulus values and their *P*-derivatives. Furthermore, to the best of our knowledge, no simultaneous *in situ* *P*-*T* studies have been conducted on amphiboles so far. This lack of knowledge prevents a detailed description of the behaviour of amphiboles that are stable at *HP*-*HT* conditions and consequently it is still difficult to assess their petrological implications. In this light, we have selected crystals of pargasite from the peridotite of the "phlogopite peridotite unit" of the Finero mafic-ultamafic complex (Ivrea-Verbano Formation, Italy) (Cowthorn, 1975), in order to describe: *a*) the *HP* elastic behaviour of this amphibole and its deformation mechanisms at the atomic scale up to 20 GPa, by single-crystal synchrotron X-ray diffraction with a diamond anvil cell, *b*) its *HT* behaviour, along with its potential de-hydroxilation, by *in situ* X-ray synchrotron powder diffraction using a hot air blower device (up to 823 K), and *c*) its phase stability field at simultaneous *HP*-*HT* conditions, by single-crystal synchrotron X-ray diffraction with a resistive-heated diamond anvil cell (P_{max} = 16.5 GPa, T_{max} = 1200 K). The thermal and compressional behaviour of pargasite are now fully described within the *P*- and *T*-range investigated and the petrological implications of our experimental findings are discussed.

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A high pressure phase transition in chalcostibite, $CuSbS_2$

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Keywords: chalcostibite, high pressure, phase transition, diamond anvil cell.

Sulphosalts are a group of minerals important for the extraction of metals (Cu, Pb, Ag, Fe) and semimetals, whose general formula is $(Me^{+}, Me^{2+}, \text{etc.})_x\ [(Bi, Sb, As)^{3+}, Te^{4+}]_y\ [(S, Se, Te)^{2-}]_z$. They may represent new technological materials with peculiar optical, magnetic and electric properties and can have potential applications as thermoelectric materials, semiconductors for photovoltaic devices and infrared detectors.

As many of them have modular crystal structures, their chemical and structural building units allow material engineering and designing in several ways. The knowledge of the evolution of their structure with pressure may give important suggestion for technological applications.

The crystal structure of chalcostibite α-$CuSbS_2$ was investigate at *P* between 0 and 13.2 GPa by synchrotron single-crystal X-ray diffraction data, compressing the sample in an ETH-type DAC equipped with diamond backing plates at GSECARS-BM13 (APS, Argonne, USA). The *V-P* data, collected up to 10.8 GPa where fitted to a third order Birch-Murnaghan equation-of-state , yielding $V_0 = 332.4(4)$ Å^3, $K_0 = 50(3)$ GPa, and $K' = 6.9\ (9)$ GPa^{-1}. The compressibilities of the lattice parameters, up to 10.8 GPa, were calculated by fitting the data to a second order Birch-Murnaghan EOS and the following values were found: $K_{0a} = 49.0(6)$ GPa, $a_0 = 6.0(2)$Å, $K_{0b} = 76(3)$ GPa, $b_o = 3.80(8)$ Å, and $K_{0c} = 57(3)$ GPa, $c_0 = 14(9)$ Å.

At pressure higher than 11 GPa the evolution of crystal lattice and geometrical parameters indicates that a phase transition occurs, from orthorombic *Pnma* space group to monoclinic $P2_1$. The single crystal was retained after the reversible phase transition despite the contraction of the unit cell of 2.2% and the anisotropic change of the lattice parameters, which affected mainly the *a* lattice parameter. The high pressure structure of β-$CuSbS_2$ was solved in $P2_1$ space group. The phase transition violates the mirror plane perpendicular to α-$CuSbS_2$ **b** axis and occurs in the sense of a "2 Å shear" along this axis suggested as a possible structural modification in the emplectite homologous series by Makovicky (1981). The shearing occurs between the (001) infinite slabs of Sb and S atoms corresponding in structure to the (101) and (10-1) SnS type and influences mostly the coordinations of Cu atoms that interconnect the slabs. The coordination achieves a configuration halfways between the starting tetrahedral and a square-bi-pyramidal. The coordination of Sb retains its general monocapped trigonal prism form largely influenced by its lone electron pair, with five short and 2 long bonds. The activity of the lone electron pair is constantly decreasing with equalization of short bonds and significant shortening of one of the long ones, with a movement of lone-electron pairs closer to Sb nucleus.

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High-temperature studies on Fe-dominant amphiboles: what do we see with each technique?

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Keywords: Fe-rich amphiboles, *HT* studies, deprotonation, Fe-oxidation, XRD, spectroscopy.

The crystal-chemical/structural response of Fe-dominant amphiboles to high-*T* conditions was approached since the 1960's (Addison & Sharp, 1962, Ungaretti, 1980) mostly due to the increasing technological relevance of Fe-asbestos ("crocidolite") as thermic insulators. The oxidation of ferrous iron at high *T* was found to be balanced by the loss of H at the O(3) site.

We have studied a synthetic *A*-site full (potassic-ferro-richterite, PFR; Oberti et al., 2016; Della Ventura et al., 2017a) and a natural *A*-site vacant (riebeckite, RI; Della Ventura et al., 2017b) amphibole and discuss here results obtained combining X-ray diffraction and spectroscopic (FTIR, Raman, Mössbauer and XAS) methods. *In situ HT*-XRD shows a drastic drop of the cell parameters at 350°C for PFR and at 450°C for RI. Structure refinement (SREF) done at *HT* shows that the oxo amphibole structure is stable up to 800°C. Both SREF and Mössbauer spectroscopy show that iron oxidation occurs only at the *M*(1) sites, while the other OH-coordinated *M*(3) site, and *M*(2) are unaffected. Single-crystal *HT*-FTIR experiments systematically detect a loss of intensity of the O-H stretching absorption at *T* 50-100°C higher than XRD, but this shift is smaller when working on powders. Also, the band intensities increase significantly at the onset of deprotonation when collected *in situ*, but are constant when collected after quenching. *In situ HT*-Raman spectroscopy on RI shows complete deprotonation at $T > 450$°C, whereas FTIR spectroscopy on the same crystal shows no hydroxyl loss until 550°C. Because Raman spectroscopy probes only the most surficial layers (a few mm) of the sample, these data definitively confirms that the deprotonation process mainly occurs at the crystal surface. This implies that the process needs a continuous diffusion of both protons and electrons across the silicate matrix to proceed. Based on all the available data, a general model for the dynamics of Fe-oxidation at *HT* in these compounds is presented and discussed.

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The behavior at non-ambient conditions of colemanite: a hydrous Ca-borate

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Keywords: colemanite, borates, phase transition, high pressure, hydrogen bonding.

Colemanite, $CaB_3O_4(OH)_3 \cdot H_2O$, is a common hydrous borate of large economic relevance, as it is one of the major commodities of boron with applications in the fields of glass and ceramic industries. Colemanite-rich layers are usually found in stratigraphic successions related to lacustrine basins in semi-arid to arid environments, associated to a local volcanic activity, which provides the source for boron. Despite the large economic relevance, the behavior of this mineral at non-ambient conditions of temperature and pressure was almost unexplored, which can provide a basis for understanding its stability during diagenetic and metamorphic processes. In this contribution, we report the high-pressure behavior of colemanite (Lotti et al., 2017), based on *in situ* single-crystal synchrotron X-ray diffraction data up to 24 GPa, and its low-T behavior by *in situ* X-ray and neutron single-crystal diffraction.

Colemanite was found to be stable up ~ 14.5 GPa, where a reconstructive phase transition towards a high-pressure polymorph (colemanite-II) with same symmetry (space group $P2_1/a$), but a six times larger unit cell volume, occurs. The elastic behavior of colemanite was described by fitting the experimental data with a III-order Birch-Murnaghan equation of state, yielding the following refined elastic parameters: K_{V0} = 64(4) GPa and K_V¢ 5.5(7). The colemanite-to-colemanite-II phase transition induces an increase in the average coordination number of both the Ca and B cations. In particular, a fraction of the boron sites increases its coordination from triangular to tetrahedral by making a further bond with a H_2O-oxygen atom. Although the phase transition occurs (at ambient temperature) at pressures far from those associated with the usual geologic environments of colemanite, the reported results disclosed flexible deformation mechanisms that borate compounds may adopt to accommodate pressure, thus providing new insights on the behavior of borate minerals at non-ambient conditions. The complex hydrogen-bonding network of colemanite has also been characterized, at ambient and low temperature conditions, by means of *in situ* single-crystal synchrotron X-ray and neutron diffraction experiments. A positional disorder, related to the presence of two mutually exclusive configurations of the H_2O-molecule hydrogen atoms, was found both above and below ~ 0°C, where a displacive phase transition from the $P2_1/a$ to the $P2_1$ space group occurs.

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Crystal-fluid interaction and compressional behavior of chabazite with Li^+, Na^+, Ag^+, K^+, Rb^+, and Cs^+ as extra-framework cations

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Keywords: chabazite, compressibility, phase transition, crystal-fluid interaction.

The high-pressure behavior of monovalent-cation-exchanged chabazites from Rubendorfel (Bohemia) ($Ca_{1.6}Na_{0.5}Si_{8.4}Al_{3.6}O_{24}\cdot 14.3H_2O$), in the form of Li^+, Na^+, Ag^+, K^+, Rb^+, and Cs^+ chabazite, was investigated by means of *in situ* synchrotron X-ray powder diffraction using pure water as penetrating pressure-transmitting fluid up to 5.5 GPa (at room temperature). The experiments were conducted: i) under hydrostatic consitions in the low-*P* range (< 1-5 GPa), and ii) under non-hydrostatic conditions in the higher *P* range (*P* > 1.5 GPa), in order to describe potential transformation phenomena even with sample compressed in solid H_2O. *In situ* high-pressure synchrotron X-ray powder diffraction experiments on the as-prepared cation-forms of chabazites were performed at beamline 10-2 at the Stanford Synchrotron Radiation Light source (SSRL) at the SLAC National Accelerator Laboratory. At beamline 10-2, the synchrotron radiation from the wiggler insertion device impinges on a Si(111) crystal followed by two pinholes in order to create an approximately 200 micrometer diameter beam of monochromatic X-rays with a wavelength of 0.61992(5) Å. A Pilatus 300K-w Si-diode CMOS detector manufactured by DECTRIS was used to collect powder diffraction data. The detector held at distance of *ca*. 1032(2) mm from the sample was stepped to produce scattering angle coverage in 2-theta up to *ca*. 40°. A modified Merrill-Bassett diamond anvil cell (DAC), with two opposing diamonds supported by tungsten-carbide plates, was used for high-pressure XRD measurements. The pressure of a sample in the DAC was measured by detecting the shift in the R1 emission line of the included ruby chips (uncertancy: +/-0.05 GPa). Pressure-dependent changes in the unit-cell lengths and volumes were derived from a series of whole profile fitting procedures using the EXPGUI suite of programs. Rietvel structure refinements are in progress. In all cases, except for Na-chabazite, a phase transition from the original rhombohedral to triclinic symmetry is observed in the range between 3.0 GPa and 5.0 GPa. The phase transition is accompanied by an abrupt decrease of the unit-cell volume by up to 10%. The apparent drasticaly different compressibility of the low-*P* rhombohedral forms suggests: i) *P*-induced penetration phenomena of H_2O molecules, which lead to an anomalous stiffnes of the structure, ii) a drastic control of the extraframework population on the compressional behaviour and crystal-fluid interaction.

The crystal structure of dolomite-IV, a high-pressure polymorph of dolomite, at 115 GPa

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Keywords: high-pressure, single crystal diffraction, dolomite.

We report the crystal structure of dolomite-IV, a high-pressure polymorph of Fe-dolomite stabilized at 115 GPa and 2500 K. It is orthorhombic, space group *Pnma*, a = 10.091(3), b = 8.090(7), c = 4.533(3) Å, V = 370.1(4) Å^3 at 115.2 GPa and ambient temperature. The structure is based on the presence of 3-fold C_3O_9 carbonate rings, with carbon in tetrahedral coordination. The structure of dolomite-IV has not been predicted, but it presents similarities with the structural models proposed for the high-pressure polymorphs of magnesite, $MgCO_3$. A ring-carbonate structure match with spectroscopic analysis of high-pressure forms of magnesite-siderite reported in the literature, and, therefore, is a likely candidate structure for a carbonate at the bottom of the Earth's mantle, at least for magnesitic and dolomitic compositions.

The thermal behavior of armstrongite from Khan Bogdo (Mongolia)

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Keywords: mesoporous Zr-silicates, thermal behaviour, TGA, *HT*-FTIR, *HT*-XRD.

Armstrongite is a mesoporous Zr-silicate with a mixed framework of silicate sheets and Zr-octahedra forming cavities occupied by Ca atoms. The studied sample has $(Ca_{0.96}Ce_{0.01}Yb_{0.01})Zr_{0.99}Si_6O_{14.97}\cdot 2.02H_2O$ crystal chemical formula (Mesto et al., 2014); the two water molecules display different local environments, as also found for other zeolite-like zircon-silicates (Mesto et al., 2014; Yakubovich et al., 2013; Zubkova et al., 2011; Grigor'eva et al., 2011). Single-crystal structural refinement (Mesto et al., 2014) showed the mineral to be monoclinic [s.g. $C2/m$, a = 14.0178(7), b = 14.1289(6), c = 7.8366(3) Å, β = 109.436(3)°] and twinned with two individuals rotated around a twin twofold axis parallel to [100]. In the present work, the thermal behavior of armstrongite was investigated in the range 30-700°C by combining TGA, *HT*-XRPD, *HT*-SCXRD and *HT*-FTIR.

Both TGA and *HT*- FTIR show that armstrongite dehydrates at $T > 370°C$ in agreement with the evolution of the *HT*-XRPD that indicates a discontinuity in the variation of the cell parameters at the same temperature. The following changes were observed upon heating from 25 to 375°C: $\Delta a \sim 0.15$ Å, $\Delta b \sim 0.07$ Å, $\Delta c \sim 0.05$ Å and $\Delta\beta \sim 0.2°$. The latter result is compatible with *HT*-SCXRD data. In addition, *HT*-SCXRD shows that the heating does not affect the s.g., although the dehydrated phase has a different coordination environment for the Ca^{2+} ions with respect to the hydrated one. Work is in progress to define the structural details of the dehydrated phase.

HT-FTIR shows, in agreement with Mesto et al.(2014), two water molecules for the hydrous phase; careful analysis of the spectra indicates that one of these is most affected during the heating experiment and is lost at lower temperature. Slight but significant frequency shifts of the framework modes are also observed.

An analysis of the thermal expansion tensors shows that the major expansion occurs along the [010] direction, whereas the maximum contraction direction was normal to [010].

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Intracrystalline "geothermometry" assessed on clino- and orthopyroxenes bearing synthetic rocks

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Keywords: pyroxenes, intracrystalline thermometry, synthetic samples, closure temperature.

Ongoing discussion on the application of intracrystalline "geothermometers" to Martian nakhlite samples indicates that the available calibration equations that express the lnk_D as a function of 1/T(K) for clino- and ortho-pyroxenes (cpxs and opxs) require further validation. This can only be done using crystals grown in rock analogues synthesized under controlled temperature conditions. On these samples, it is possible to compare the closure temperature (T_C) of the intracrystalline Fe^{2+}-Mg ordering process for each of both phases (cpx and opx), with the quenching temperature (T_Q) of the synthesis experiments. Intracrystalline thermometry records the last thermal event experienced by a single mineral phase if the system remains closed for the entire cooling process, as expected for our synthesized samples, which are subjected to a rapid quenching.

For this purpose, we measured by single crystal X-ray diffraction the Fe^{2+}-Mg order degree, expressed as the intracrystalline distribution coefficient k_D, on three pairs of synthetic samples containing both clinopyroxene and orthopyroxene as separated crystals. Each of these synthetic samples was experimentally grown from a hydrous nepheline basanite under conditions that ranged from 1050°C at 2.0 GPa to 1170 °C at 3.0 GPa.

Our results, obtained by applying for cpx and opx the calibration equations by Murri et al. (2016) and that by Stimpfl et al. (2015), respectively, demonstrate for the first time the quite remarkable agreement between calculated closure temperatures (T_C) and actual quenching temperatures (T_Q) for synthesis products over which we have complete control. The smallest discrepancy between calculated and actual temperature is of the order of degrees (*e.g.*,12°C and 4°C for clinopyroxenes and orthopyroxenes, respectively), whereas the largest is of the order of tens of degrees (*e.g.*, 22°C and 55°C for clinopyroxenes and orthopyroxenes, respectively). These values are well within the intrinsic estimated standard deviations (e.s.d.'s) that arise from the structural refinement (*e.g.*, about 28°C for the sample with the highest e.s.d. on the Fe site occupancy).

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The stability of eclogitic clinopyroxene in the Earth's mantle: an experimental investigation

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Keywords: multianvil press, high pressure, Earth's mantle, polymorphic transformation, breakdown.

The transport of chemical elements down into the Earth' s transition zone and lower mantle is strongly affected by the stability of minerals as function of pressure and temperature. Whether the slab stagnates or sinks depends on the density and viscosity of the subducted portions that links with the mineralogy and associated phase transitions and decomposition reactions, which have important implications for the origin of deep earthquakes. Clinopyroxene (cpx) is known to dissolve as majoritic component in garnet during subduction. However, the associated slow diffusion can result in metastable cpx at high pressure. To date, experimental studies on the stability of omphacitic cpx as function of pressure are few and sparse in literature. We performed high pressure and temperature experiments to investigate the fate of omphacite during subduction.

The experiments were carried out at temperatures between 800 and 1300°C and pressures of 3 and 6 GPa using the Voggenreiter 840 t, Walker-type multi anvil press available at *HPHT* Lab at National Institute of Geophysics and Volcanology (INGV, Rome). The starting material employed was a mixture of synthetic omphacitic glass, quartz, dolomite and graphite representative of a carbonated eclogite, which was loaded in a graphite capsule. Tungsten carbide (WC) anvils (F grade) with 17 and 11 mm truncation edge lengths (TEL) were used with chromium-doped MgO octahedra (25 and 18 mm edge length) as pressure media.

In a second set of experiments, a synthetic omphacitic glass was mixed with Re and ReO_2 to act as redox buffer, all loaded in a Re capsule of ~1 mm in diameter. WC anvils (F grade) with TEL of 3 mm were used with cobalt-doped MgO octahedra and pyrophyllite gaskets as pressure media both optimized to generate pressures above 25 GPa (Tange et al., 2008). The temperature during the experiments was monitored with a W-5%Re/W-26%Re thermocouple. In all experiments, olivine (San Carlos) or quartz powder were used as pressure marker (Ito, 2007). The sample was compressed applying a ram load up to ~450 ton, then heated and kept at a constant temperature within ±10°C for a period of 20-360 minutes. The recovered samples were mounted in epoxy resin, sectioned and polished for textural observation and chemical analyses with a field-emission scanning electron microscope.

Preliminary results from experiments at 3 and 6 GPa show a strong temperature dependence of the content of sodium and aluminum in tetrahedral coordination that is consistent with previous studies. Isothermal runs at higher pressures show the formation of a Na-poor rim in the recovered cpx likely corresponding to the nucleation of a post-clinopyroxene phase (Oguri et al., 2007).

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New high pressure Raman spectroscopy data on diopside: a comparison with other *C*2/*c* synthetic pyroxenes

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Keywords: Raman spectroscopy, high pressure, crystal structure and vibrational modes, pyroxenes.

Recent advances in quantum mechanical calculation made assignment of the vibration frequencies in Raman spectroscopy by-product of energetic calculation. It is now possible to relate structural features and Raman peaks with pressure. Aiming at determining in pyroxenes the relations with well described peaks and structural changes, we collected the high-pressure Raman spectra of diopside ($CaMgSi_2O_6$), along with other three synthetic pyroxenes of composition $CaCoSi_2O_6$, $CaMgGe_2O_6$ and $CaCoGe_2O_6$, up to P = 7.6 and 8.3 GPa, respectively for silicates and germanates.

The spectra of the investigated silicates show few major peaks, between 300 and 400 cm^{-1}, and mostly related to stretching and bending in the *M*2 and *M*1 polyhedra, a single feature at ~ 660 cm^{-1}, and a further intense peak at about 1010 cm^{-1}, related to bending and stretching of the tetrahedra, respectively. In germanates, we find similar features albeit downshifted in energy. No phase transition or change in the compressional behaviour was observed within the *P*-range investigated. The peak wavenumbers increase almost linearly with pressure; the slope $d\upsilon_i/dP$ is greater for the modes at higher wavenumbers. The strong dependence of the peak position with pressure of the high-energy stretching modes is due to the high sensitivity of the vibrational frequencies probed by Raman spectroscopy to subtle changes in the tetrahedral deformation, which are overlooked by single crystal X-ray diffraction.

We observed a higher *P*-induced variation of intermediate wavenumber modes in Mg- *vs.* Co-pyroxenes, and of higher wavenumber modes in Ge- *vs.* Si-pyroxenes. These findings are likely related to the different compressional behavior of the polyhedron hosting Co or Mg and the tetrahedron hosting Ge or Si.

The well-resolved relation between the *M*1-O2 bond distances and the 660 cm^{-1} peak in diopside, hedenbergite and enstatite Raman spectra provides a clue to interpret changes in Raman peak position and crystal structure. In diopside and enstatite, with *M*1 occupied only by Mg, the Raman peak position *vs.* *M*1-O2 bond distances follow the same trend, which is parallel to that found in hedenbergite, with Fe at the *M*1 site.

Towards a reliable equation of state for zircon

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Keywords: zircon, equation of state, bulk modulus, thermal expansion.

Zircon ($ZrSiO_4$, tetragonal, space group *I*4_1*/amd*) has a wide range of stability over upper mantle conditions and is a ubiquitous phase in metamorphic rocks, especially as an inclusion phase in metamorphic garnets, in which it is often trapped from the protolith. The remnant pressures exhibited by zircons trapped inside garnets could be used to determine the conditions of entrapment, and thus constrain the *P*-*T* paths of ultrahigh-pressure metamorphic rocks (Angel et al., 2015).

Accurate values elastic parameters are crucial in order to apply the elastic geobarometry method. However, the elastic properties found in the literature for zircon are extremely variable and are derived from a variety of different datasets and experimental measurements. Therefore, we have reassessed all of the literature data, and we have obtained a self-consistent set of data from which we obtained EoS parameters for a Birch-Murnaghan 3rd-order EoS combined with a Holland-Powell thermal pressure model with the procedure implemented in EoSFit7 (Angel et al., 2014); isothermal bulk modulus K_T = 225(2) GPa, $dK_T/dP = K'$ = 6.1(1.2), volume thermal expansion α_V = 1.048(7)x10^{-5} K^{-1}. The Einstein temperature (θ_E) is set to 566 K (Dutta & Mandal, 2012).

Because of the small contrast between the bulk modulus of zircon and garnet, zircons trapped on the prograde path during subduction will experience pressures within 0.2 GPa of the external pressure during metamorphism, and remnant pressures of 0.3 GPa (when the inclusion and host are measured at room conditions) starting from an entrapment pressure in the range 1.9-4.3 GPa considering a temperature range of 500-800°C. For a typical early prograde pressure of 0.5 GPa and a temperature of 400°C, a remnant pressure of 0.38 GPa is predicted from our zircon EoS.

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Session S6:

Advances in fundamental understanding of structure, properties and uses of ordered porous materials

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The thermal behaviour of erionite series

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Keywords: erionite, ERI, zeolites, *HT*-XRPD, Rietveld method, thermal behaviour.

Erionite (ERI) is a naturally occurring zeolite, often characterized by fibrous morphology that pertains to the ABC-6 family. In recent years, it has been the object of several papers aimed at investigating its health effects in humans as erionite has been classified in 1987 as a Group-I carcinogen by the International Agency for Research on Cancer (IARC). Erionite is hexagonal, space group $P6_3/mmc$. Owing to its large chemical variability (Passaglia et al., 1998), erionite was elevated to group status and its member species were reclassified as erionite-K, -Na, and -Ca, conforming to the most abundant extraframework (EF) cation. The thermal behaviour of erionite-K and -Na from Rome (Oregon, USA), characterized by an R = Si/(Si+Al) of 0.807 and 0.796, respectively, has been analysed by Ballirano & Cametti (2012) and Ballirano & Pacella (2016).

The present work reports the results of the analysis of the thermal behaviour of a sample of woolly erionite-K from Lander County (Nevada, USA), with chemical formula $(Ca_{2.03}Na_{0.73}K_{2.52}Mg_{0.26})[Al_{8.22}Si_{27.78}O_{71.80}]\cdot 29.71H_2O$, R = 0.722, investigated in the 303-1173 K thermal range by *in situ* laboratory focussing-beam transmission X-ray powder diffraction. Present data suggest the existence of a well-defined dependence of the thermal induced variation of cell parameters and volume as well as on the temperature of dehydration (T_{dehydr}) and of breakdown (T_{break}) from R ratio. In particular, we notice a general temperature-induced volume contraction whose magnitude increases as the R becomes smaller. An inverse correlation between R and T_{dehydr} is observed because higher R values are associated to lower dehydration temperatures. A positive dependence exists between R ratio and T_{break}. A higher Si content results in a higher thermal stability, in agreement with the general trend observed in zeolites. On the contrary, no correlation has been found between T_{break} and weighted ionic potential $(Z/\mathrm{r})_{\mathrm{wt}}$ as suggested by reference data. Temperature increase produces a general depletion of the Ca1, Ca2, Ca3 and K1 sites, which is counterbalanced by an increase of the K2 site scattering even though the latter is not populated at RT. No "internal ion exchange" mechanism was apparently acting in the present sample differently from other erionite samples analysed in the past. At 303 K approximately 20 e^- allocated at OW sites might be assigned to EF cations. Such fraction increases due to their migration from the EF cation sites following the same mechanism reported in reference data.

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Detection of Brønsted acid sites in zeolite l: a combined neutron and synchrotron diffraction study

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Keywords: acidic L zeolite, neutron characterization, Brönsted sites.

Due to their catalytic activity, excellent chemical and thermal stability and their reaction selectivity, acidic zeolites are preferred as catalysts in petroleum and chemical industries (Corma, 1995). Synthetic L zeolite (empirical formula $K_9[Na_3Al_9Si_{27}]O_{72}$ $21H_2O$) is a large pore material with LTL framework topology and hexagonal symmetry (*P*6/*mmm* space group). Its framework is built from columns of cancrinite cages stacked with double six membered rings (D6R) along the **c** axis. This peculiar arrangement creates large undulating 12-ring (12MR) channels, which are separated from each other by elliptical 8-membered ring channels, parallel to the original columns along the **c** axis. Its acidic and structural features are suitable for technological applications, such as innovative optical devices (*e.g.*, luminescent probes, optical lens and filters) and photonic antenna systems based on dye–zeolite host–guest materials (Albuquerque & Calzaferri, 2007). The aim of the present study is: firstly, to determine the number and location of Brønsted sites in zeolite L and secondly, to study the interaction of water with hydroxyl groups in the rehydrated D-form. These informations provide a complete understanding of the hydrogen-bonding network and allow speculations on the degree of confinement of zeolitic water in LTL. A sample of untreated L zeolite (LTL), purchased by Tosoh Corporation (500KOA code, SiO_2/Al_2O_3 ratio = 6.1, Na_2O = 0.25 wt.%, K_2O = 16.8 wt.% and BET = 290 m^2/g), was used in this study. The acidic form (D-LTL) was prepared as follows: 1) exchanging in a 1 M solution of ND_4Cl on D_2O for 192 h at 40°C (ND_4-LTL); 2) washing with D_2O and drying overnight at 96ºC; 3) and then calcining at 550ºC for 2 hours under a flux of air in order to obtain the acidic form. The D-LTL powder pattern was measured at 2.25 K at the D2B line (ILL, Grenoble). Thereafter, the rehydrated D-form (RD-ILL) was collected at the high resolution ID22 (ESRF) Beam Lines, as a function of temperature, from *RT* to 800°C (heating rate of 8°C/min). Rietveld refinements revealed the presence of two Brønsted acid sites (corresponding to 7.6 hydroxyl groups). The first one was on framework oxygen O5, not far from the center of the 8-ring of the cancrinite cage. The second one was on the framework oxygen O1, heading towards the center of the 12 MR channel. The RD-LTL refinement highlighted the presence of six additional extraframework sites attributed to re-adsorbed H_2O molecules. Very interestingly, these last form water-chains interacting strongly with the framework oxygens. These results are of paramount importance as the presence of water molecules, even in undetectable amounts, is crucial in the zeolitic catalyst in catalytic processes.

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Red mud as aluminium source for zeolite synthesis

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Keywords: red mud, aluminium source, FAU- and GIS- type zeolite structures, magnetic properties.

Zeolites are hydrated aluminosilicate minerals with a three-dimensional open structure consisting in aluminium and silicon tetrahedra linked by sharing oxygen atoms. The synthesis of these minerals typically requires batch systems in which pure aluminate and silicate solutions are mixed and then subjected to hydrothermal treatment for different times. Red mud is a waste material formed during the production of alumina when the bauxite ores are subjected to caustic leaching. It is mineralogically characterised by the presence of iron oxy-hydroxides (*i.e.*, primarily hematite and goethite) with a minor aluminium hydroxides (*i.e.*, boehmite). The red mud consisting mainly of iron-based oxides was used to induce magnetic properties in the microporous materials.

In this work, we report on the synthesis of zeolites using colloidal silica (Ludox HS-30) and red mud as sources of silicon and aluminium, respectively. The conditions of synthesis were varied in order to obtain pure synthetic products with defined microporous structures. The physicochemical properties of the synthetic products were characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), thermogravimetry (TG), and nitrogen adsorption/desorption isotherms.

Two types of zeolites with FAU- and GIS- type structures were synthesized using the red mud alumina source. Moreover, two different morphologies for GIS- type zeolites were determined, *i.e.*, wool ball-like and cactus-like shapes. The results confirm the important role of the Si/Al ratio of the precursor mixtures on the synthesis of zeolites with different morphology, crystalline structure and porosity. More importantly, the synthetic products displayed magnetic properties.

Thermal transformations of (NH_4,Cs)-clinoptilolite: what happens for compositions in between the end-members?

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Keywords: $CsAlSi_5O_{12}$, mullite, zeolite, ceramics.

Mono-cationic zeolites have been used to obtain aluminosilicate-based products useful in the ceramic field (Subramanian et al., 1993). Some composite ceramics have been prepared also from bi-cationic forms, hitherto only of synthetic zeolites, but the couple of cations Cs^+/NH_4^+ has been not yet considered. On the other hand, it has been demonstrated that a clinoptilolite-based material can be transformed to ceramics if the zeolite is in Cs- or NH_4-form (Brundu & Cerri, 2015; Brundu et al., 2017). This work investigates the thermal transformations of the same material (90% in clinoptilolite) for zeolite compositions in between the NH_4, Cs end-members.

Three samples (A, B, C) have been prepared by ion exchange and subjected to chemical, TG-DTA and X-ray analyses. The Cs and NH_4 contents, and the Cs/NH_4 atomic ratios, are, respectively: A) 19.02%, 0.51%, 5.00; B) 13.20%, 1.54%, 1.16; C) 8.76%, 2.31%, 0.51. The materials have been heated for 2 h from 200 to 1200°C, making steps of 100°C and performing XRD analyses after each step. Further treatments have been executed at 1100°C for 4, 8, 16 and 32 h. QXRD analyses (RIR-Rietveld method; Bruker Topas 5) have been performed on the samples heated at 1200°C for 2 h and at 1100°C for 32 h.

The amorphization of the zeolite occurs at 900°C in C, and at 1000°C in A and B. After 2 h at 1200°C, 66% of $CsAlSi_5O_{12}$ (CAS) and traces of pollucite nucleate in A, an incipient crystallization of cristobalite and mullite occurs in C, whereas B remains substantially amorphous.

In all samples, the crystallization at 1100°C increases with time and, after 32 h, A is composed by about 91% of CAS, 7.5% of glass and traces of pollucite. In B and C, mullite and silica polymorphs form besides CAS and pollucite but, after 32 h, the residual glass is 6.7% in B and 59.7% in C. Only in the sample richest of ammonium (C), mullite nucleation anticipates CAS's one, thus reducing the amount of Al available for the crystallization of the latter phase, which does not exceed 13.8%, whereas CAS attains 74.2% in B.

By considering the cesium content of samples, the quantities of Cs-phases nucleated after 32 h at 1100°C and their Cs^+ occupancies, it turns out that in A and B the cesium is almost completely contained in the crystalline structures of CAS and pollucite, whereas in C about 67% of the element remains in the glassy fraction.

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Thermal behavior of stilbite and stellerite revisited and dehydration of their Na-exchanged forms: considerations on the memory effect of the STI framework type

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Keywords: STI framework, thermal stability, Na-stellerite, Na-stilbite.

In this study, the thermal behavior of Na-exchanged stellerite and stilbite was investigated by *in situ* single crystal X-ray diffraction under dry conditions. For comparison with the exchanged forms new data were also collected on natural samples of stellerite and stilbite under the same experimental conditions. With the increase of temperature, strong disorder at T and O sites of the tetrahedra of the four-membered ring developed in both natural forms. Such disorder was associated with the rupture of T-O-T connections and transition from the A to the B phase. Differently from previous studies (Arletti et al., 2006), stellerite B occurring between 300°C to 400°C was found to be monoclinic in space group $A2/m$. In addition, at 400°C, a new T-O-T connection occurred in the B phase of stellerite, analogous to that in the B phase of barrerite (Alberti & Vezzalini, 1978; Ori et al., 2009).

The dehydration behavior of stilbite developed through a mechanism similar to that observed in stellerite. In contrast to previous findings (Cruciani et al., 1997) stilbite remained monoclinic and at 75°C transformed from space group $F2/m$ to $A2/m$.

Na-stellerite and Na-stilbite were at *RT* monoclinic, space group $F2/m$, confirming our previous results on Na-barrerite (Cametti et al., 2016). Upon heating from 50 to 400°C, they also displayed the same structural modifications as observed in natural barrerite and Na-barrerite and adopted space group $A2/m$. Compared to natural stellerite and stilbite different T-O-T connections ruptured leading to a different topology of the B phase. The total volume contraction was 16% at 350°C compared to 8% of pristine materials. The highly-condensed D phase (Sacerdoti, 2007), which does not form in natural stellerite and stilbite, was obtained by heating a Na-stellerite crystal *ex-situ* at 525°C. The structure corresponded to the D phase of natural barrerite and Na-barrerite.

All STI members, after being exchanged with Na, have identical symmetry and demonstrate corresponding behavior upon heating and associated dehydration. Thus, a previously assumed memory effect of the symmetry of the natural parent structure (Passaglia et al., 1982), is not confirmed.

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New insights on the hydration of the zeolite laumontite: a natural nano-sponge

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Keywords: zeolite, laumontite, high pressure, H_2O adsorption.

Laumontite, $|(Ca_{4-x}Na_x)K_x(H_2O)_n|[Al_8Si_{16}O_{48}]$, space group *C*2/*m*, is one of the most common natural zeolite occurring in a wide range of geological environments, including sedimentary deposits and deep-sea sediments. Remarkably, it is also present in oceanic basalts as well as in vugs of plutonic and volcanic rocks and in sedimentary rocks. Fully hydrated laumontite contains 18 H_2O molecules per formula unit, although it can lose up to 4 H_2O molecules per formula unit if exposed to air at relative humidity RH < 50%. Such a partially-dehydrated laumontite is formally referred as leonhardite (Yamazaki et al., 1991).

To date, laumontite has been studied mainly *via* X-ray powder diffraction, in order to investigate the processes of hydration/dehydration controlling the RH or submerging samples in pure water or increasing temperature (*e.g.*, Yamazaki et al., 1991; Fridriksson et al., 2004). Lee et al. (2004) investigated the high-pressure behavior of laumontite up to 7.5 GPa, by *in situ* synchrotron powder diffraction with a diamond anvil cell, using the 16:3:1 methanol-ethanol-H_2O pressure medium, and observed an instantaneous over-hydration effect at a relatively low pressure (< 0.5 GPa) with a potential additional phase transition at about 3 GPa (Lee et al., 2004). However, a number of open questions remain still open about: i) the possible phase transition observed by Lee et al. (2004) at about 3 GPa, ii) the elastic parameters of leonhardite, which both thermodynamic calculation and geological observations suggest being the stable form of laumontite under diagenetic and low- grade metamorphic conditions (*e.g.*, Neuhoff & Bird, 2001; Coombs et al., 1959), and iii) the single-crystal hydration kinetics in H_2O mixture.These parameters are critical considering the fact that laumontite is one of the most common zeolite in the oceanic basalts and, thereby, it can be an important H_2O-carrier in subduction zones. In this light, we performed *in situ* single-crystal synchrotron X-ray diffraction experiments using different pressure transmitting fluids, as well as a number of *in situ* single-crystal experiments at ambient pressure in different H_2O rich-mixture. On the basis of these studies, we are able to describe: 1) the hydration mechanisms and kinetics of laumontite in large single-crystals, 2) the bonding configuration of the adsorbed H_2O molecules and the structural deformation of the framework in response to the overhydration at ambient pressure; 3) the elastic parameters of leonhardite; 4) the different deformation behavior between leonhardite and the hydrated-laumontite.

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Synthesis and structural characterisation of woodwardite and its relationships with rare earth elements

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Keywords: woodwardite, Layered Double Hydroxides, Rare Earth Elements.

Woodwardite [$(Cu_{1-x}Al_x)(OH)_2(SO_4)_{x/2}\cdot nH_2O$] occurs as stalagmites or loose precipitates, often as poorly crystalline aggregates, in Cu mining areas (Witzke, 1995). It is a member of the hydrotalcite group (Mills et al., 2012), also known as Layered Double Hydroxides (LDH) or anionic clays, due to the capacity of these compounds to sorb and exchange anions. The structure of woodwardite is composed by brucite-like octahedral sheets characterised by Al-to-Cu substitutions causing a net positive charge, balanced by the presence of sulphate in the interlayer.

Natural samples of woodwardite collected at the Libiola mine (north west Italy) were found to have anomalously high concentrations of rare earth elements (*REE*s), compared to the value of such elements in the surrounding rocks. A selective capacity of woodwardite to scavenge *REE*s from solutions is suggested by the work of Kameda et al. (2013), which reported that Cu-Al LDH are able to scavenge *REE*s. In solution, *REE*s can form both cations [$REE(H_2O)_6]^{3+}$ and anions [$REE(SO_4)_2]^{-}$ (Brookins, 1989), and therefore can be hosted in the structure of woodwardite in the octahedral layers or in the interspace between them. The aim of the present work was to understand the relationships between woodwardite structure and rare earth elements in order to assess the possibility to use this mineral for the recovery of such elements.

In order to achieve this goal, pure woodwardite and *REE*-doped woodwardite samples were synthesised and analysed by means of different techniques. The synthesis routine gave a blue powder, composed by nanosised woodwardite crystals. Among the tested *REE*s (Y, La, Ce, Nd, and Gd), only La and Ce^{4+} were not incorporated in woodwardite, whereas the other tested elements were captured by woodwardite in different amounts (between 3.5 and 8 wt%). X-ray diffraction showed the presence of a turbostratic structure, and a model for different polytypes with a different number of layers (from 1 to 4) was developed. Basing on X-ray absorption spectroscopy results, *REE*s should be hosted inside the interlayer, making woodwardite a promising material for the recovery of *REE*s from solutions.

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Syntheses of melanophlogite (type I clathrate)

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Keywords: melanophlogite, syntheses, X-ray diffraction, clathrate, gas storage.

Melanophlogite (MEP) is a tectosilicate belonging to SiO_2 type I clathrate compounds, zeolite–like materials with microporous framework of corner–sharing $[SiO_4]$ tetrahedra with tetrakaidecahedral $[5^{12}6^2]$ and pentagonododecahedral $[5^{12}]$ isolated cavities between them. Its chemical formula is $46SiO_2 \cdot 8(CO_2,CH_4,H_2S)$, in which tetrakaidecahedral $[5^{12}6^2]$ and pentagonododecahedral $[5^{12}]$ cages, with volume of 136 and 97 $Å^3$ respectively, are present in a typical ratio of 6:2. Guest gases can fill the structural voids and act as templates for MEP crystallization process (Gies, 1983; Gunawardane et al., 1987; Kolesov & Geiger, 2003).

MEP, potentially interesting for gas storage, is found in few localities all around the world and some of them are in Italy: Fortullino (Livorno), Racalmuto (Agrigento) and Varano Marchesi (Parma), each of them with characteristic guest gases in the structural voids (CO_2, CH_4 and H_2S and only CH_4 in MEP from Fortullino, Racalmuto and Varano Marchesi respectively).

The implementation of MEP syntheses methods is still under improvement and refinement. In the literature, information are rare and lacking of important practical details. A study indicates tetramethyl orthosilicate (TMOS) as crosslinking agent and methylamine as guest gases source (Gunawardane et al., 1987). In this work, tetraethyl orthosilicate (TEOS), safer than TMOS, is used as crosslinking agent. Chemically purified water is used as medium.

The reagents are placed into quartz vials, which preservation is linked to pressures developed inside them during thermal increase, when pressures can become high and cause vials explosion. It is decided to decrease the amount of the reagents and employ tubes of lower diameter and higher thickness: this combination of factors seems to ensure an increased vials stability.

Increasing methylamine concentrations (0.3, 0.6, 0.9, 1.2, 1.8, 2.4 and 4.8 ml/ml solution) are investigated and for each of them various ratios of chemically purified water and TEOS (4:1, 2:1, 1:1, 1:2 and 1:4) are considered. Till now, only the synthesized samples obtained using the first 4 methylamine concentrations are examined and XRPD analyses have shown MEP crystallization for methylamine concentration of 1.2 ml/ml solution and ratios of chemically purified water and TEOS of 4:1 and 2:1. It seems higher methylamine concentrations and higher ratios of chemically purified water and TEOS can promote MEP crystallization. Further analyses on all other synthesized samples are in progress.

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Mechanochemistry immobilization of organic and inorganic pollutants into clay minerals: a suitable technology for soil remediation

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Keywords: smectite, kaolinite, heavy metals, organic pollutants, mechanochemistry, remediation.

The presence of organic pollutants as well as of heavy metals in the environment is a potential risk for water and soil quality due to their toxicity. Lots of technologies have been developed to remove them from the environment. Among these, mechanochemistry is quite suitable for it allows activation of chemical reactions by inducing different kinds of mechanical stress and without any other energy supply. Clay minerals have been employed in this technology due to their low cost, availability, and low toxicity. In the present study were investigated-by X-ray diffraction, FTIR, solid-state NMR, XPS, and TG-DTA-the effect of dry milling on the ability of dioctahedral smectites (Bentolite H) and trioctahedral smectites (Laponite RD) to immobilize heavy metals cations (Cd and Cu). The mechanochemical reactions of both smectites and well crystallized kaolinite (Kga-1b) with organic molecules (phenols) – as representative of pollutants with enhanced polarity, *i.e.*, cathecol (CAT) and pentachlorophenol (PCP) – were also investigated. Strong milling treatments gradually reduces crystallinity in clay minerals by causing diffusion of atoms ("prototropy"), delamination, and layer breakdown, therefore affecting the surface and colloid properties clay minerals and causing the increase of their catalytic activities and sorption capability. Heavy metal immobilization degree was evaluated by ICP/OES analysis of extracts. Organic pollutant removal efficiency of clay minerals was evaluated by chromatographic analysis (HPLC-DAD). To this purpose the dioctahedral smectite "bentolite L" and the trioctahedral one "laponite RD" were ground with six distinct amounts of Cd and Cu chloride in dry conditions by means of zirconia planetary ball mill. Increasing milling time and heavy metal/clay minerals mass ratio were selected for experimental tests whereas grinding energy and ball to powder ratio were hold to constant value. Heavy metal immobilization degree was evaluated by ICP/OES analysis of extracts (deionised water and 1M $MgCl_2$ solution) as difference between the amount of heavy metal spiked in the mixture and its amount in the extracted fraction. Mechanochemical dry milling activates chemical reactions between clay minerals surface and heavy metals cations by inducing different kinds of mechanical stress. Time depending experiments pointed out an increased of Cd and Cu retention as time increases for both smectites. Long time experiments (24 h) showed otherwise that laponite RD exhibits stronger Cd retention capability than bentolite. Milling facilitates heavy metal sorption in sites in which the cation is relatively tightly bonded to the TOT layers of the smectite structure. With respect to the organic pollutants, prolonged high energy grinding likely promotes intense sequestration of PCP and CAT by both smectites with respect to the simple contact between sorbants and pollutants. The type of mechanochemical interaction of PCP with the trioctahedral smectite is weak, mainly occurs on the external surfaces, and does not involve the OH-phenolic group or any complexation of the interlayer cation. Such interaction only causes amorphization of Laponite by formation of a double film of PCP molecules adsorbed on the external clay mineral surfaces. On the contrary, the dioctahedral smectite exhibits strong mechanochemical interactions with PCP molecules via the phenolic group. Prototropy, induced in Bentolite by milling, is responsible for the PCP molecule perturbation and the enhanced capability of Bentolite to promote formation of intermediate products via OH groups. Mechanochemical interactions of CAT with both smectites mainly occur in the interlayers: they are stronger for the dioctahedral smectite than for the trioctahedral one, and likely involve inner-sphere complexation of Bentolite interlayer cation by CAT phenolic groups. Mechanochemical interactions of both pollutants with kaolinite mainly occurs via adsorption on external clay mineral surfaces through the phenolic group and, in the case of PCP, do not involve the chlorine atoms of the ring. The fundamental understanding of solid-state reactions for organic and inorganic pollutants is thus potentially useful to achieve soil remediation.

Synthesis condition influence on fly ash zeolites properties

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Keywords: synthesis, fly ash, zeolite, hydrothermal treatment.

The present study was undertaken to discuss experimental results of the utilization of F-class fly ash for synthesis of zeolite. The transformation of this solid waste into useful material like zeolite with high application possibilities is possible. Synthesis of zeolites with the use of fusion method with NaOH at 550°C followed by hydrothermal treatment enables the possibility of receiving materials of high yield of zeolites. In the performed experiments the influence of a series of parameters was examined in correlation to received zeolitic material. However, temperature, reaction time, type of water used (distilled water and seawater), and action of acid pre-treatment in the stage of the synthesis zeolite are also considered important variables to obtain highly crystalline zeolite. Different instruments were used to characterize the properties of fly ash and zeolite product as X-ray fluorescence spectrometry (XRF), X-ray diffraction analysis (XRD), scanning electron microscopy (SEM), Brunauer-Emmett-Teller method (BET) and Fourier transform infrared spectroscopy (FTIR).

XAS investigation of La in montmorillonites

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Keywords: *REE* recovery, XAS, La-enriched montmorillonites.

This work aims at characterizing La structural environment in clay minerals in order to better understand how rare-earth elements (*REE*) are hosted in clay minerals during uptake treatments of *REE* solutions. REE play indeed an essential role in several fields of applied sciences (Binnemans et al., 2013) and the recent development of the green economy is making *REE*s recovery increasingly popular. In particular, the use of natural clays as sorbents in treating aqueous wastes containing *REE* was recently investigated (Iannucelli-Zubiani et al., 2015).

Two samples of source clays, Ca-Montmorillonite from Texas (STx) and Na-Montmorillonite from Wyoming (SWy), have been tested as sorbents for the removal of La ions from liquid solutions (Iannicelli-Zubiani et al., 2015).

In the present work, Lanthanum L_3-edge XANES and EXAFS spectra have been collected at the BM08 beamline (LISA) on the La-enriched STx and SWy samples. Preliminary analysis of the EXAFS spectra provided distances in the range 2.56-2.62±0.02 Å. No systematic difference has been found according to sample type and La concentration indicating that the La environment does not show marked differences in the studied samples. The large value of the distance is compatible with the incorporation of La the interlayer site (Trillo et al., 1992).

Understanding *REE* bonding environment inside crystalline hosts is a prerequisite for better evaluating the feasibility of using these hosts for *REE* recovery from electronic waste. Such knowledge is indeed crucial for tailoring uptake and release processes in order to obtain a more efficient and environmentally friendly procedure.

Given the low costs involved in the processes for La uptake in clay materials, the location of *REE* in the interlayer make these kinds of materials promising for recovering *REE*.

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Synthesis of zeolitic materials from Sardinian kaolin

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Keywords: zeolites, kaolinite, Sardinia.

The search of synthetic materials, with specific built-in properties, has promoted basic research particularly in the field of zeolites because of their uses in catalysis, gas sorption, or ion exchange (Barrer, 1982). In this way, several authors have studied the synthesis of zeolites from kaolinite and metakaolinite, after their reaction with alkaline solutions (generally sodium or potassium hydroxides).

North-western Sardinia (Italy) is characterised by the occurrence of several partially exploited kaolin deposits, known as "district of Romana" deposits, with reserves estimated in 2-3 million tons (Oggiano & Mameli, 2012). Chemical and mineralogical analyses of the raw materials indicate that these kaolins are quite homogeneous, being characterised by the presence of kaolinite ± dickite, cristobalite/opal-CT, and scarce quartz ± alunite/natroalunite ± hematite.

Particularly the Donigazza kaolin, characterized by the presence of abundant kaolinite and amorphous silica, scarce quartz and low iron content, have encouraged to investigate the conversion of this raw material into zeolites.

The perspective is to draw a better exploitation of this mineral resource, as the deposits of NW Sardinia were mainly exploited to manufacture vitrified tiles and/or sanitaryware and now are unexploited.

The rock was powdered and hydrothermally treated at 100°C in sealed teflon-lined stainless steel vessels, under autogeneous water vapor pressure. A set of 30 experiments were performed by varying the concentration of the NaOH solution (1, 2, 3, 4 and 5 mol L^{-1}) and the reaction time (12, 24, 48, 72, 96, 168 hours), for a 1:5 liquid/solid ratio. Mineralogical analysis of the final products revealed the growth of several types of zeolites, depending on time and NaOH concentration: GIS-type zeolites, sodalite-cancrinite, and analcime. NaP1 crystallizes at NaOH concentration of 3 M or below, being transformed in NaP2 after long time in 1 M solutions. At higher concentration of NaOH (4 M or above) the main product is a mixture of hidroxycancrinite and hydroxysodalite, accompanied of sodalite a 4 M concentration formed at short reaction time. Analcime is the major mineral only in 4 solutions at time longer than 72 hours.

Varying synthesis conditions Donigazza kaolin can be transformed in different zeolites for potential applications.

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Synthesis of vishnevite analogue from alunite-bearing kaolin

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Keywords: synthesis, kaolinite, sulfate, cancrinite.

Cancrinite-group compounds cannot be grouped along with the materials showing good zeolitic properties, such as high cation exchange capacity or molecular sieving (Fechtelkord et al.2003). On the contrary, being extraframework ions diffusion limited by the presence of fairly strong bonds, CAN can be considered as ion sequestrating materials. The absence of a significant ion exchange capacity can be exploited in several processes of relevant environmental and industrial interests.

Cancrinite-group compounds are usually synthesised under hydrothermal conditions in highly alkaline solution with an excess of NaOH. Nucleation of the cancrinite structure is promoted by the presence in solution of anions such as NO_3^-, $S_2O_3^{2-}$ and SO_3^{2-}, which act as structure-driving agents (Hackbarh et al., 1999). In this study, (SO_4^{2-})-cancrinite, synthetic analogue of the mineral vishnevite, has been synthesised from volcanogenic sulfate-bearing kaolin, labelled L02. Syntheses were conducted by melting kaolin with NaOH (1:1.2 weight ratio) at 550°C and afterwards, incubating samples in vessels with distilled water at 50°C for 96, 360 and 720 hours. Syntheses have been started from an alunite-bearing kaolin (alunite 13 wt%) as well as from synthetic mixtures of alunite and high-grade kaolin in different proportions. Products have been compared to those obtained by using a high-quality kaolin without alunite. Three different Si/Al ratio have been used: 1.0; 1.8 and 2.3, by adding fumed SiO_2 to the kaolin-NaOH mixture. All resulting samples have been characterized by XRD, FT-IR and SEM-EDS. Zeolites Y and A crystallizes only in samples without alunite, as expected, while sulfate bearing CAN is the main reaction product of all alunite-containing batches. Traces of sodalite crystals have been observed at SEM. No sulfate salts have been observed and the absence of SO_4^{2-} in the supernatant liquid after incubation have been confirmed by ICP-OES.

Recently, the feasibility of using the same L02 sulfate-bearing kaolin to synthesize geopolymers has been assessed (Gasparini et al., 2015). Sulfur seems to be retained in the aluminosilicate gel, likely in amorphous or nanosized zeotype phases. The results of this study suggest that vishnevite analogue is, with nosean, one of the candidate phase for trapping sulfur in geopolymers, considering structure-directing role shown by the SO_4^{2-} anion towards the [CAN]-framework.

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Azobenzene/$AlPO_4$-5 hybrid material: synchrotron X-ray powder diffraction structural characterization

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Keywords: AFI, $AlPO_4$-5, azobenzene, dye/zeolite hybrid materials.

The regular pore systems of nanometric openings exhibited by zeolite frameworks make these porous materials ideal host matrices for achieving supramolecular organization of photoactive species (Calzaferri, 2012). Organic/inorganic hybrid materials (such as zeolites + colorants) are currently used in strategic areas, from sustainable energy technologies to biomedical sciences. In these systems, photoactive molecules are organized in one-dimensional nanostructures inside the zeolite channels (Gigli et al., 2014). It is known that the properties of these hybrids depend on the packing of molecules inside the channels, which controls the intermolecular interactions and the interactions of the dyes with the framework. Studies on zeolites with AFI topology demonstrated that the confinement and the consequent alignment of dyes into $AlPO_4$-5 porosities induces new spectroscopic properties, such as laser emission with properties tunable over a wide range (Ihlein et al., 1998; Lei et al., 1998). However, up to now detailed information on the crystal structure and on the host/guest and guest/guest interactions of these systems are completely lacking.

$AlPO_4$-5 (s.g. *P6cc*, $a = b = 13.827$ Å, $c = 8.580$, V= 1420.64 Å^3) is characterized by 12-ring channels with 0.73 nm free diameter. The calcined $AlPO_4$-5 and the composite material, obtained upon penetration of the trans-azobenzene dye, were analyzed by thermogravimetric (TG) analyses and synchrotron X-ray powder diffraction at the beamlines ID22 at ESRF (Grenoble) and X-Press at Elettra Synchrotron (Trieste). Moreover, UV-Vis and FT-IR spectroscopies were employed to give specific information about the dye-zeolite interactions.

The TG curves show that a portion of the water molecules present in the calcined sample (16.5 H_2O p.u.c., corresponding to 16.8% weight loss) is substituted by the dye-molecules (0.5 molecule p.u.c., corresponding to 5.1% weight loss).

Our structural refinements show that the penetration of azobenzene induces an increase of *a* cell parameter, while *c* remains almost constant. Azobenzene molecule is confined in the 12-ring channels and is tilted by 36° with respect to the channel axis. These results, compared with other data reported in literature (Megelski et al., 2001), confirm the structure-directing influence of the host matrix on the guest molecule arrangement. UV-Vis spectrum of the composite material put in evidence that a fraction of the azobenzene molecules is protonated on the azo group. Ammonia adsorption followed by FT-IR spectroscopy confirmed that the host $AlPO_4$-5 shows Brönsted acidity responsible for the azo group protonation.

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Intrusion-extrusion of water/alcohol molecules in Si-chabazite: structural interpretation of the energetic performance

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Keywords: Si-chabazite, high pressure behavior, penetration of guest molecules.

The demand for low cost, efficient and sustainable energy is ever increasing. Since fifteen years, absorption or energy storage using pure-silica zeolites has been developed and opened a new field of applications for these exciting microporous solids (Eroshenko et al., 2001) . The basic idea is that to penetrate water into a hydrophobic porous material a certain pressure must be applied. During this forced penetration (intrusion), the mechanical energy can be converted into interfacial one. Depending on various physical parameters related to the porous material-such as its pore system, its dimensionality and pore size-when the pressure is released (extrusion) the "zeosil-water" system is able to restore, dissipate or absorb the supplied mechanical energy accumulated during the compression step with a more or less significant hysteresis. As a consequence, it displays a spring, shock-absorber or bumper behavior, respectively. In the present work, the energetic performances of the pure-silica Si-chabasite (CHA) zeolite were preliminary tested.

The water/alcohol intrusion of synthetic zeolite Si-chabazite-CHA framework type, s.g. $R\text{-}3m$, a = 13.5454, c = 14.7635 Å (Diaz-Cabañas et al., 1998) was explored in the pressure range P_{amb}-4.82 GPa by *in situ* synchrotron X-ray powder diffraction (XRPD) experiments, using a mixture of methanol:ethanol:water = 16:3:1 (mew) as penetrating *P*-transmitting medium.

No phase transitions were observed in the investigated *P*-range. The cell volume decreases of about 3.7% up to 4.8 GPa and the P_{amb} volume is almost completely regained upon pressure release.

The structural refinements indicate a significant penetration (corresponding to about 270 extraframework electrons) of the *P*-transmitting medium even at 0.1 GPa, the lowest investigated pressure. On the basis of the interatomic distances and of the steric hindrances, both alcohol and water molecules seem to penetrate the zeolite porosities. However, impressively, a segregation between methanol and ethanol was observed, since the two molecules cannot occupy simultaneously the same CHA cage.

The reversibility of the intrusion process, with the extrusion of the medium molecules upon *P* release was already noted by porosimetric experiments performed by using pure water (Trzpit et al., 2007). Our and literature results suggest that Si-CHA can be used as a "spring device", able to store and restore mechanical energy. Preliminary results on the effects of changes of the medium composition on the intrusion/extrusion process will be shown, as well.

Acknowledgements: The study is part of the project ZAPPING, financed by Italian MIUR (www.zapping-prin.it).

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Toluene and *n*-hexane competitive adsorption on high-silica zsm-5 zeolite

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Keywords: high silica zeolites, hydrophobic, water pollution, toluene, *n*-hexane.

Fuel-based compounds, such as toluene and *n*-hexane, are common pollutants present in water and wastewater. Due to their tendency to persist in air, water and soil and to bioaccumulate through the food chain, they are included among the most hazardous compounds for human health and environment. Acquatic ecosystems are especially vulnerable because of the frequent use of water bodies as recipients of potentially toxic liquids and solids from domestic, agricultural and industrial wastes. Hence, the removal of fuel-based compounds, through adsorption onto inorganic sorbents is of considerable interest. Due to their selectivity towards organic contaminant and fast adsorption kinetics, it has been recently highlighted that High Silica Zeolites are hydrophobic sorbent materials suitable for adsorption processes (Martucci et al., 2015; Pasti et al., 2016). The aim of this work is to determine the ZSM-5 zeolite degree of selectivity and its structural changes when a competitive adsorption of toluene and *n*-hexane occurs. A sample of ZSM-5 zeolite (MFI topology, SiO_2/Al_2O_3 ratio=280), was provided by Tosoh Corporation and loaded with a binary mixture of toluene and *n*-hexane. Kinetics and adsorption isotherm data were obtained via Headspace Solid Phase Microextraction-GC. Powders patterns were collected before and after adsorption on a Bruker D8 Advance diffractometer equipped with SOL-X detector. Thermal (TG and DTA) analysis were performed in air up to 900°C at 10°C/min. This multidisciplinary approach allowed us to: 1) measure the sorption capacity of zeolite materials weighed against organic pollutants dissolved in water; 2) characterise the sorbent structure after pollutant adsorption; 3) localise the organic species in the zeolite channel systems; 4) probe the interaction between the adsorbate and zeolite framework. Rietveld refinements provide information about the relative position of molecules inside the structure after toluene, *n*-hexane and their mixture adsorption. Data reveal that 1) *n*-hexane and toluene are preferentially adsorbed whether as single components than as binary mixture; 2) zeolite selectivity is higher towards the *n*-hexane than toluene. Differences Fourier maps analysis shows that *n*-hexane, water, and toluene have been adsorbed at about 8.95%, 2.2%, and 1.59%, respectively, in good agreement with both adsorption data and thermal analysis. As a matter of fact, ZSM-5 zeolite preferably adsorbs *n*-hexane, even in presence of a competitor, such as toluene.

Martucci, A., Braschi, I., Bisio, C., Sarti, E., Rodeghero, E., Bagatin, R., Pasti, L. (2015): Influence of water on the retention of methyl tertiary-butyl ether by high silica ZSM-5 and Y zeolites: a multidisciplinary study on the adsorption from liquid and gas phase. RSC Adv., 5, 86997-87006.

Pasti, L., Rodeghero, E., Sarti, E., Bosi, V., Cavazzini, A., Bagatin, R., Martucci, A. (2016): Competitive adsorption of VOCs from binary aqueous mixtures on zeolite ZSM-5. RSC Adv., 6, 54544-54552.

Adsorption and desorption of fuel-based compounds from water through synthetic zeolite ZSM-5

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Keywords: *in situ*, high temperature, time resolved, zeolite, fuel-based compounds.

The expansion of chemical and petrochemical industries in response to the increasing demand of energy and consumer goods of different topologies, has generated in the recent years a significantly increase of the water contamination. The major pollutants, that deriving from this industrial processes are included among the Emerging Organic Contaminants, specifically Volatile Organic Compounds (VOCs) require the most attention due to their harmful effects both on the environment and human health, even at very low concentrations. Due to the toxic effects of these chemicals also at long term, the removal or the reduce of concentrations of these class of pollutants from water bodies is today a very important objective. Often, the traditional water treatments (*i.e.*, vaporization, dilution, decomposition, and reactions to sunlight action) need to be supported by new technologies and methods. For instance, adsorption technologies based on the use of adsorbent materials have been shown to be an effective and eco-friendly alternative to substitute or support the traditional methods. Among the adsorbent materials, hydrophobic zeolites have proven to be very promising materials, regarding the successful removal of several representatives of VOCs (Pasti et al., 2016). By an environmental impact point of view, zeolites also have another very interest aspect. In fact, they can be easily regenerated by thermal processes without changing their initial adsorption features. On the basis of the above statements, to contribute to the growth of knowledge on these materials applied in this field, the combination of chromatographic, diffractometric and thermogravimetric techniques has been employed to investigate the fuel-based compounds adsorptive-desorptive process. In particular, the behaviour of ZSM-5 (hydrophobic and synthetic zeolite) has been studied. Concerning the study of the desorption process, time-resolved high-temperature synchrotron X-ray powder diffraction was used as a tool to understand the structural modification undergoing on ZSM-5 framework during the desorption of 1,2 dichloroethane, toluene, and methyl tert-butyl ether. Specifically, the X-ray powder diffraction patterns are collected from room temperature to 600°C. The results achieved by means of Rietveld refinements of the investigated compounds highlight the "out-of-equilibrium effects" that govern the adsorption/desorption dynamic conditions in ZSM-5 powders (Rodeghero et al., 2017).

Pasti, L., Rodeghero, E., Sarti, E., Bosi, V., Cavazzini, A., Bagatin, R., Martucci, A. (2016): Competitive adsorption of VOCs from binary aqueous mixtures on zeolite ZSM-5. RSC Adv., 6, 54544-54552.

Rodeghero, E., Pasti, L., Sarti, E., Cruciani, G., Martucci, A. (2017): Temperature-induced desorption of Methyl tert-butyl ether confined on ZSM-5: a combined in situ synchrotron XRD powder diffraction and chromatographic study. Minerals, 34, 1-9.

Chromium and arsenic removal from contaminated waters: environmental application of maghemite nanoparticles – preliminary results

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Keywords: toxic metal release, SAMNs, hexavalent chromium, arsenic.

Toxic metal release, transport and dispersion into the biosphere have a direct impact on the environment and on human health. Arsenic and hexavalent chromium are highly toxic agents, so the reduction of these pollutants in soils and waters to acceptable levels is of great importance.

In this field nanoparticles emerge as one of the most promising new techniques for soil and water remediation. In this work, a new type of iron nanoparticles called SAMNs (Surface Active Maghemite Nanoparticles) is used. It is a novel superparamagnetic nanoparticle constituted of maghemite (Magro et al., 2010), characterized by specific surface chemical behavior, without any coating or superficial modification, high surface-area-to-volume-ratio, low toxicity, strong absorption ability and are stable in water for months as colloidal suspensions. The removal efficiency of SAMNs in respect of hexavalent chromium it was tested in laboratory solutions, with variable testing conditions in terms of pollutant concentrations, temperature and *p*H of the solution.

From these tests emerged that SAMNs can remediate water also with high concentrations of hexavalent chromium (22 mg/L) with a strong *p*H dependence; they are able to bind 99% Cr(VI) at *p*H 3.0, while this amount decreased to about 40% at *p*H 9.0. SAMN@CrVI complex was also characterized, as well as the covalent nature of the absorption was unequivocally proved (Magro et al., 2016). For arsenic removal the same methodology is applied, supported by several studies that demonstrate the ability of zero valent iron nanoparticles (nZVI) to reduce arsenic concentration in groundwater (Chowdhury & Yanful, 2010).

For arsenic determination in water the modified molybdenum blue colorimetric method has been applied (Tsang et al., 2007). This analytical procedure enable to determine concentration of arsenic in groundwater, at concentrations below 10 µmol L^{-1}, by means of a UV-vis Spectrophotometer.

Further experiments are in progress to validate the efficiency of SAMNs for the removal of arsenic from groundwater.

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Magro, M., Domeneghetti, S., Baratella, D., Jakubec, P., Salviulo, G., Bonaiuto, E., Venier, P., Malina, O., Tuček, J., Ranc, V., Zoppellaro, G., Zbořil, R., Vianello, F. (2016): Colloidal surface active maghemite nanoparticles for biologically safe CrVI remediation: from core-shell nanostructures to pilot plant development. Chem. Eur. J., 22, 14219-14226.

Tsang, S., Phu, F., Baum, M.M., Poskrebyshev, G.A. (2007): Determination of phosphate/arsenate by a modified molybdenum blue method and reduction of arsenate by $S_2O_4^{2-}$. Talanta, 71, 1560-1568.

Study of adsorption/desorption process of p-HBA into Y zeolite: a model system for water treatment contaminated by humic acids

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Keywords: humic acid, p-HBA, Y zeolite, adsorption/desorption process, regeneration.

Due to their biological origin, humic monomers, such as p-hydroxybenzaldehyde (p-HBA), are usually present in soils and water. Phenolic and aromatic compounds, such as p-HBA, arise from the degradation of natural organic matter (NOM), which can assume different molecular structures creating natural and synthetic compounds. The removal of these compounds from water is of increasing interest due to the possibility of negative interference with water remediation systems. Indeed, they usually assume the role of intermediary or precursor of many hazardous contaminants. Moreover, when high concentrations are present in water, they become phytotoxic for plants. It has been highlighted that hydrophobic zeolites are eco-friendly materials, which can be exploited for their adsorption properties in the removal of contaminants from water bodies and their possibility of regeneration through thermal treatment, without changing their initial adsorption capacity (Braschi et al., 2016; Wang et al., 2016). Since the presence of natural organic matter (NOM) can affect organic pollutants adsorption, the effect of lignin-derived phenolic monomers on the adsorption properties was investigated. The aim of this work is to study the structural modifications induced by adsorption/desorption process undergoing on a hydrophobic Y zeolite (HSZ-390HUA, SiO_2/Al_2O_3 = 200, Tosoh Corporation) loaded with p-HBA upon thermal treatment. To obtain this goal, chromatographic, diffractometric and thermal (TG and DTA) analysis were carried out. Kinetics and adsorption isotherm batch data were obtained via Headspace Solid Phase Microextraction-GC in order to quantify the amount of p-HBA adsorbed into zeolite channels system.The desorption process was continuously monitored at the ID22 beamline (ESRF-Grenoble) as a function of temperature (heating rate 20 °C/min, from room temperature to 600°C) to investigate high-temperature structural modifications and probe the host-guest interactions. Experimental results confirm that p-HBA is highly adsorbed on zeolites. Rietveld refinements reveal that the extraframework content is completely desorbed at about 570°C; these results are in good agreement with the total weight loss registered by thermal analysis. After thermal treatment, zeolite does not show any significant loss of crystallinity and non-equilibrium distortions in the framework are relaxed. Moreover, the regenerated zeolites regain almost the same unit-cell parameters of the bare material and no relevant structural deformations are registered in channel geometry.

Braschi, I., Blasioli, S., Buscaroli, E., Montecchio, D., Martucci, A. (2016): Physicochemical regeneration of high silica zeolite Y used to clean-up water polluted with sulfonamide antibiotics. J. Environ. Sci., 43, 302-312.

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Unidirectional zeolites as hosts for the high-pressure synthesis of conducting polymer nanocomposite

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Keywords: zeolites, high-pressure, nanocomposites.

Polymerization of simple organic molecules under high pressure in the subnanometric pores of high-silica zeolites can be used to produce novel nanocomposite materials, which can be recovered at ambient *P* and have remarkable mechanical, electrical or optical properties. In order to target novel electrical and optical properties, isolated chains of conducting polymers have been prepared in the pores of zeolite hosts at high pressure, such as polyacetylene, which was polymerized under pressure in the pores of the 1-D zeolite TON (Santoro et al., 2016). The structure of this nanocomposite was determined by synchrotron X-ray powder diffraction data with complete pore filling corresponding to one planar polymer chain confined in each pore with a zig-zag configuration in the *yz* plane. This very strong confinement can be expected to strongly modify the electrical properties of polyacetylene. This new material is susceptible to have applications in nanoelectronics, nanophotonics and energy and light harvesting. Completely novel nanocomposites were prepared by the polymerization of carbon monoxide CO in TON (Santoro et al., 2015). In this material, isolated, ideal polycarbonyl chains are obtained in the 1-D microporosity of the zeolite, in contrast to the non-stoichiometric, branched bulk polymers obtained by high pressure polymerization of this simple system. These polyCO/zeolite composites could be interesting energetic materials. In both nanocomposites, the presence of the polymer guest significantly modifies the mechanical properties of the host zeolite which, in absence of the guest, underwent a phase transition and amorphisation under pressure (Thibaud et al., 2017).

Santoro, M., Dziubek, K., Scelta, D., Ceppatelli, M., Gorelli, F., Bini, R., Thibaud, J.M., Di Renzo, F., Cambon, O., Rouquette, J., Hermet, P., van der Lee, A., Haines, J. (2015): High pressure synthesis of all-transoid polycarbonyl $[-(C{=}O)-]_n$ in a zeolite. Chem. Mater., 27, 6486-6489.

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High pressure behaviour of GIS-type zeolite amicite

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Keywords: zeolite, amicite, high-pressure, LS-XRPD, over hydration.

We report the results of a study (Arletti et al., 2017) performed by *in situ* synchrotron X-ray powder diffraction of the high pressure behavior of the natural zeolite amicite [$K_4Na_4(Al_8Si_8O_{32})\cdot 10H_2O$], the GIS-type phase with ordered (Si,Al) and (Na,K) distribution. The experiments were carried out at the SNBL1 (BM01a) beamline at ESRF, up to 8.13(5) GPa in the penetrating pressure transmitting medium methanol:ethanol:water = 16:3:1 (m.e.w.), and up to 8.68(5) GPa in the non-penetrating medium silicone oil (s.o.). The crystal structure refinements of the patterns collected in m.e.w. were performed up to 4.71(5) GPa, while for the patterns collected in s.o. only the unit cell parameters were determined as a function of pressure. A number of microporous materials with GIS topology have been investigated under *HP*: i) the natural zeolite gismondine (Ori et al., 2008; Betti et al., 2007), the Ca member of this group; ii)the synthetic phase potassium gallo silicate K-GaSi-GIS (Lee et al., 2008); iii) the synthetic phase potassium alumino germanate K-AlGe-GIS (Jang et al., 2010). The framework deformation mechanism of amicite-similar to that reported for the other phases with GIS topology-is essentially driven by the distortion of the double crankshaft chains and the consequent changed shape of the 8-ring channels. The pressure-induced over-hydration, observed in amicite compressed in m.e.w., occurs without unit-cell volume expansion and is substantially reversible upon pressure release. The comparison of the high pressure behavior of amicite with that of the other GIS-type phases confirms that the compressibility of microporous materials is not simply related to their framework density and topology, but is also greatly affected by the type, amount, and location of the framework and extra-framework species.

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Multianalytical study of sauconite from the Skorpion (Namibia) nonsulfide supergene orebody

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Keywords: sauconite, Zn-rich smectite, Skorpion ore deposit, ICP-OES, TG/DTA, XRPD, FTIR, TEM.

Sauconite, a Zn-bearing smectite, generally occurs in nonsulfide supergene deposits (Boni & Mondillo 2015). In the Skorpion ore (Namibia), sauconite predominates over the other Zn-oxidized mineral (Borg et al., 2003). A characterization of sauconite from the Skorpion ore was undertaken by combining ICP-OES, TG/DTA, XRPD, FTIR, TEM/HRTEM and AEM. Chemically the clay is nearly stoichiometric and homogenous: Zn^{2+} shares the octahedral site with small quantities of Al, Fe and Mg cations, while the interlayer contains Ca^{2+} and traces of K^+ and Na^+. Contrary to Peru nonsulfide ores (Mondillo et al., 2015), at the micro- and nanoscale the occurrence of Zn-beidellite is very minor at Skorpion. The DTA curve exhibits double endothermic breaks in the temperature range 100-250°C, ascribable to dehydration and loss of adsorbed water. Dehydroxylation is represented by the endothermic break in the 600-740°C range, whereas an exothermal peak at ~ 820°C points to the formation of new phases (Zn-orthosilicate, Zn_2SiO_4, gahnite, $ZnAl_2O_4$), in agreement with previous studies (Faust, 1951). A total weight loss of *ca.* 17% was measured. The XRPD random-mount pattern the Skorpion sauconite exhibits two-dimensional *hk* diffraction bands typical of disordered (faulted) clays. The 001 reflection occurs at about 14.72 Å, as in di-hydrated Ca^{2+}-rich smectites. The peak at 7.48 Å is asymmetric towards lower *d* spacings (~ 7.13 Å). The 060 reflection at 1.54 Å confirms the trioctahedral nature of the sample and the absence of Zn-beidellite. A weak sharp peak at 3.62 Å suggests the presence of K-feldspar. After ethylene glycol [EG]-solvation, a shift of 001 to 16.84 Å was observed. Broad and weak maxima at ~ 7.33 and 3.58 Å were also detected, compatible with the presence of kaolinite and K-feldspar traces. The IR spectrum shows a well-resolved band at 3640 cm^{-1}, due to 3Zn-OH stretching (Petit et al., 2008), and a weak band around 3690 cm^{-1} compatible with the presence of kaolinite. The TEM suggests that Skorpion sauconite forms from fluids, meteoric and/or hydrothermal processes, in two textural contexts: epitaxially grown on previously deposited phyllosilicates (mica), and/or directly nucleated from Zn-rich solutions.

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Session S7:

New minerals, systematic mineralogy, crystal chemistry, new mineralogical localities

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As-V minerals of hydrothermal origin in the Mn-ore deposits of Eastern Liguria (northern Apennine, Italy): where crystal chemistry meets geochemistry

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Keywords: As-V minerals, Mn-ores, geochemistry, crystal chemistry.

Manganese ores of eastern Liguria are mostly known for the great variety and rarity of secondary mineral species of hydrothermal origin (Cortesogno et al., 1979; Cabella et al., 1998). Although the crystal chemistry of those mineral assemblages is well-studied and characterized in detail, the genetic link with the geochemical conditions of formation is often poorly understood. In this work we studied the possible origin of As-V mineralization associated with hydrothermal veins in the Mn-ore deposits of Graveglia Valley, Monte Alpe and Cerchiara mine (northern Apennines, Italy). Different occurrences in ophiolites have been considered: secondary veins cross-cutting the Mn or Fe-Mn ores in low-grade Jurassic metacherts; diffuse mineralization within silicified fossil woods. It can be demonstrated that some peculiar crystal-chemical features displayed by As-V secondary minerals provide important clues on the genetic environment and thus reflect the geochemical conditions under which those elements are precipitated by hydrothermal fluids and incorporated into crystal structures. It turns out that even small variations in the redox state and *p*H conditions of the fluids can determine abrupt changes or the cycling occurrence of unusual Mn-As-V mineral parageneses in the veins, hence the close association in space and time of "geochemical spots" with completely different and highly variable mineralogical features.

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The collection of type mineral specimens of the Natural History Museum of the University of Pisa

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Keywords: type mineral specimens, new mineral, natural history museum.

Type mineral specimens are reference samples for the definition of mineral species (Dunn & Mandarino, 1987). The importance of their preservation in museum is well-known in the scientific community, since any further investigation dealing with the status of a mineral species should be carried out on type material.

Following the long-established tradition of crystal-chemical study of the "mineralogical school" of Pisa, the Natural History Museum of the Pisa University preserves an important mineralogical collection, formed by more than 19900 specimens.

Among them, the collection of type mineral specimens has an outstanding relevance, being constituted by ninety-nine type mineral specimens, representative of seventy-two different mineral species. In addition to type material used for the description of new mineral species, the collection includes samples used for the definition of new polytypes (*e.g.*, stibivanite-2*O*; Merlino et al., 1989) and the redefinition of not-well characterized minerals (*e.g.*, dinite; Franzini et al., 1991). Moreover, some species defined by mineralogists of the XIX Century were not adequately described and the modern investigations proved they corresponded to other known minerals. Consequently, they were formally discredited. Such specimens used for the discreditation of formerly accepted mineral species are known as necrotypes and some of them are stored in the collection (*e.g.*, the portite necrotype; Franzini & Perchiazzi, 1994).

The type mineral specimen collection of the Natural History Museum of the Pisa University does not only preserve type specimens for the future generations of scientists; indeed, it gives also an interesting picture of the evolution of the studies of the mineralogical school in Pisa.

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Thallium in potassium sulphates: crystal structure of alum-(K) and voltaite from Fornovolasco mine, Apuan Alps, Tuscany, Italy

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Keywords: alum-(K), voltaite, thallium.

The identification of the thallium-rich nature of several pyrite ore bodies from the southern Apuan Alps, Tuscany, Italy (Biagioni et al., 2013; D'Orazio et al., 2017), poses serious environmental concerns about the potential passage of Tl from the litosphere to the hydrosphere and biosphere following the pyrite oxidation and the genesis of a suite of secondary sulfate minerals. The latter could play an important role in acid drainage and metal sequestration and consequently their knowledge is crucial for evaluating the environmental impact of these ore bodies.

Several well-crystallized species, representing high-quality samples for crystallographic investigations, were collected in the old tunnels of the Fornovolasco mine. Eighteen different sulfates have been identified so far. Among them, alum-(K) and voltaite have shown detectable amounts of Tl.

Alum-(K), ideally $KAl(SO_4)_2 \cdot 12H_2O$, occurs as anhedral colorless aggregates or, rarely, as {111} individuals, up to 1 mm in size, associated with melanterite, römerite, copiapite, halotrichite, krausite, voltaite, and alunogen. Its unit-cell parameter is $a = 12.2030(2)$ Å, s.g. Pa-3. The crystal structure refinement converged to $R_1 = 0.059$ for 977 reflections with $F_o > 4\sigma(F_o)$ and 62 refined parameters. In agreement with qualitative EDS chemical analysis showing detectable amounts of Tl, the refinement of the site occupancy factor (s.o.f.) at the K site points to an occupancy ($K_{0.90}Tl_{0.10}$). In addition, these results are confirmed by X-ray absorption spectroscopy measurements, carried out at Tl L_3 edge (12658 *e*V). The position and shape of the main absorption edge indicate that Tl is present as Tl^+; EXAFS fit parameters indicate a first shell formed by O atoms with a shorter Tl-O shell [R = 2.69(2) Å, coordination number (CN) = 2.0(4)] and a longer one [R = 2.86(2) Å, CN = 6(1)]. The large Debye-Waller factor [0.033(5) Å^2] suggests a large structural disorder.

Voltaite, ideally $K_2Fe^{2+}{}_5Fe^{3+}{}_3Al(SO_4)_{12} \cdot 18H_2O$, occurs as euhedral {100} and {110} crystals, dark green in color, with a vitreous luster. They are associated with römerite, copiapite, halotrichite, krausite, alum-(K), rhomboclase, coquimbite, and alunogen. Its unit-cell parameter is $a = 27.3201(6)$ Å, s.g. Fd-3c. The crystal structure refinement converged to $R_1 = 0.026$ for 830 reflections with $F_o > 4\sigma(F_o)$ and 93 refined parameters. As in alum-(K), the refinement of the s.o.f. at the K site of voltaite confirms the minor replacement of K by Tl (s.o.f. = $K_{0.90}Tl_{0.10}$), in agreement with qualitative EDS chemical analysis.

Alum-(K) and voltaite could represent two possible sequestrators of thallium in Acid Mine Drainage systems, temporarily immobilizing this heavy element and avoiding its dispersion in the environment.

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Raman spectroscopy of the new Mo minerals from Su Seinargiu, Sardinia, Italy

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Keywords: molybdenum-bismuth oxides, molybdates, Raman spectroscopy.

The Su Seinargiu prospect, located on the southern coast of Sardinia, has recently become a reference locality for the study of Mo secondary minerals. Indeed, seven new mineral species containing this element have been described.

The Raman spectra of the bismuth-molybdenum oxides gelosaite, mambertiite, and sardignaite are characterized by the occurrence of strong Raman bands in the region 800–1000 cm^{-1}, related to the stretching of the shortest Mo–O bonds. Other weaker bands occurring between 400 and 800 cm^{-1} can be interpreted as due to longer Mo–O bonds as well as Bi–O bonds (*e.g.*, Hardcastle & Wachs, 1991, 1992). Further bands, related to bending modes, occur in the region between 200 and 400 cm^{-1}. In the region between 3000 and 4000 cm^{-1}, weak bands are related to O–H stretching vibrations. Whereas sardignaite can be easily distinguished from gelosaite and mambertiite, having two strong bands at 859 and 913 cm^{-1}, the distinction between these two latter minerals seems to be not possible through Raman spectroscopy only. Indeed, gelosaite and mambertiite are both characterized by three strong bands at 845, 899, and 940 cm^{-1}.

The two thorium molybdates ichnusaite and nuragheite cannot be distinguished on the basis of Raman spectra only. They both show Raman bands at the same positions in the regions 700-950 cm^{-1}(the most important feature is a strong band at 945 cm^{-1}) and 300-450 cm^{-1} that can be related to the stretching and bending of MoO_4 tetrahedra, respectively. Weak and broad bands occur in the 3000-4000 cm^{-1} region.

Similarly, the Raman spectrum of the iron-cerium hydrated molybdate tancaite-(Ce) is characterized by two groups of bands, *i.e.*, those in the range 700-950 cm^{-1} (stretching modes) and those between 300 and 450 cm^{-1} (bending modes).

Finally, the Raman spectrum of suseinargiuite is similar to that of the related mineral wulfenite, with a strong band at 876 cm^{-1}, agreeing with those of synthetic $Na_{0.5}Bi_{0.5}MoO_4$ (Hanuza et al., 1997).

Raman spectroscopy is a useful tool for identifying the rare molybdenum minerals found at Su Seinargiu, even if some mineral pairs (*i.e.*, mambertiite-gelosaite and ichnusaite-nuragheite) require further studies through X-ray diffraction for an accurate characterization.

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The CNMNC procedures: spreading more and more information in a faster way, without losing accuracy

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Keywords: new minerals, nomenclature, classification.

The procedures set up by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA-CNMNC) are, for some respect, obsolete. They date back to the pre-Internet era, a period in which the exchange of information between the chairman of the CNMNC and the voting members was based on photocopies distributed by surface – more rarely air – mail. The voting members were allowed two months to vote and comment on new mineral proposals, and return them again by mail. The notice of the approval of a given new mineral reached the wide scientific community only after the publication of the paper. The CNMNC used to publish on the major mineralogical journals a yearly report containing basic info on new minerals approved, without the names of the minerals.

In the last years things have changed a bit. Aiming at accelerating the dissemination of info on new minerals, the CNMNC executive issues every second month a report (CNMNC Newsletter) with some more info, *e.g.*, the full authorship, details on the type locality, and the mineral name. The Newsletter also gives notice of other actions taken by the CNMNC, such as re-definitions, discreditations, approval of nomenclature reports on selected mineral groups. These pieces of info go to the *European Journal of Mineralogy* and the *Mineralogical Magazine*, therefore they are citable, and precede, on average by several months, the publication of the full papers by the authors.

All this information is then summarized in the official "IMA List of Minerals", which is maintained and kept updated as soon as a new CNMNC Newsletter has been released, and freely distributed through the CNMCN web site [http://nrmima.nrm.se/]

Within the CNMNC, the voting procedure has been modified a bit. Now the voting members must give their votes and comments within one month, then they can read the comments made by the other members and may decide to change their vote within the second month.

The net result of this modified procedure has little or no effect outside the CNMNC. The main feeling by some researchers towards the procedures for approval of new minerals and for re-definitions of existing minerals is that they are time-consuming and out-to-date.

Therefore in the last years it happened sometimes that research groups did prefer to ignore the authority of the CNMNC on all issues related with the status of valid mineral species, and published papers which, *e.g.*, included the re-definition *de facto* of a mineral species without passing through the correct comment + voting procedure.

The net result of this behaviour is that some oddities still enter the mineralogical literature, *e.g.*, the same mineral is cited with different end-member formulae, the same chemical formula is named in different ways, the hierarchy and the relationships among supergroups, groups, and subgroups is often ignored outside the close circle of systematic mineralogists.

Piccoliite, a new mineral of the pilawite group

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Keywords: piccoliite, manganese arsenate, crystal-structure, new mineral, Montaldo di Mondovì mine, Valletta mine, Piedmont, Italy.

Piccoliite (IMA No. 2017-016), ideally $NaCaMn^{3+}_2(AsO_4)_2O(OH)$, is a new mineral topologically equivalent to pilawite-(Y) ($CaYAl_2(SiO_4)_2O(OH)$, Pieczka et al., 2015). The two minerals have a very similar structure even if the latter is monoclinic, $P2_1/c$, with unit-cell parameters a = 8.56, b = 7.26, c = 11.18 Å, β = 90.6°, V = 694.7 Å^3, whereas piccoliite is orthorhombic, *Pbcm*, with a = 8.88, b = 7.52, c = 11.69 Å, V = 780.1 Å^3. Piccoliite has been found in quartz-calcite veins at two Italian Piedmontese localities in Cuneo province: Montaldo di Mondovì mine (MM) at Borgata Oberti, Corsaglia Valley (type locality) and Valletta mine (VM), Maira Valley (cotype locality). At MM piccoliite is associated with calcite, berzeliite/manganberzeliite and, very rarely, with unnamed *REE* analogues of chernovite-(Y). At VM it is associated with quartz, hematite, grandaite, tilasite/adelite, and, rarely, with thorianite. At both localities several other arsenates have been found (VM is also the type locality of 4 arsenates plus a silico-arsenate). Another common feature is the presence of Mn minerals bearing Mn in different oxidations states Mn^{2+}, Mn^{3+}, and Mn^{4+}.

Piccoliite occurs in aggregates of black anhedral crystals, embedded in the quartz matrix, and rarely as black well-developed prisms. It is brittle with irregular fracture and has brown streak and resinous lustre. It is transparent in thin section although very deep red coloured. Mohs hardness is 5-5 ½. Reflectance percentages (R_{min} and R_{max}) at 589 nm are 7.4 and 9.3. Electron microprobe analysis resulted in the piccoliite empirical formulae, based on 10 anions per formula unit (pfu) and 6 cations pfu, $Na_{0.87}Ca_{1.20}Mg_{0.20}Mn^{3+}_{1.08}Fe^{3+}_{0.59}(As_{2.03}V_{0.03}Si_{0.01})O_9(OH)$ (MM) and $Na_{0.76}Ca_{1.29}Mg_{0.48}Sr_{0.01}Mn^{3+}_{0.63}Fe^{3+}_{0.49}\ Mn^{4+}_{0.34}(As_{1.97}P_{0.01}Si_{0.01})O_9(OH)$ (VM). Raman spectroscopy confirmed the presence of (OH) groups with a band at 3140 cm^{-1}.

The crystal structure of piccoliite was solved by single-crystal X-ray diffraction on a crystal from MM and refined to R = 2.5%. Piccoliite and pilawite-(Y) show $[^{[6]}M_2(^{[4]}TO_4)_4\varphi_2]$ chains (φ = OH) topologically similar to those occurring in the phosphate minerals palermoite $Sr_{0.5}LiAl_2(PO_4)_2(OH)_2$ and bertossaite $Ca_{0.5}LiAl_2(PO_4)_2(OH)_2$, and in the arsenate minerals carminite $PbFe^{3+}_2(AsO_4)_2(OH)_2$ and sewardite $CaFe^{3+}_2(AsO_4)_2(OH)_2$, which are all isostructural. Notwithstanding the topological similarity between their octahedral-tetrahedral chains, the structures of piccoliite and pilawite-(Y) are not congruent with those of the other species, differing in the cross-linking in the 8.5 Å direction of piccoliite.

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Micro-tomography, LA-ICP-MS and electron microprobe investigation of garnet from Val Codera granitic pegmatite (central Alps, Italy)

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Keywords: pegmatite, garnet, Val Codera, central Alps.

Selected crystals of garnets from a granitic pegmatite dike located in the Codera Valley (Novate Mezzola, Sondrio Province, Italy) have been analysed by synchrotron X-ray computed micro-tomography, laser ablation ICP-MS and electron microprobe with the aim to describe and quantify their texture and chemistry, including trace elements and *REE*. The analyses were carried out on a suite of nine trapezohedral garnets, ranging from 0.2 to 1 cm in size and from wine red to reddish brown in colour. The pegmatite dike is reported in literature as "the garnet dyke" (De Michele, 1974) and outcrops for more than 30 m in length in the glacial circle of the upper Val Codera. The dike is discordant with the foliation of both Bergell tonalite and granodiorite and it is classified as "Rare Elements Pegmatite" belonging to the mixed LCT-NYF family. The main minerals, feldspar, quartz and biotite, are associated with beryl (aquamarine) and red garnet. Other subordinate minerals are tourmaline, columbite, euxenite, monazite, xenotime, uraninite, zircon and magnetite (Guastoni et al., 2014). The garnet crystals may be considered as gem materials but they are commonly broken and contain too many inclusions. The examined samples are mainly a solid solution of almandine (30-54%) and spessartine (36-64%), less pyrope (3-7%) and 1% of grossular with the spessartine content decreasing considerably from the core to the rim together with the decrease of MnO/(MnO+FeO) ratio. All the crystals contain inclusions of niobates, tantalates, chlorite, K-feldspar and mica. The shape, spatial distribution and dimension of the inclusions have been characterized by synchrotron X-ray computed micro-tomography that allows a 3*D* imaging and identification of microstructural features of the crystals.

The rare earth elements show the chondrite-normalized pattern characteristic of magmatic type garnets, presenting considerable enrichment of heavy *REE* and strong negative Eu anomaly. The substitution of *REE* and Y in garnet occurs in the eightfold coordinated {X} site that, in these garnets, is mainly occupied by Mn^{2+} and Fe^{2+}, so the variation of both these elements controls *REE* and Y distribution. The *SREE* and Y contents increase at the crystal rim (up to 900 and 1200 ppm, respectively) showing a well definite negative correlation with Mn which presents its maximum value at the core of the crystals. This result suggests that the spessartine-rich garnet crystallisation took place from a Mn-rich melt in presence of volatiles which prevented the incorporation of Y and *REE* in the structure favouring the crystallisation of Y and *REE*-rich accessory minerals.

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Thermessaite-(NH_4): another piece of the puzzle of the evolution of sublimate deposition at "La Fossa" crater fumaroles

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Keywords: aluminum fuoride sulfates, sublimates, fumaroles, Vulcano, La Fossa crater, burning-coal steams, Anna mine.

The Al-fluoride sulfate thermessaite-(NH_4), ideally $(NH_4)_2AlF_3(SO_4)$, was deposited in 2005 as a medium to high-temperature (250-300°C) fumarole mineral at the rim of "La Fossa" crater, Vulcano, Aeolian Islands, Italy. Its mineralogical association and crystal morphology suggests it was formed by direct deposition from the fumarole gas steam as a primary phase (volcanic sublimate), and not as a secondary product formed by the interaction of liquid condensates of the gas and mineral phases previously formed (fumarolic encrustation), as always happens in fumaroles for Al-sulfates which are mainly hydrous. The mineral is the (NH_4)-analogue of thermessaite, $K_2AlF_3(SO_4)$, and corresponds to an anthropogenic phase found in the burning Anna I coal dump of the Anna mine, Aachen, Germany. The thermessaite-(NH_4) discovery at Vulcano crater fumaroles is a remarkable event, not just because of the simultaneous presence in it of NH_4, Al, and F as essential constituents, which is in itself an extremely rare feature, but also because it is the key to discussing the evolution of the mineralogical depositional processes at Vulcano fumaroles. "La Fossa" crater high temperature fumarole mineralization is worldwide known for its unique Pb-Bi sulfide and sulfosalt assemblages which deposited, starting back 1988-1990 years, throughout the thermal crisis characterizing the area. Neverthless, since the beginning of the 21st Century, although the always high temperatures at the vents, sulfides and sulfosalts reduced gradually their deposition, and the metals begun to deposit as simple chlorides and complex halide-sulfates, the latter here interpreted as the intermediate stage of the transition from halide to sulfate assemblage after the incorporation of atmospheric oxygen into the volcanic gaseous steam. The changed mineralogical associations among Vulcano sublimates and the progressive sulfosalts disappearance is interpreted as indicative of the more oxidizing conditions, probably favored by a reduction of the gas fluxes connected to the evolution of the volcanic activity and consequent mixing processes of the volcanic fumarole steam with the atmosphere in proximity of the surface. At least, the finding of thermessaite-(NH_4) in the burning Anna I dump of the Anna coal mine in Aldsdorf (Germany) stresses the similarity of volcanic exhalations with the burning-coal steams, and confirms the strong analogies in the mineralogy of the La Fossa crater fumaroles and the burning dump at Anna mine.

Platinum group minerals (PGM) in Italy

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Keywords: platinum group minerals, Ivrea Verbano Zone, sulfides, chromitite, Italy.

Platinum group minerals (PGM) are the carriers of the platinum group elements (PGE): osmium (Os), iridium (Ir), ruthenium (Ru), rhodium (Rh), platinum (Pt) and palladium (Pd). PGM occur naturally, as alloys, native elements or combinations with other elements, mainly S, As, Te, Bi, Sb, Se and O. The PGM are rare, representing only less than the 3% of the approved minerals by the International Mineralogical Association (IMA). In Italy, the occurrence of PGM have been reported only in the Ivrea-Verbano zone, located in the Italian western Alps. The Ivrea-Verbano Zone (IVZ) consists of a sequence of metasediments (the kinzigite formation), ultramafic mantle tectonites (Finero, Balmuccia, and Baldissero) and an underplated igneous complex (the basic complex). The IVZ is considered a lower continental crust section that experienced thinning, underplating, mantle plume and high-temperature regional metamorphism during the uppermost Palaeozoic. The PGM found in the IVZ form small grains, generally less than 10 µm, and occur as accessory phases in two different ore deposits: magmatic Ni-Cu-Fe sulfides and chromitite. The Ni-Cu-Fe sulfides were mined for Ni in the past, from 1855 to 1948. They can be grouped in three distinct types of mineralizations: 1) layers in the peridotite-pyroxenite-gabbro-anorthosite of the basic complex, 2) ultramafic sills intruding metasediments, 3) ultramafic discordant pipes in gabbros and metasediments. The mineralizations are composed of base metals sulphides (BMS) such as pyrrhotite, pentlandite and chalcopyrite. The discovered PGM consist of abundant tellurides of the merenskyite-moncheite-melonite series and minor sperrylite and irarsite. They occur associated with the BMS. Trace amounts of platinum group elements have been detected in the BMS. These mineralogical data indicate that PGE and chalcogenides were initially trapped in an immiscible sulfide liquid. After, they were exsolved together with Te and As to form discrete PGM. Small pods and schlieren of chromitites have been described in the peridotites of the subcontinental metasomatic mantle of the Finero. Due to their small size, the Finero chromitites were only prospected but never mined. The PGM recognized in Finero generally occur included in chromite. They comprise laurite, thiospinels of the cuproiridsite-cuprohodsite-malanite series, Ru-rich pentlandite, Pt-Cu and Ir-Rh alloys. Two potential new PGM have been also analyzed. Their composition corresponds to the following formula: $(Rh,Ir,Ru)(Sb,S)_2$ and Rh_3S_2. The Finero PGM crystallized at high temperature during the magmatic stage, under relatively high sulfur fugacity. The PGM described in the IVZ indicate that their host deposits may represent an uncommon type of mineralization formed in an extensional regime during an underplating and mantle plume event occurred in the deep crust.

The crystal structure of kaliophilite, KAlSiO$_4$, solved on the basis of electron diffraction tomography data

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Keywords: electron diffraction, structure solution, polytypism, nanomaterials.

Kaliophilite has been the first polymorph with composition near to KAlSiO$_4$ to be identified exactly 130 years ago (Mierisch, 1887). Until the advent of X-ray diffraction, this mineral was thought to be the K end-member in a simple isomorphous series with nepheline at the Na-rich side. Yet, in the following century ten further polymorphs were discovered and it eventually became clear that kalsilite is the actual K end-member of the nepheline series, both having a simple tridymite topology. Kaliophilite must instead be characterized by a significantly different structure, requiring the surprisingly large hexagonal unit cell 27.06 27.06 8.57 Å, 27 times larger than kalsilite (Gregorkiewitz, 1986).

Previous attempts to determine the kaliophilite structure by X-ray diffraction were unsuccessful. Synchrotron data from micro-crystals suggested that pseudo-symmetry and twinning could be major issues already at this scale. The problem could only recently be overcome using electron diffraction tomography (Mugnaioli et al., 2009), which allowed collecting data from a real single crystal of few hundreds of nanometers.

Kaliophilite crystallizes in space group $P3c1$, and not $P6_3$ as previously assumed. Its framework consists of alternating Si and Al tetrahedra (as confirmed by ^{29}Si MASNMR) and can be topologically described in terms of six-membered rings of tetrahedra arranged in sheets perpendicular to **c**. In tridymite all rings are equivalent, whereas in kaliophilite there are three different types of ring topologies. From a conformational point of view, kaliophilite rings can have trigonal or oval appearance, while tetrahedral bases are always eclipsed along **c**. The so-determined structure furnishes also an intuitive and straightforward explanation of the observed twinning.

The five distinct framework topologies found so far in KAlSiO$_4$ can be compared using an order parameter, FTO, defined as the order of the topological space group divided by the number of K$_2$Al$_2$Si$_2$O$_8$units (the cell content of kalsilite). FTO assumes the values 24 for kalsilite, 8 for KAlSiO$_4$-*Icmm* (Minor et al., 1978), 6 for megakalsilite (Khomyakov et al., 2002), 4/3 for KAlSiO$_4$-O1 (Gregorkiewitz, 1980) and 4/9 for kaliophilite, showing that the latter has by far the most complicated framework.

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Defining new minerals in a rapidly changing world (and in a careless community)

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Keywords: IMA, nomenclature, classification, new minerals.

The IMA Commission on New Minerals Nomenclature and Classification (CNMNC) is very efficiently taking over the complex task of defining rules for mineral nomenclature and of checking proper characterization of new mineral species. Recently, a couple of issues were raised which will strongly engage the Commission itself and the mineralogical community in general.

The first is the need of a wider acceptation of the concept of "mineral", especially since we have realized to live in the Anthropocene, where human behaviour-or misbehaviour-produces an incredible number of compounds which are proxy to minerals (Heaney, 2017). The second is the need of procedures which make easier but compulsory the use of the schemes for mineral nomenclature and classification in force. This latter is a requirement not only for the correct dissemination of science but also for an effective use of big data analysis also for Earth sciences.

Some years ago, the IMA-CNMNC Subcommittee on amphiboles defined new rules to classify and name end-member compositions in this huge but widespread and petrologically important mineral supergroup. The new rules were kept as simple as possible, and were strongly connected to the crystal-chemical rationale of the dominance of (homovalent) cations/anions involved in the crucial heterovalent exchanges. Rootnames were assigned to the ideal ^{A}(Na/vacancy) ^{C}(Mg/Al/Ti) ^{W}(OH) compositions with the charge arrangements available in the different subgroups, and prefixes were defined to highlight the dominance of other homovalent substituents. Few exceptions recognized the importance of names well embedded in the mineralogical/petrological literature.

The final report was published in 2012 (Hawthorne et al., 2012). Since then, about 15 new amphibole end-members were characterized by the same authors and approved by IMA-CNMNC, also spreading information on the new scheme. However, the report is still sporadically cited (~100 entries), the most of the petrological community still being "loyal" to Leake et al. (1997), who obtained more than 250 citations in the same period.

Hawthorne, F.C., Oberti, R., Harlow, G.E., Maresch, W.V., Martin, R.F., Schumacher, J.C., Welch, M.D. (2012): Nomenclature of the amphibole supergroup. Am. Mineral., 97, 2031-2048.

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Leake, B.E., Woolley, A.R., Arps, C.E.S., Birch, W.D., Gilbert, M.C., Grice, J.D., Hawthorne, F.C., Kato, A., Kisch, H.J., Krivovichev, V.G., Linthout, K., Laird, J., Mandarino, J.A., Maresch, W.V., Nickel, E.H., Rock, N.M.S., Schumacher, J.C., Smith, D.C., Stephenson, N.C.N., Ungaretti, L., Whittaker, E.J.W., Guo, Y. (1997) Nomenclature of amphiboles: Report of the subcommittee on amphiboles of the IMA-CNMMN. Can. Mineral., 35, 219-246.

Incorporation of Co in dolomite structure: coupled single crystal and EPMA investigations of cobaltoan dolomites from Tenke-Fungurume, D.R. of Congo

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Keywords: cobalt, dolomite, crystal structure, single crystal study, EPMA study.

Cobaltoan dolomite from Tenke-Fungurume, D.R. of Congo, can host up to 20% mol Co (Barton et al., 2014). Incorporation of Co in dolomite is definitely more relevant than in cobaltoan calcite, because of the closeness in ionic radius between Mg^{2+} (0.72) and Co^{2+} (0.745) (Shannon, 1976). A set of crystals from this locality was studied through coupled EPMA and single crystal structural refinements to investigate structural changes induced by Co incorporation in dolomite structure. As expected, Co incorporation reflects in a clear direct trend in cell volume expansion, with the *a* cell parameter more sensible than the *c* cell parameter to Co content.

Dolomite structure can be described (Reeder & Wenk, 1983) through "layers" of Me^{2+} alternating with "layers" hosting CO_3 groups along the **c** axis, approximating an hexagonal close packing. Both the Mg and Ca polyhedra are trigonally distorted, namely elongated along the threefold axis. A scrutiny of Me-O bond distances shows a direct correlation between the volume of (Mg,Co) coordination polyhedron and the unit cell volume, whereas the volume of Ca polyhedron is inversely related to the Co content hosted in Mg polyhedron. In fact, when the (Mg,Co) polyhedron expands, the oxygen atom is shifted towards Ca cation, resulting in a contraction of the Ca coordination polyhedron.

The distortion of Ca and (Mg,Co) coordination polyhedra is less pronounced in "basal" edges, namely those polyhedron edges lying perpendicular to the **c** axis, respect to "lateral" edges. The expansion of the "basal" edges of the Mg polyhedron with increasing Co content is more relevant than the slight expansion of the Mg lateral edges; the same holds for the contraction of Ca polyhedron. This is in agreement with the pronounced variation of the *a* cell parameter, directly related to the length of the "basal" edges. In dolomites, because of the difference in length between the longer Ca-O and shorter (Mg,Co)-O bonds, a "rotation" of the octahedra and of the CO_3 groups along the ternary axis, is necessary to accomplish a fit. Their orientation in calcite structure, hosting Ca octahedra all of the same size, can be assumed as starting zero point for comparison. Following Reeder & Wenk (1983) the mean rotation angle of CO_3 groups is a convenient measure of the net rotations of all the components: in cobaltoan dolomites the net rotation angles of CO_3 groups decreases with increasing Co content.

Barton, I.F., Yang, H., Barton, M.D. (2014): The mineralogy, geochemistry, and metallurgy of cobalt in the rhombohedral carbonates. Can. Mineral., 52, 653-669.

Reeder, R.J & Wenk, H.R. (1983): Structure refinements of some thermally disordered dolomites. Am. Mineral., 68, 769-776.

Shannon, R.D. (1976): Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Crystallogr., A32, 751-767.

A crystal structural study of gabrielsonite from Långban, Sweden

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Keywords: Långban, gabrielsonite, crystal structure solution, lead, arsenic coordination, arsenite.

Långban is a worldwide famous mineralogical locality, almost unique for its mineral diversity and the peculiarities of the occurring minerals.

The largest number of rare minerals occur in late-stage Pb–Mn–As–Sb-bearing fissures, typically oxychlorides, arsenates and arsenites. The great species diversity is due to the unusual, almost unique co-presence of Mn^{2+}, Mn^{3+}, Sb^{5+}, As^{3+}, As^{5+}, Pb^{2+}, Ba^{2+} and Be^{2+}. Gabrielsonite was here established as a new species by Moore (1967), with chemical formula $PbFe(AsO_4)(OH)$, space group $P2_1ma$, a = 7.86, b = 5.98, c = 8.62 Å. During the SYNTHESYS SE-TAF-5983 research visit to the Naturhistoriska riksmuseet, gabrielsonite crystals were extracted from a museum specimen (NRM#19250353), with the aim of investigating its crystal structure. Single crystal intensity data were collected at Elettra synchrotron facility, XRD1 beamline, with wavelength 0.59043 Å, resulting in 2490 unique reflections, with R_{int} = 0.0796. The gabrielsonite structure was solved in space group $Pmc2_1$, with a = 6.006(1), b = 8.661(2), c = 7.909(2) Å, and refined up to R_1 = 0.0344, wR_2 = 0.1140, S = 1.042. Two independent Pb cation sites, with half occupancy, are found in gabrielsonite structure, showing distorted four coordination, with bond lengths ranging from 2.203(5) to 2.606(7) Å. The two independent As sites have both a half partial occupancy, and present the typical trigonal pyramidal coordination, with bond lengths ranging from 1.785(6) to 1.814(5) Å. Fe shows octahedral coordination, with bond lengths ranging from 1.936(5) to 2.118(6) Å. About the anionic part, two of the four independent oxygen sites show half partial occupancy, while the two remaining anionic sites are fully occupied; a bond valence analyses allowed to identify one of these sites as a hydroxyl. The crystal structure of gabrielsonite is made up by chains of edge sharing Fe octahedra (FOC) running along **a**, whereas Pb1 and As1 polyhedra form through corner sharing “layers” (PAL) parallel to (010). As2 and Pb2 polyhedra link by corner sharing to form chains (PAC) running along **a**, with Pb and As polyhedra regularly alternating along the chain.

The structure of gabrielsonite can be described through a regular alternation along **b** of slabs hosting PAC, FOC, and PAL structural elements. Alternatively, by analogy with the minerals of the adelite-descloizite group, it can be described through a “framework” made up by FOC linked by corner sharing to AsO_3 groups, with Pb atoms hosted in the framework channels running along **a**. Present structural analyses indicate for gabrielsonite the new chemical formula $PbFeAsO_3(OH)$, to be confirmed through appropriate EPMA, EXAFS, FTIR and Raman studies.

Moore, P.B. (1967): Gabrielsonite, $PbFe(AsO_4)(OH)$: A new member of the descloizite-pyrobelonite group, from Långban. Arkiv. Mineral. Geol., 4, 401-405.

Session S8:

Naturally occurring asbestos: state of the art and strategies for investigation and management

Conveners:

Rosalda Punturo (Univ. di Catania)
Andrea Bloise (Univ. della Calabria)
Elena Belluso (Univ. di Torino)
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Workers' risks in naturally occurring asbestos contaminated sites

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Keywords: naturally occuring asbestos, workers' risks.

Naturally Occuring Asbestos (NOA) refers to fibrous minerals contained in rocks, either cropping out or buried, potentially hazardous for population and workers because of their spreading as an effect of atmospheric agents, natural, geomorphological and tectonic processes, anthropic activities.

Italian legislation (m.d. 101/2003, l. 93/2001) disciplines mapping of national areas in which asbestos may be detected. These rules classify the areas into 4 categories; category 3 is specific for areas where natural asbestos may occur in metamorphic rocks, defined "Green Stones" by m.d. 14/5/1996, Annex 4.

Green Stones mainly crop out in several areas in central and western Alps and in overlapping slopes of northern Appennines; in addition, some outcrops may be also observed in southern Italy, not yet included in the mandatory mapping, and in other lithotypes containing amphibole fibrous varieties in central Appennines, where the orogenic context determines different geological conditions.

The results of the Italian mandatory mapping provide georeferred sites included in a national database; at the present, information about Naturally Occurring Asbestos were officially transmitted to the Ministry of the Environment and the Protection of the Territory and Sea (MATTM) by only some regions such as Piemonte, Liguria, Emilia-Romagna, Toscana and Lazio.

Inail (National Institute for Insurance against Accidents at Work) is carrying out the mapping to find out all of the possible hazardous situations for workers in those sites where Naturally Occurring Asbestos may be observed and detected, and finally to provide the adequate safety actions and practices to be applied during the different working activities (*e.g.*, infrastructure and buildings construction, agriculture, excavation, mining).

The researches of the Department of Biological, Geological and Environmental Sciences of University of Catania are addressed to characterize Green Stone and derived soils by a mineralogical, geochemical and petrographic point of view, with the aim to identify and characterize the minerals of asbestos potentially present.

In this item, authors present two case studies referred to mining and urban development works and describe monitoring, risk assessment and preventive actions performed *in situ*.

Serpentinite-derived soils as carriers of toxic elements: potential for hazardous exposure in southern Italy

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Keywords: southern Italy, Naturally Occurring Asbestos (NOA), mineralogical characterization.

The aim of the present study was to investigate the concentration levels of toxic elements in twelve serpentinite-derivative soils samples developed within San Severino Lucano village (Basilicata region, southern Italy), in order to understand their possible contribution to the health problems caused by asbestos exposure. The human health risks are based on the potential fibres inhalation, when they become airborne through rocks (*e.g.*, serpentinite) weathering or human activities producing dust (Punturo et al., 2015; Bloise et al., 2016a). Moreover, asbestos minerals, for different structural reasons, have an high capability to host a large number of toxic elements and some researchers claimed that asbestos fibres may play a passive role in producing diseases as carriers of trace elements (Bloise et al., 2016b). An association with neighborhood exposure to asbestos and an increased risk of deaths from lung diseases has been documented among the persons who live near Naturally Occurring Asbestos (NOA) deposits around the world including in Basilicata region (Italy). Agricultural soil samples have been collected mainly within to urban centre and characterized by using different analytical techniques such as XRF, XRPD, ICP-MS, TEM/AEM, TG/DSC. Results pointed out as all the collected soil samples contain asbestos minerals (*e.g.*, chrysotile asbestos, tremolite-actinolite) clay minerals, plagioclase and oxides in various amounts. The values of trace metals in our soils samples are very high, four elements (Cr, Co, Ni, V) exceeds the regulatory thresholds for public, private and residential green use. A high amount of Cr and Co were present in chrysotile while Ni was predominantly found in asbestos tremolite. It is generally accepted that none of the theories alone is adequate to explain the pathogenic mechanism of asbestos. However, these data suggest that the cytotoxicity of asbestos may be also related to the minor and trace elements present as impurities in their structure. In our opinion, since the dispersion of fibres could be associated with carcinogenic lung cancer, in areas where NOA can be found, the institutions should publish local maps indicating areas with mineralogical concern and take precautions to avoid hazardous exposures of population.

Bloise, A., Punturo, R., Catalano, M., Miriello, D., Cirrincione, R. (2016a): Naturally occurring asbestos (NOA) in rock and soil and relation with human activities: the monitoring example of selected sites in Calabria (southern Italy). Ital. J. Geosci., 135, 268-279.

Bloise, A., Barca, D., Gualtieri, A.F., Pollastri, S., Belluso, E. (2016b): Trace elements in hazardous mineral fibres. Environ. Pollut., 216, 314-323.

Punturo, R., Bloise, A., Critelli, T., Catalano, M., Fazio, E., Apollaro, C. (2015): Environmental implications related to natural asbestos occurrences in the ophiolites of the Gimigliano-Mount Reventino Unit (Calabria, Southern Italy). Int. J. Environ. Res., 9, 405-418.

Monitoring of asbestos fibres both airborne and respired in Torino (Italy): identification and quantification by SEM-EDS

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Keywords: asbestos, environmental risks, SEM-EDS.

Asbestos fibres, when released into the air, can determine serious health hazards to exposed people. This research was conducted to assess the backgroung of airborne asbestos in Torino (Piedmont, Italy) with the aim to evaluate the subsequent risk of exposure for the population. These results have been correlated with the data of a previous investigation where the burden of asbestos in the lungs of subjects resident in Torino all their life and without professional exposure were detected.

Torino is surrounded by the western Alps, where natural asbestos (chrysotile, tremolite asbestos and actinolite asbestos) occur in serpentinitic bodies as accessory minerals. This geographical position and the presence of asbestos containing materials widely used in building constructions, make Torino a suitable area of study.

Air samples were collected in the 24 districts of Torino. Subsequently, morphological, dimensional and chemical data of asbestos were detected by Scanning Electron Microscopy (SEM) with annexed Energy Dispersive Spectroscopy (EDS). Because the SEM-EDS technique does not allow to discriminate some species chemically very similar, were considered as a group: tremolite/actinolite asbestos, tremolite/horneblende/edenite and chrysotile/antigorite.

The only fibers identified as asbestos belong to the group tremolite/actinolite (the presence of which is due only to natural sources, since in Italy they have not been industrially used).

Crocidolite, grunerite asbestos and anthophyllite asbestos, present in many asbestos-containing materials, were not detected in any district.

Some fibers have been identified as possible asbestos; they belong to the groups of tremolite/horneblende/edenite and chrysotile/ antigorite.

Chrysotile/antigorite fiber group was present in all districts.

The results show that, although asbestos and possible asbestos have been detected, their concentrations are lower than the limit (2 ff SEM f/l) recommended by Italian legislation (DM06/09/1994). None of the areas under examination would present a pollution situation in place.

Also among the respired fibers in lung tissue of 10 subjects the only identified as asbestos belong to the group of tremolite/actinolite. Chrysotile/antigorite fibers were detect only in lung tissue of women.

The maximum concentration of tremolite/actinolite and chrysotile/antigorite fibers detected was respectively 0.38 x 10^5 ff/gdt and 0.28 x 10^5 ff/gdt.

These values are lower than the quantities reported by the European Respiratory Society guidelines exposition (De Vuyst et al., 1998) as indicative of significant asbestos exposure for amphiboles (1 x 10^5 ff/gdt).

De Vuyst, P., Karjalainen, A., Dumortier, P., Pairon, J.C., Monsó, E., Brochard, P., Teschler, H., Tossavainen, A., Gibbs, A. (1998): Guidelines for mineral fibre analyses in biological samples: report of the ERS Working Group. European Respiratory Society. Eur. Respir. J., 11, 1416-1426.

DM06/09/1994 (allegato 2B). Normative e metodologie tecniche per campionamento e analisi mediante microscopia elettronica in scansione. In: Supplemento ordinario della Gazzetta Ufficiale n. 220.

Naturally occurring asbestos in serpentinite quarries: the Valmalenco case history

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Keywords: serpentinite, asbestos, quarries, NOA.

The Valmalenco serpentinite, a worldwide marketed dimension and decorative stone, derives from the Malenco unit (central Alps, northern Italy), a huge ultramafic body exposed over an area of 130 km^2, at the Penninic to Austroalpine boundary zone. However, the same area was once subject to chrysotile mining, from the XIX Century till 1975: for these reasons, the Valmalenco district is an excellent "naturally occurring asbestos" (NOA) case history. To evaluate asbestos exposure and contamination, extensive sampling of rocks, stream sediments, soils and airborne particulate was carried out since 2004, in cooperation with INAIL. The asbestos quantification in massive samples was performed by SEM-EDS, considering specific criteria for the NOA environment (careful sample preparation and morphological – dimensional criteria). All commercial stone varieties can be considered virtually asbestos-free, largely below the 1000 ppm threshold. On the contrary, there is a slight chrysotile contamination close to the lode selvages, micro-fractures and veins. Little amounts of chrysotile (generally < 400 ppm) were detected in stream sediments and soils, as well as traces of asbestiform tremolite (< 150 ppm, probably linked to talc lodes). The analysis of air samples (PCM, SEM-EDS and TEM) showed a complex environment, with significant analytical difficulties, especially due to abundant pseudo-fibrous antigorite fragments (falling into the WHO fibre definition criteria). The assessed occupational exposure levels (quarries) were mainly below 100 ff/L, except for some specific cases. Critical issues were detected during stone processing (especially gangsaw cutting): even the presence of small chrysotile contamination on the block surfaces can generate a lot of airborne fibres, due to the extreme mechanical fragmentation of the cutting process. The chrysotile concentrations at quarry property borders and at nearest villages were always below the Italian environmental exposure limit (2 ff/L). SEM-EDS and PCM results show no agreement, because of the abundance of extremely thin chrysotile fibrils (< 0.1 µm), undetectable by PCM. TEM investigations highlighted in some cases abundant chrysotile "micro-fibrils" (< 5 µm, not countable per WHO criteria), supposedly linked to "high-energy" mechanical processing (*e.g.*, diamond disk and block-cutter). To reduce the exposure risk, it is of crucial importance to avoid the interception of chrysotile veins during quarrying, as well as performing the block squaring-off directly in the quarry: a key issue is the continuous structural and petrographic control of quarry fronts and commercial blocks. Prevention actions were planned based on the analytical results, and are still in progress, under coordinated supervision of the local authorities. A specific protocol for airborne asbestos determination in NOA environment was recently released by INAIL.

Innovative unattended SEM-EDS analysis for fiber quantification

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Keywords: asbestos fibers, SEM-EDS.

The most widespread method for asbestos detection, *i.e.*, the phase-contrast microscopy (PCM), cannot clearly define tiny asbestos fibers and occasionally yields inaccurate results due to the subjectivity of the operator. X-ray diffraction method is useful only for concentration > 1%. Transmission electron microscopy (TEM) offers the highest resolution and the best fiber identification, but it is the most expensive method, not at all friendly to use. The scanning electron microscopy (SEM) is systematically used in health labs to analyze both the airborne asbestos and soil fibers.

Several papers on the automatic counting of asbestos fibers have been published, all of them based on optical microscopy techniques, especially phase contrast (PCM). However, as far as we know, nobody tried to use for an automatic counting of the asbestos fibers the SEM-EDS, a more reliable technique where higher resolution is coupled with the possibility to obtain a complete chemical composition of the particles. The new method is based on the matched use of the SEM-EDS analytical potentialities, *i.e.*, by identifying the particle shape first and determining their chemical composition later.

The suggested procedure consists of the following steps.

1. Particle detection is performed by thresholding Back Scattered Electron (BSE) image: threshold levels are carefully calibrated, at fixed time intervals, on appropriate standards.
2. During the image acquisition, the only particles exceeding an appropriate threshold value (morphometric filter), are classified as "fibers". In case of single straight and regular fibers, the classical maximum and minimum Feret diameters work correctly. In other more complex cases, such as bent chrysotile fibers, another method is used which accurately approximates length and diameter of the fibers. By assigning a score to the percentage of the areas overlapping, obtained from these two methods, a single fiber can be easily discriminated from an aggregate of multiple fibers.
3. The fibers are assigned to a specific asbestos mineral species by means of EDS quantitative analyses.

According to the suggested protocols, fiber counting is carried out on a limited portion (1 mm^2) of the whole filter, a significant error may result from an inhomogeneous distribution of the fibers. However, repeating n-times the counting on an equal number of fields but with random arrangement, the homogeneity of the fiber distribution is tested.

Conclusions. In addition to the reproducibility of the results, our procedure significantly enhances the productivity, consequent to the reduction of analysis time, which allows the possibility of obtaining automatic results without the presence of an operator. Using the best available resolution conditions, an average acquisition time of 2 hours per sample is estimated, *i.e.*, 8 samples could be processed during a night run.

Potential toxicity of non-regulated asbestiform zeolites

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Keywords: zeolite, fibers, hazard, cytotoxicity.

Several fibrous minerals are known in nature, some of which have physical-chemical features very useful in various industrial processes and applications. However, some of them are considered highly hazardous to human health, because of their capability to split into inhalable fibres, and of their biopersistence in the lungs. This is the case, for example, of the well-known asbestos, but also of fluoro-edenite, balangeroite and erionite. Nevertheless, there are many other fibrous minerals, not sufficiently investigated from a toxicological point of view so far, having physical and chemical features very similar to those of asbestos, such as attapulgite, "bissolite", carlosturanite, clinoptilolite, jamesonite, mesolite, mordenite, natrolite, nemalite, offretite, palygorskyte, phillipsite, picrolite, scolecite, sepiolite, thomsonite and wollastonite. Notably, several of these fibrous minerals belong to the zeolite group. Zeolites occur worldwide, including Italy, and are widely used in a great number of industrial and agricultural applications. Therefore, a potential exposure to zeolite fibres may arise during their mining, production and use.

Toxicological studies have evidenced that the mechanism by which inhaled fibres induce pathological response is strongly dependent on: (a) physical features of the fibrous mineral particles such as diameter, length and aspect ratio; (b) chemical-mineralogical features (crystal structure, bulk and surface chemical composition); (c) surface reactivity, *i.e.*, the ability to generate reactive oxygen species (ROS); (d) biopersistence. In spite of this, there are insufficient evidences in humans for the carcinogenicity of zeolites other than erionite, and there are very few data from *in-vivo* experiments for the carcinogenicity of clinoptilolite, phillipsite and mordenite, as well as the other fibrous zeolites. On this basis, due to the need to improve the knowledge on their toxicological aspects, a systematic investigation on fibrous zeolite samples by means a multidisciplinary approach is in progress. In particular, asbestiform erionite, offretite, thomsonite and mesolite have been isolated and prepared for mineralogical, chemical, biochemical, and cellular tests.

Mineralogy and textures of riebeckitic asbestos (crocidolite): the role of single *vs.* agglomerated fibres in toxicological experiments

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Keywords: asbestos, amphibole, texture, agglomeration, toxicity.

Exposition to asbestos may cause adverse effects, but a clear relationship between mineralogy and texture of fibres *vs.* toxicity is still lacking. Toxicological studies can be properly interpreted and compared only if quantitative textural, morphological and mineralogical features of fibres are determined. In this work, riebeckitic ("crocidolite") amphibole fibres were analysed by XRPD, FTIR, SEM-EDS and EMP-WDS, showing that only crystals with stoichiometry close to ${}^{A}\square\square{}^{B}\mathrm{Na}_2{}^{C}(\mathrm{Fe}^{2+}{}_{2.5}\mathrm{Mg}_{0.5}\mathrm{Fe}^{3+}{}_{2}){}^{T}\mathrm{Si}_8\mathrm{O}_{22}{}^{W}(\mathrm{OH})_2$ were present in the staring material used for *in-vitro* experiments.

Fibres deposited from solutions of 0.1, 1, 10, 25, 50, 75 and 100 mg/L were automatically counted by image analysis using SEM micro-photographs; we used equal-area ellipses of measured objects and their aspect ratios to discriminate between single and agglomerated fibres. At 0.1 and 1 mg/L the fibres are well separated, whereas between 1 and 10 mg/L they start to agglomerate. *In-vitro* tests performed on fibres deposited at these concentrations show that the toxic potential, quantified by the MTT test, increases following a curvilinear trend, with a decreasing rate at the higher concentrations, in agreement with previous studies. Therefore, an increasing amount of fibres does not induce automatically a proportional increase of toxicity; combination with image analyses on deposited fibres allows explaining this feature based on the increasing amount of agglomerated fibres. Considering that the asbestos mineralogy is constant, the main conclusion of this study is that the relationships between the amount of riebeckitic fibres *vs.* their toxic potentials cannot be properly interpreted without a careful characterization of textural data. We believe that the analytical protocol proposed here is valuable for any aero-dispersed dust in polluted environments, as well as for the interpretation of experimental *in vitro* studies.

Comparison among Italian normative methods for asbestos quantification in massive lithotypes by SEM-EDS

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Keywords: NOA concentration, grain size, excavated soils and rocks.

LD 161/2012 assessed at 1000 mg/kg the threshold to define excavated soils and rocks as asbestos-contaminated. The decree states that analyses are to be performed on the fraction undersize 2 mm and the concentration (mg/kg) has to be determined referring to the weight of the whole sample undersize 2 cm. These parameters are not considered "precautionary" from Regional Agencies for Environmental Protection, as do not provide an evaluation of the total airborne fibres potentially released from a massive rock. In fact the airborne fibres concentration depends on the initial concentration (mineralogical composition) but also on the technical processes (*e.g.*, excavation, grinding) to which the rock will be subjected.

The aim of this study was to compare how sample preparation (milling of a representative sample fraction < 2 cm or < 2 mm) and calculation of asbestos fibers concentration according to LD 161/2012 affect the result, in order to infer the most reliable method.

Selected samples from metamorphic (serpentinites, metabasalts and schists) and sedimentary rocks (clays, debris materials and soils), outcropping along the Sestri-Voltaggio Zone (central Liguria, Italy), were analysed. About 100 g of bulk rock-samples below 2 cm were sieved at 2 mm and 0.106 mm; then, the coarse (grain size > 2 mm) and medium (grain size > 0.106 mm) fractions were mechanically milled to obtain powders below 0.106 mm. The three final powdered fractions were characterized and quantified by Scanning Electron Microscopy (SEM) coupled with Energy Dispersive Spectroscopy (EDS), according to MD 06/09/94. Only fibres with length:diameter 3:1 and length > 8 µm were counted.

Preliminary results show that when chrysotile and tremolite-actinolite fibres are present, they occur in all fractions, increasing in milled coarse and medium fractions. On the whole, length and diameter of countable fibers were not significantly different between natural and milled powders. In serpentinites, chrysotile bundles occurred in natural powders, whereas milled powders were characterized by a high number of chrysotile fibrils below counting dimensions.

On the whole, the results of calculations according to LD 161/2012 decreased the concentration from 80% to 50% compared with total asbestos analyses.

Italian Legislative Decree No. 161/2012. Regolamento recante la disciplina dell'utilizzazione delle terre e rocce da scavo

Italian Ministerial Decree No. 06/09/1994. All. 2B. Determinazione quantitativa delle concentrazioni di fibre di amianto aerodisperse in ambienti indoor mediante microscopia elettronica a scansione.

Correction factors for the effect of shape and thickness of SEM-EDS microanalysis of asbestos fibres by Monte Carlo analysis

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Keywords: asbestos, SEM-EDS microanalysis, Monte Carlo simulations, correction factors.

SEM-EDS quantitative micro-analysis of asbestos mineral fibres still represents a complex analytical issue because of the variable fibre shape and small thickness (< 5 µm) compared with the penetration depth of the incident electron beam (Paoletti et al., 2011; Moro & Valdrè, 2016).

Size and shape of micro- and sub-micrometric particles may cause large errors in the quantification due to particle effects on the generation and measurement of X-rays from the sample. These effects are related to the elastic scattering of electrons in the finite size (mass) of the fibre, which is strongly influenced by the average atomic number. The thickness of the particle is key, for a given mean atomic number, with a shape component affecting the absorption and fluorescence contributions to the correction routine.

To overcome these issues empirical methods were developed, however they are cumbersome and need characterized standards for thickness, geometry and composition (Paoletti et al., 2011).

Here we present correction factors obtained by Monte Carlo analysis for the thickness and shape effect of SEM-EDS and microprobe microanalysis of chrysotile, crocidolite, amosite, anthophyllite, tremolite and actinolite asbestos.

NIST DTSA-II (Ritchie, 2017) was used to simulate electron transport, X-ray generation and detection in asbestos bundles and fibres of variable thickness and shape on a pure carbon holder. We report the results obtained on 100 µm long fibres and bundles of circular and square section and thicknesses from to 0.1 µm to 10 µm. Realistic experimental conditions, such as sample geometry, SEM set-up and detector physics were taken into account. An electron probe of 40 nm in diameter was simulated, focussed in parallel illumination onto the surface of the fibre or bundle, in a mid position with respect to the edges. The modelled EDS detector has a resolution of 130 *e*V measured at Mn*K*α, an elevation angle of 40°, and an azimuthal angle of 0°. The influence of thickness and shape on the simulated spectrum was investigated for electron beam energies of 5, 15 and 25 k*e*V. A strong influence of the asbestos fibres and bundles thickness and shape was observed. In general, the X-ray intensities as a function of fibre thickness showed a considerable reduction below about 0.5 µm at 5 k*e*V, 2 µm at 15 k*e*V, and 5 µm at 25 k*e*V, with a non-linear dependence. Specific correction parameters, k-ratio, for the asbestos fibre thickness effect are here presented.

Moro, D. & Valdrè, G. (2016): Effect of shape and thickness of asbestos bundles and fibres on EDS microanalysis: a Monte Carlo simulation. IOP Conf. Series: Mater. Sci. Eng., 109, 012011.

Paoletti, L., Bruni, B.M., Gianfagna, A., Mazziotti-Tagliani, S., Pacella, A. (2011): Quantitative Energy Dispersive X-Ray Analysis of Submicrometric Particles Using a Scanning Electron Microscope. Microsc. Microanal., 17, 710-717.

Ritchie, N.W.M. (2017): NIST DTSA-II software: www.cstl.nist.gov/div837/837.02/epq/dtsa2/index.html

Fibrous minerals in New Caledonia: a comparison of different analytical strategies for environmental monitoring

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Keywords: asbestos, antigorite, Raman portable, monitoring, New Caledonia.

The New Caledonia is one of the largest world producers of nickel ore which is formed by the alteration of ultramafic rocks. Mining activity, focused on nickel extraction from lateritic ore deposits, must deal with the natural occurrence of asbestos and fibrous minerals. Almost all outcrops of geological units and open mines contain serpentine and amphibole, also as asbestos varieties (Lahondère, 2007). Owing to humid tropical to sub-tropical conditions, weathering processes and supergene mineralizations are ones of the main responsible for fibres realise of asbestos minerals.

The presence of fibrous minerals in mining exploitation and storage sites requires attention due to health problems and for the safety of the operators. In order to decrease the risk due to the exposition, the prevention plan followed by the mining sector involves a classification based on colour, morphology and release of fibres. These parameters depict an alteration status where the major risk is linked to an increasing degree of alteration, and to a greater capacity in the emission of fibres.

This work aims to test and compare different mineralogical and petrological methods to improve the diagnostic strategy required for the establishment of an effective environmental monitoring system.

A set of about fifty asbestos samples including serpentine (chrysotile, antigorite) and amphibole (tremolite), all fibrous and sorted by their different degree of alteration, was analysed. A particular attention has been dedicated at the study of fibrous antigorite, recognized as asbestos only by Caledonian legislation, but still not by European law.

Data obtained with the more traditional techniques-such as polarized light microscopy, X-ray diffraction, scanning electron microscopy (SEM-EDS), and transmission electron microscopy-have been completed by the employment of more specialized tools as phase contrast microscopy (PCM), Raman spectroscopy, and thermal analysis (DTA). Moreover, analytical performances of a Raman portable equipment, to be used in field observation, were assessed against other laboratory methods. Portable Raman was successfully tested on the mining front at the open mines of Balangero (Italy) and Tontouta (New Caledonia) under normal environmental conditions (sun, strong wind, high temperature, etc.).

Preliminary results have confirmed PCM and Raman spectroscopy as the decisive tools in the detection and characterization of asbestos fibres for both serpentine and amphibole. Furthermore, these methods have proved to be extremely effective even in presence of strongly fibrous and altered samples.

Lahondère, D. (2007): L'amiante environnemental en Nouvelle Calédonie: Expertise géologique des zones amiantifères. Evaluation des actions engagées. BRGM/RP-55894-FR.

Physical-mechanical and petrophysical properties of serpentinite rocks employed as stone material and environmental implications

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Keywords: serpentinite, physical-mechanical properties, petrophysics, historical quarries, Naturally Occurring Asbestos, Calabria, Italy.

The present study focuses on serpentinite rocks, which have been widely employed and marketed for building and ornamental purposes since pre-historical times.

For this reason, we chose some serpentinite key outcrops (Punturo et al., 2015; Bloise et al., 2016), such as those ones located at quarries and road cut in the area of Gimigliano and Conflenti towns (Sila Piccola, northern Calabria), to collect representative samples for specific laboratory analyses. However, they could potentially be rich in asbestos minerals and, as a consequence, have a negative impact on the environmental quality.

In order to highlight the release, if any, of asbestiform minerals from serpentinites we carried out salt crystallization tests and measured the physical-mechanical as well as petrophysical properties of serpentinites before and after the deterioration tests. In particular, we carried out seismic investigation ad Uniaxial Compression tests together with porosity determination. Furthermore, the serpentinite rock samples have been also investigated by means of Polarized Light Microscopy (PLM), X-ray powder diffractometry (XRPD), Scanning Electron Microscopy combined with Energy-Dispersive Spectrometry (SEM/EDS).

Results revealed that, when natural outcrops are disturbed by human activities, the weathering processes and consequent release of NOA in the environment may be enhanced. This also holds after the "change in service" of serpentinites from natural outcrops to artefact and monuments.

Finally, obtained results can be used to take decisions for the realization of health protecting measures during human activities such as road construction and quarry excavations and may also provide new data for the compulsory Italian mapping of natural sites that are characterized by the presence of the asbestos commonly known as NOA (Naturally Occurring Asbestos).

Bloise, A., Punturo, R., Catalano, M., Miriello, D., Cirrincione, R. (2016): Naturally occurring asbestos (NOA) in rock and soil and relation with human activities: the monitoring example of selected sites in Calabria (southern Italy). Ital. J. Geosci., 135, 268-279.

Punturo, R., Bloise, A., Critelli, T., Catalano, M., Fazio, E., Apollaro, C. (2015): Environmental implications related to natural asbestos occurrences in the ophiolites of the Gimigliano-Mount Reventino Unit (Calabria, Southern Italy). Int. J. Environ. Res., 9, 405-418.

Mineralogy as useful tool for medicine: the study of hazardous materials in biological tissues

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Keywords: asbestos fibers, scanning electron microscopy, micro-Raman spectroscopy, biological tissues.

The relationship between the minerals defined by the Law "asbestos" – actinolite, amosite, anthophyllite, crocidolite, tremolite, chrysotile – and the development of severe diseases of the respiratory system (*e.g*., asbestosis, mesothelioma, pulmonary carcinoma) is now universally accepted. Moreover other fibrous minerals are identified responsible of asbestos-related diseases and recognized even more carcinogenic than asbestos. A deep characterization of the fibers and of the impurities and phases lying on the fiber surfaces is essential to the comprehension of the carcinogenicity mechanisms of these mineral phases. On the other hand, more and more studies are devoted to study the relationship between asbestos and development of cancers affecting other parts of the human body, in particular gastrointestinal system. The mineralogy may be a very useful support to these studies by identifying the presence of asbestos fibers, or fibers considered carcinogenic, in tissues of patients affected by these diseases and by identifying the tissues in which the fibers are incorporated.

During the last years, our research group applied Environmental Scanning Electron Microscopy and micro-Raman spectroscopy, two techniques not requiring particular preparation of the samples, to identify fibrous mineral phases directly in histological sections. The samples were sections from patients affected by different diseases, not only respiratory, or from mice in which asbestos fibers were injected in the peritoneum. The results obtained on the different cases analyzed will be presented (Rinaudo et al., 2010; Musa et al., 2012; Croce et al., 2013; Grosso et al., 2015, 2017).

Croce, A., Musa, M., Allegrina, M., Rinaudo, C., Baris, Y.I., Dogan, A.U., Powers, A., Rivera, Z., Bertino, P., Yang, H., Gaudino, G., Carbone, M. (2013): Micro-Raman spectroscopy identifies crocidolite and erionite fibers in tissue sections. J. Raman Spectrosc., 44, 1440-1445.

Grosso, F., Randi, L., Croce, A., Mirabelli, D., Libener, R., Magnani, C., Bellis, D., Allegrina, M., Bertolotti, M., Degiovanni, D., Rinaudo, C. (2015): Asbestos fibers in the gallbladder of patients affected by benign biliary tract diseases. Eur. J. Gastroenterol. Hepathol., 27, 860-864.

Grosso, F., Croce, A., Trincheri, N.F., Mariani, N., Libener, R., Degiovanni, D., Rinaudo, C. (2017): Asbestos fibres detected by scanning electron microscopy in the gallbladder of patients with malignant pleural mesothelioma (MPM). J. Microsc., 266, 48-54.

Musa, M., Croce, A., Allegrina, M., Rinaudo, C., Belluso, E., Bellis, D., Toffalorio, F., Veronesi, G. (2012): The use of Raman spectroscopy to identify inorganic phases in iatrogenic pathological lesions of patients with malignant pleural mesothelioma. Vibr. Spectrosc., 61, 66-71.

Rinaudo, C., Allegrina, M., Fornero, E., Musa, M., Croce, A., Bellis D. (2010): Micro-Raman Spectroscopy and VP-SEM/EDS applied to the identification of mineral particles and fibres in histological sections. J. Raman Spectrosc., 41, 27-32.

Asbestos tremolite contamination in a feldspar sand quarrying site: considerations

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Keywords: tremolite, feldspar, "ban asbestos".

In 2015 has been recorded the presence of contamination by asbestos tremolite fibers in a feldspar mine in Sardinia. Feldspars are minerals common in the world and used in great amount in different productive processes.

Among these, an important use is in the ceramic industry, as well as in those of glass, cement and steel industry. The tremolite asbestos, which is an amphibole mineral, is notoriously present as a contaminant of other minerals (as talc, as vermiculite and also as a natural contaminant of chrysotile).

The presence of tremolite in feldspars has not been significantly reported to human health aspects, except some studies of strict geological nature.

Starting from investigations, in the Lazio region, in companies that used feldspar from a mine in Sardinia, an important problem of environmental and occupational exposure to asbestos fibers, has been highlighted in traditionally "unsuspicious" materials.

Identifying and confirming the presence of tremolite fibers is complicated and it requires many instrumental analisys (MOCF, MOLP, SEM, DRX), but, at the same time, the attention must also be focused on the protection of public health. For this reason, as a precaution, the mine is currently on Lockdown.

Therefore we suggest the discussion on banning the use and marketing of asbestos-containing products as recalled in article 1, paragraph 2, Law 257/92 and, in particular, their mining and their handling must be related to the risk for health and regulated by specific law.

NOA, natural soil contamination: what analyzes, what assessment

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Keywords: contaminated sites, earth and rock excavation, asbestos wastes.

Physical chemical characterization and environmental quality assessment of soil is required in many situations and it is regulated by several norms depending on the context, mainly in the case of: "contaminated sites" DLgs 152/06 and "earth and rocks for excavation" Decree 161/12.

In soils with the natural presence of asbestos-NOA, characterized by concentrations of asbestos fibers, chrysotile and /or amphibole, which are often very different from zone to zone, there are analytical difficulties about the identification and quantification of a parameter that requires a specific and specialistic approach.

There is, at the moment, a lack of an official method, as also of accurate concerning the environmental and health aspects.

In regard to materials made up of stones, we can have different situations:

- excavating, moving the soil for infrastructural works directly in those areas or sites with natural presence of asbestos-NOA (*e.g.*, executing: road and motorway works, engineering plants as water, telephone or energy network, etc.);
- use of serpentinitic crushed stone "conform" to DM 14/5/1996 in geographic areas different from those of origin;
- management of areas where stones have been used as mentioned above.

In cases of anthropogenic contamination of wastes containing asbestos (*e.g.*, fragments of slabs, insulating residues, residues of various articles) found on the soil or subsoil, the characterization and the reclamation of the soils become complicated in geologically sites with NOA.

Geographical areas with NOA presence are easily identifiable by national and regional geological maps. The areas affected by the presence of NOA have been mapped under DM 101/2003 (in particular mining sites) and some regions carried out specific studies.

This communication is intended to present some considerations and some procedural proposals.

Airborne fibers monitoring during railway tunnelling across a serpentinite lens (Voltri Massif, Italy)

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Keywords: chrysotile, NOA, airborne fibers monitoring, SEM-EDS.

The tunnelling of Terzo Valico, TAV between Genoa and Milan involves excavation across a complex geological setting characterized by ophiolitic formations, potentially containing naturally occurring asbestos (NOA).

International organizations of health and safety agree on the absence of a "safe" level of asbestos fibres in air and require keeping as low as possible their concentration (IARC, 2012; WHO, 2014). Therefore, the management of tunnelling activities in rocks containing NOA presents critical issues for occupational and environmental exposure to asbestos.

In this work, data of 871 airborne monitoring carried out during 100 m of tunnelling excavation across a serpentinite lens, intercalated within calcschists, in the Cravasco adit (Voltri Massif), are reported.

Airborne dusts, collected on polycarbonate membrane, were analysed by Scanning Electron Microscopy (SEM) equipped with Energy Dispersive Spectroscopy (EDS), according to MD 06/09/94 All. 2B.

Serpentinite occurrence at the front and our results of fibres concentration above 2 ff/L caused the stop of excavation. Therefore, a new system of exhaust ventilation, a dedusting equipment and a physical compartmentation of tunnel in 3 zones (A-B-C) were installed, in order to reduce the asbestos concentration and resume the activities.

Results of sampling, carried out in different zones of the tunnel during the first 27 cycles of excavation, were discussed in working tables constituted by Contractor, ARPAL, ASL, DISTAV. This allowed us to obtain information about the chrysotile fibres dispersion from the rock front to the exit of the tunnel, detect the significant parameters of monitoring and analysis (stations number, frequencies, membrane diameter, volume sampling, personal *vs.* static environmental sampler, high analytical sensitivity *vs.* quick results) and identify acceptable levels of fibres in air according to used personal protective equipments (LD 81/2008).

Asbestos concentration was above 10 ff/L in 75% of samples coming from zone A during excavation, but this value quickly decreased in time (5.4% for zone A during no-excavation) and space (2% for zone B and none for zone C), demonstrating the effectiveness of the actions carried out to reduce fibres dispersion from the excavation zone to other zones of the tunnel and the outside. In particular, the asbestos concentration was below 1 ff/L in 54%, 80% and 100% of analyses performed in zone B, C and outside square (zone D), respectively.

IARC (2012): International Agency for Research on Cancer . Asbestos. IARC Monogr. Eval. Carcinog. Risks Hum., 100C, 219-309.

Italian Ministerial Decree No. 06/09/1994. All. 2B. Determinazione quantitativa delle concentrazioni di fibre di amianto aerodisperse in ambienti indoor mediante microscopia elettronica a scansione.

Italian Legislative Decree No. 81/2008. Testo unico sulla salute e sicurezza sul lavoro.

WHO (2014): Chrysotile Asbestos. World Health Organization, Geneva, Switzerland.

Naturally Occurring Asbestos in Calabria

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Keywords: Naturally Occurring Asbestos, Calabria, tremolite.

Naturally Occurring Asbestos (NOA) can form in several types of geologic settings depending on the rock types and geologic history of an area. Calabria region has many settings that are favorable for the presence of NOA because of the variety of older metamorphic and igneous rocks and by the multiple episodes of deformation that many of these rocks have undergone.

This paper reports a contribute to the first map data on a regional scale of NOA, according to the Italian Decree 101/2003, related to mining activities in use or disused (quarries for inert materials and ornamental stones extraction), and to natural outcrops with no economic use.

In Calabria NOA are mainly concentrated in the ophiolitic sequences belonging to the Gimigliano-Mount Reventino Unit in Sila Piccola (Punturo et al., 2015) and along the Coastal Chain.

Identification of fibrous mineral material collected during fieldwork was obtained by different analytical techniques: optical microscopy, scanning electron microscopy combined with energy dispersive spectroscopy, X-ray diffraction and Fourier transform infra-red spectrometry analyses.

The amphibole-group asbestos minerals are the most common type of asbestos found in Calabria, where it frequently occurs such as overlapping slicken-fibres and/or slip-fiber veins in areas of ultramafic rocks and serpentinite and in areas of faulting and shearing (Campopiano et al., 2015).

Chrysotile also occurs, but is less common, in serpentinite mostly derived from peridotite. Other asbestiform minerals as antigorite and chlorite, suspected of posing a health risk, were also found.

In order to identify the risk levels of the individual sites and establish risk analysis, a specific procedure was adopted, implicating the use of a specific algorithm development of which was entrusted to Inail Dipia by the Ministry for the Environment.

Moreover, a map of ophiolitic rocks and NOA occurrence was developed. The map is intended to aid cities, special districts, and state agencies in determining where they may wish to consider actions to minimize generation and exposure to dust that may contain NOA. Geologic information may also be useful in designing site development to avoid potential long term exposure to NOA or in developing monitoring or mitigation plans to minimize potential short term NOA exposures during construction activities.

Angelosanto, F., Bruno, M.R., Campopiano, A., Conte, M., De Vincenti, F., Fera, N., Giardino, R., Iannò, A., Iavicoli, S., Olori, A., Oranges, T., Spadafora, A., Villella E. (2015): Amianto presente in alcuni affioramenti ofiolitici della regione Calabria. Atti del 32° Congresso Nazionale AIDII, Varese, 24-26 giugno 2015.

Apollaro, C., Bloise, A., Catalano, M., Critelli, T., Fazio, E., Punturo, R. (2015): Environmental implications related to natural asbestos occurrences in the ophiolites of the Gimigliano-Mount Reventino Unit (Calabria, Southern Italy). Int. J. Environ. Res., 9, 405-418.

Airborne monitoring in tunnel excavation, a highly dusty environment with Elongated Minerals Particles (EMP)

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Keywords: mineral dust, EMP, air tunnelling monitoring, asbestos.

The Terzo Valico railway project is part of the Rhine-Alpine Corridor, within the trans-European transport network, connecting the most populated and industrialised European regions. The new line will be 53 km long, 37 km of which under tunnels, and will improve transports between Genoa harbour and rest of northern Italy.

This paper reports the results of 719 sampling of airborne fibres collected inside tunnels under construction, aimed to assess and prevent asbestos professional exposure, according to an environmental monitoring protocol drawn up for Terzo Valico tunnelling.

The data refer to the first 7.25 km of tunnels excavated in Liguria from September 2014 to April 2017. The concentration of asbestos fibres was determined by means of a Scanning Electron Microscope equipped with Energy Dispersive X-ray Spectroscopy device (SEM-EDS).

Tunnelling air is characterized by high dustiness caused by presence of carbonaceous particles and elongated minerals particles (EMP) such as titanium dioxide, calcite, chlorite, mica and feldspar and amphiboles cleavage fragments with dimensions in agreement to parameters described in the LD 81/2008 (length > 5 mm, diameter < 3 mm and length to diameter ratio > 3:1).

In 719 analysed samples during excavation, asbestos fibres concentration was below detection limit (DL 0.3 ff/L), between DL and 2 ff/L and above 2 ff/L in 559 (77.75%), 119 (16.55%) and 16 (2.3%), respectively. Moreover, 25 samples (3.47%) were unreadable due to the excessive particulate deposited on the membranes.

The overload of filters with mineral dust was the most significant problem of the analytical activity during tunnelling excavation. Italian legislation (MD 06/09/1994) establishes an air sampling volume of 3000 L, however this decree is designed for indoor environments after remediation. Therefore, a compromise between sampling protocol, analytical method and improvement of measures on ventilation systems was necessary to obtain readable filters in order to assure time-effective monitoring and workers safety.

Our results showed that air monitoring can objectively confirms in a relative short time the presence of asbestos minerals and other EMP providing information about the nature of the lithotype at the rock front.

Italian Legislative Decree No. 81/2008. Testo unico sulla salute e sicurezza sul lavoro.

Italian Ministerial Decree No. 06/09/1994. All. 2B. Determinazione quantitativa delle concentrazioni di fibre di amianto aerodisperse in ambienti indoor mediante microscopia elettronica a scansione.

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The methodological restoring of Rhegion Greek eastern walls by analysing their components: clay and sandstone

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Keywords: walls, raw clay, sandstone, restoration.

The Greek eastern *Rhegion* walls were constructed in two successive periods each of them characterized by different techniques. The most ancient-dating back to the 5th Century b.C. – made with raw clay, the other – dating back to the 4th-5th Century b.C. – built in sandstone squared blocks. The study of this architectonic monument has the aim of analysing in detail the material used for its construction in order to spot the place of origin of the material themselves and, in the meantime, to suggest the best restoring method to avoid the time wear.

Tarquinia's "macco" as a pictorial substrate and processes of degradation in hypogea linked to seasonal cycles

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Keywords: macco, painted tombs of Tarquinia, meteoclimatic cycles, seasonal cycles, degradation, hypogeum.

The meteoclimatic cycles are able to damage the materials of Cultural Heritage as to them many classical chemical reactions are associated: redox, acid/base, complexation, dissolution. More, it is enough a bias of 1-2 degrees to bring to evaporation/condensation cycles of water able to combine their effects with those ones of the above reactions. Macco is a complex material which suffers from the described situation (Paribeni, 1970). Particularly acid base and complexation reactions are involved, both relating to the Lewis's theory. Macco's composition with a relevant presence of acid metals such as Al, Fe, Si, combined with porosity and ability to adsorb water, brings to two peculiar characteristics: higher resistance to acid pollutants, the most present in the anthropic zones and media, and ability to bind basic oxide pigments, so stabilizing paintings on it. Really water adsorption is still favoured by the above said acid nature of metal as able to bind water through the lone pair of oxygen atom. This water can dilute superficial aggressive conditions without damage of dissolution due to the macco's determined insoluble composition.

In this research we characterized macco for its chemical and physical properties and the obtained results are the basis for the above conclusions. Methods used for its characterization were the determination of water absorption by full immersion, the determination of water absorption by capillarity, the determination of the drying index, the determination of moisture content in painted walls, resilient modulus tests under repeated freeze-thaw cycles, analysis of mercury porosimetry for the evaluation of pore shape and intrusion-extrusion hysteresis, TGA, XRD, Raman and IR Spectroscopy, SEM-EDS.

Paribeni, M. (1970): Cause di deperimento e metodi di conservazione delle pitture murali delle tombe sotterranee di Tarquinia. Sistema, Roma

Petrography and source origins of the main rock-types used for architectural and sculptural elements of the Alexandria Lighthouse archaeological site (Alexandria, Egypt)

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Keywords: Egypt, Alexandria Lighthouse, architectural elements, petrography, provenancing.

The Alexandria Lighthouse archaeological site is located just off the coast of the modern city of Alexandria and it is basically underwater today. Its ruins consist of three thousand architectural and sculptural elements which lie on the seabed at depths of six to eight meters.

During a field inspection of the stone blocks, column shafts and bases, sculptures and obelisks that have been salvaged from the seabed since 1994 and are currently displayed or stored at different locations in Alexandria City, a series of samples (also from objects that are still under water) was collected and studied.

This work summarizes the results of a detailed petrographic and geochemical characterization (OM, XRD, XRF/ICP-AES, $\delta^{13}C$ and $\delta^{18}O$ analyses) of some of the Alexandria Lighthouse monumental objects made of sedimentary and magmatic rocks; it also offers pointers to their corresponding ancient quarries of origin. The studies reveal that these archaeological items are made of local granite/alkali-granite, diorite/granodiorite, quartzitic sandstones (orthoquartzite) and greywacke (siltstone or sandstone). The source area of each type of constituent stone of the archaeological samples is established, and the corresponding ancient quarries identified where possible (Aswan Neoproterozoic granitoids, Gebel Ahmar and Wadi Hammamat). The results expand the knowledge of the real nature of the Alexandria Lighthouse building and ornamental stones and provide inspiration for future investigations and researches.

In situ Raman and pXRF spectroscopic study on the mural paintings of Etruscan Tarquinia tombs

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Keywords: XRF, Raman spectroscopy, pigments Etruscan painting.

The painted graves of Tarquinia are the more important existing pre-Roman record of classical painting in the Mediterranean. The monumental series of funereal paintings, dated between the seventh and second Century BC, faithfully reflect the Etruscan civilization, of which they form a unique source of knowledge. They also represent indirect evidence of Greek paintings, which were almost completely lost. These subterranean chambers are a significant chapter in the history of restoring ancient paintings. In fact, some of the most important interdisciplinary studies regarding the deterioration in underground environment, and possible preventive measures, have been based on these tombs (Cecchini, 2012).

The main goal of this research is the identification of pigments and their substrates in order to clarify the unknown aspects of the materials and techniques used and, therefore, to furnish fundamental information in order to plan suitable restoration and conservation. With this aim in mind, complementary non-destructive and *in situ* handheld X-ray fluorescence and Raman spectrometers for the investigation of wall paintings from nine of the more important Tarquinia graves (Leonesse, Fior di Loto, Cacciatore, Barone, Bartoccini, Tori, Giocolieri, Caccia e Pesca and Gioglioli) allowed us to provide a new perspective on the use of color in Etruscan art.

In particular, the combined mineralogical and chemical approach evidenced the use, together with common pigments of precious dyes in some of the more notable paintings. The value of these pigments gives additional importance to the Etruscan Necropolis.

Further information was obtained on the white-gray preparatory layer, that plays a key role in the comprehension of the painting technique that is one of the most debated aspects about the Tarquinia wall paintings.

On the whole, the obtained results will be useful for future restoration and conservation strategies. In conclusion, the Tarquinia site is an open-air laboratory where new diagnostic needs are essential to innovative technical approaches.

Cecchini, A. (2012): Le tombe dipinte di Tarquinia. Vicenda conservativa, restauri, tecnica di esecuzione. Nardini, Firenze, 231 p.

Mineralogy, the hedgehog, and the fox: the contribution of Mineral Sciences to Archaeometallurgy in the light of a new conceptual framework

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Keywords: mineralogy; archaeometallurgy; metal production and manufacturing; case studies.

The recent advances and noteworthy contribution of Mineralogy to a relatively novel discipline like Archaeometallurgy are a good demonstration of the validity of the "fox" approach, in the sense of the famous Isaiah Berlin's metaphor, *i.e.*, of a multifaced, pluralistic view of this science against the "hedgehog"'s conservative approach of a unique self-organizing principle (claiming to a quasi-ontological distinction between Mineralogy and Mineralogical Applications*)*. Archaeometallurgy deals with all aspects of metal production, distribution, and usage in the history of mankind, dating back about 10,000 years ago. Modern mineralogy is a discipline that is intrinsically suited to face archaeometric problems, especially in the field of archaeometallurgy, which requires contributions from areas as diverse as geochemistry, petrology, materials science, metallurgy, archaeology, engineering, and many more (Artioli, 2012). In fact, the characterization and identification of ore sources, the study of ancient metal production and manufacturing, and the reconstruction of the trade of raw metals and finished metallic items, requires expertize in different fields like optical microscopy, physical, chemical and isotopic analysis, and experimental reconstruction (Rehren & Pernicka, 2008), all of which are well-mastered by mineral scientists. Examples of different applications of mineralogic studies (intended in a broad sense) to different steps of the archaeometallurgical cycle will be provided.

Artioli, G. (2012): Archaeometallurgy: the contribution of mineralogy. In: "Archaeometry and cultural heritage: the contribution of mineralogy", J.M. Herrero & M. Vendrell, eds. Semin. Soc. Españ. Mineral., 9, 65-78.

Rehren, T. & Pernicka, E. (2008): Coins, artefacts and isotopes – Achaeometallurgy and archaeometry. Archaeometry, 50, 232-248.

Copper, silver and lead production in the Colline Metallifere district (southern Tuscany) in the High Middle Ages: recent results and open questions within the frame of the ERC "nEU-Med" Project

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Keywords: Colline Metallifere, High Middle Ages, copper, silver and lead production, coins, lead isotope composition.

The nEU-Med Project "*Origins of a new economic union (7th-12th Centuries): resources, landscapes and political strategies in a Mediterranean region*" has been granted from the European Research Council (ERC). The project takes place in the Maremma region of south-west Tuscany (Italy), between the Colline Metallifere and the Tyrrhenian Sea. The project, started in October 2015, is aimed to understand the processes of economic growth in this area between the 7th and 12th Centuries AD, with particular emphasis on the role played by mineral exploitation and metal production. In fact, the Colline Metallifere district hosts a number of Cu-Pb-Zn(Ag) vein deposits which fed a long-living mining and metallurgical industry (Benvenuti et al., 2014). There are still many open questions concerning, for instance, the changes and evolution of metal production in the period of interest (almost six centuries); the metallurgical chain from ore to metal, particularly for silver; whether and to what extent metal production (mainly silver and copper) in the district was purposed for coinage. We provide an up-to-date review of the state of the art of our knowledge (what we know and, mainly, what we still do not know) based on detailed archaeometallurgical surveys carried out in different sites (Montieri, Canonica di San Niccolò, the mining castle of Cugnano, and Vetricella). In addition we provide the first results obtained from analysis (lead isotope composition) of a number of silver and copper-silver coins circulating in the Colline Metallifere region. Results permit to draw some preliminary conclusions about the provenance of coinage metals used in this territory in the High Middle Ages.

Benvenuti, M., Bianchi, G., Bruttini, J., Buonincontri, M, Chiarantini, L., Dallai, L., Di Pasquale, G., Donati, A., Grassi, F. Pescini, V. (2014): Studying the Colline Metallifere mining area in Tuscany: an interdisciplinary approach. In: "Research and preservation of ancient mining areas", J. Silvertant, ed. Valkenburg aan de Geul, Trento, 261-287.

Raman spectroscopy characterization of beryls by means of portable spectrometers: a comparative study

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Keywords: Raman Spectroscopy, mobile equipment, *in situ* spectroscopy, beryl, emerald.

In recent years the use of Raman spectroscopy as a gemological tool has largely increased. In particular, in the conservation science field, the possibility to have a quick, non-destructive, contactless identification of a gem, maybe mounted on precious archaeological item, made this technique an invaluable procedure for gemologists and conservators. In addition, the use of mobile Raman spectrometers can allow an immediate identification of gemstones, directly on the outcrops, during prospection campaigns.

In this work we performed a large comparison of seven different portable Raman spectrometers to use for the first identification of gemstone minerals in non-laboratory environment. Beryls, in emerald and aquamarine varieties, in different forms and of different origin (including faceted gems, raw crystals and samples collected *in situ*) have been chosen to test the equipments. Beryl was chosen because of the strong Cr^{3+} fluorescence, making it a really testing mineral for Raman spectrometers, and for the large amount of information that is possible to collect on this mineral by Raman spectroscopy, at least using micro-Raman apparatus (Bersani et al., 2014). The possibility to obtain detailed information on the analyzed beryls also using portable spectrometer, further than the simple identification, was thoroughly investigated. The characterization of the spectrometer was completed by the analysis of some other standard minerals.

Bersani, D., Azzi, G., Lambruschi, E., Barone, G., Mazzoleni, P., Raneri, S., Longobardo, U., Lottici, P.P. (2014): Characterization of emeralds by micro-Raman spectroscopy. J. Raman Spectrosc., 45, 1293-1300.

Rupestrian churches in the Matera Unesco site (southern Italy): degradation patterns and textural characterization of the Gravina Calcarenite

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Keywords: rupestrian churches, Gravina Calcarenite, southern Italy, degradation processes, textural characterization.

Degradation of stone materials is a considerable problem that affects cultural heritage in all parts of the world. In Matera, the 2019 Culture Capital and UNESCO site, the Pleistocene Gravina Calcarenite is the main natural stone used to build. This gives a unique aspect to the ancient part of the town, called *Sassi*, and especially to the rupestrian churches. The *Sassi* are an awesome example of a rock-cut settlement where architecture is fit to the geological and geomorphological features of the area. Here grottoes, churches, crypts and houses, are partially dug and partially built (http://whc.unesco.org/en/list/670). Many constructions are in a deteriorated state due to weathering processes and to biological and anthropic factors. Degradation of the calcarenite produces different morphologies, like loss of stone materials, modifications of the original stone shape and covering by overlying materials. This study focuses on the connection between lithological features and degradation morphologies in order to obtain useful information for the preservation of prestigious two representative rupestrian churches: St.Pietro Barisano and St.Lucia alle Malve. The study consists of a detailed classification of the principal degradation patterns, on the basis of the European rules, and a petrophysical characterization of the building material. Principal degradation patterns in the crypts and external façade of St.Pietro Barisano are related to alveolization weathering and erosion, while inside the church mainly biological colonization is found. Perforation pattern is typical of St.Lucia alle Malve external façade, while biological colonization strongly affects the interior. Calcarenite in both cases is mainly lithoclastic. On a mesoscopic scale, color is whitish and the homogeneity of its appearance depends on the presence of organogenous and sedimentary structures such as levels of calcareous grains (St. Lucia alle Malve church), fossils and bioturbations (St. Pietro Barisano church). A preliminary textural characterization of the Gravina Calcarenite by optical microscopy and image analysis was made in order to observe the mutual disposition of grains and voids in relation with weathering and dissolution processes. Calcarenites are poorly to moderately sorted grainstones made up of both skeletal and subrounded lithic clasts derived from the underlying cretaceous limestone. Interparticle and intraparticle porosity is very high. Other textural analyses will be carried out in order to distinguish microfacies type recognized by Mateau-Vincens et al.(2008), in the stones used to build *Sassi*, to develop a new classification based on their textural, structural and mechanical features in relation with degradation patterns and alteration processes, for better preserving this cultural heritage.

Mateau-Vincens, G., Pomar, L., Tropeano, M. (2008): Architectural complexity of a carbonate transgressive systems tract induced by basement physiography. Sedimentol., 55, 1815-1848.

Pulsed 10.6 µm TEA CO_2 LIBS as a tool in the characterization of powdered ochres: preliminary assessments

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Keywords: TEA CO_2 laser, LIBS, Italian ochres, elemental analysis.

The provenance of raw materials is always an interesting task for both conservation scientists and archaeologists. Solving provenance issues with geological tools contributes to the delineation of executive techniques or trade routes. It fosters the comprehension of the artistic and historical value of an artwork or the detection of forgeries. At the same time, the unrepeatability of unique artworks demands non-destructive investigations.

TEA CO_2 laser-induced breakdown spectroscopy is hereby presented as a feasible technique when dealing with the provenance of pigments. Powders/fragments of Italian ochres were firstly characterized by X-ray powder diffraction. Secondly, a minimal amount of the same powdered samples was mixed with KBr to produce pellets. These samples were then analysed by LIBS, using a 10.6 µm TEA CO_2 pulsed laser. The initial pulse full width at half maximum (FWHM) was 100 ns and the net pulse duration was about 2 µs. Pulse energy was nearly 160 mJ, with a resulting output power of 80 MW. The repetition rate was 1.2 Hz

The geology of the 2nd Century A.D. amphitheater area of Catania, Italy: historical eruptions affecting the urban district

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Keywords: amphitheater area of Catania, interdisciplinary approach, lava flow hazard.

The amphitheater of Catania is one of the main architectural structures built during Roman domination of the town. It was constructed in two successive phases between the 1st and 2nd Centuries A.D. and fell into disuse from the second half of the 4th Century. Detailed geological and petrographic investigations allow better geomorphological reconstruction of the area where the monument was built. In particular, the western and eastern portions of the amphitheater are built on prehistoric lava flows, named Barriera del Bosco and Larmisi, respectively. We infer that the choice of site to build the monument was highly influenced by the morphological setting of the area. In fact, the location at the contact between two lava flow fields facilitated excavation and removal of rocks due to the incoherence of the scoriaceous lateral border of the lava flows. Integrating both archaeological and geological data has revealed that a large number of Neolithic, Greek, and Roman sites are located in the lava fields of Barriera del Bosco and Larmisi within the present urban district of Catania, indicating that during its long history the city was directly impacted by only one lava flow, namely in A.D. 1669.

Portable Instruments for *in situ* analysis of archaeological findings. Laser-Induced Breakdown Spectroscopy *vs.* X-Ray Fluorescence

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Keywords: LIBS, X-Ray Fluorescence, geochemistry, cultural heritage, archaeology.

Most of the materials of interest in archaeology (ceramics, metals, etc.) can be studied with a variety of laboratory instruments and techniques. Provenance studies can be performed using mass spectrometry techniques, for example, as well as dating of ceramics can be obtained through the application of the thermoluminescence technique. However, in some circumstances, the analysis of the samples of interest cannot be performed in the laboratory, either because sampling of material is not allowed or because the objects are difficult or impossible to move from their original location.

In those cases, it is important to have portable or mobile instrumentation capable of performing *in situ* analysis. Another important use of mobile instrumentation could be the rapid screening of archaeological findings at the site for doing archaeometric measurements 'where is needed and when is needed', *i.e.*, at the archaeological dig and during the excavation campaign.

At the moment, the most reliable mobile analytical instrumentation, capable of sustaining the harsh environment of an archaeological site, is based on the LIBS (Laser-Induced Breakdown Spectroscopy) or Energy Dispersive XRF (X-Ray Fluorescence) techniques. These methods are often considered to be alternative, since both LIBS and XRF provide elemental information on the samples of interest. Moreover, being XRF a non-destructive technique, while LIBS is intrinsically micro-destructive, the common idea is that XRF should be preferred for *in situ* analysis of archaeological findings.

While this reasoning is sometimes well founded, it should be also considered that in most cases the information obtained through XRF and LIBS analysis can be very different. XRF is commonly considered a "surface" technique, contrarily to LIBS which is often presented as a "volume" technique.

As a matter of fact, the reverse is true. A single laser shot in LIBS penetrates under the surface for fractions of microns, while the XRF primary beam can sample several tens of microns under the sample, depending on the material. However, it is exactly the surface nature of the LIBS technique that makes possible a stratigraphic analysis through repetitive removal of sub-micron layers, which is impossible to perform using XRF, since the volume information contained in a XRF spectra cannot be (easily) deconvolved.

Similarly, the ED-XRF technique does not allow the detection and measurements of light elements ($Z < 12$-13) which are critical for the analysis of some lithic materials.

In this communication, we will present several examples of *in situ* analysis where a complete understanding of the archaeological objects' composition can only be reached through the joint use of both LIBS and XRF, that should thus be considered as complementary, and not competitive, techniques.

The recent introduction of hand-held LIBS instrumentation will largely improve, in the near future, the joint use of the two techniques in museums or at archaeological excavations.

Archaeometric study of the Roman marbles reused in the late Antiquity St. Saturnino Basilica (Cagliari, Italy)

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Keywords: Roman marbles, provenance, $^{18}O/^{13}C$ stable isotope, mineralogical, petrographic, Apuan Alps, Greek quarry.

The St. Saturnino Basilica (Cagliari, Sardinia, Italy) rises over a sacred site since the origins of the town of Cagliari. The original sepulchral function of the area were consolidated and implemented during the Roman Empire and it became a Christian cemetery after the *martyrium* of St. Saturnino (beginning of the IV Century A.D.). In this period the original chapel of the church was built starting a long evolution of the building across half a millennium, until its Romanesque evolution. The basilica was abandoned and partially destroyed at the beginning of the XIV Century. The formal technical reading of its architectural structure and elements is complicated by the frequent reuse of Roman artifacts during the Byzantine and Romanesque phases as well as the presence of diachronic source materials. The naked-eye analysis of geomaterials present in the monumental highlights a significant number of lithologies (*i.e.*, various kinds of limestones and sandstones, marbles, volcanic rocks, etc.), some of which are in an advanced state of alteration. We present the results of a multi-method archaeometric study (mineralogical-petrographic observations on thin sections, XRF trace elements analysis and ^{18}O *vs.* ^{13}C stable isotope ratio investigation) concerning the architectural stone elements reused in the basilica between the late Antiquity and Romanesque periods. The majority of lithologies belongs to the local outcrops of Cagliari Miocenic geological formation (*e.g.*, limestone and sanstones). The provenance study has focused on classical marbles used for manufacturing Roman architectural elements (column shafts, bases, capitals, pilasters, slabs, etc.), which are thought to come from extra-regional sources. All the different macrofacies of marbles were sampled taking precise reference to the various construction phases and structural changes of the monument occurred in the centuries. The preliminary results show that the marbles come mainly from Apuan Alps (Italy) and subordinately from Greek quarrying areas.

Geochemical and mineralogical alteration on the stone and mortar surfaces of medieval churches (Sardinia, Italy): weathering processes, ancient conservation treatments and their microstratigraphy

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Keywords: alteration, Ca-oxalate films, SEM-EDS, LIBS, XRD, ancient treatment.

The geomaterials (*e.g.*, stones and mortars) used on the monuments when exposed to the atmosphere subjected frequently weathering and bio-deterioration processes. Thus, these latter produce various chemical and mineralogical transformations of substrate at the interface with the agents as function of intrinsic compositional and physical characteristics of the material. Moreover, if there also are ancient treatments on the surface of geomaterials, the investigation field is further complicated. This research aims to analyse the surfaces of different lithology (basalts, pyroclastic rocks, limestone, sandstone, marbles) and mortars used in the medieval churches of Sardinia (XI-XIV Cent.) having high historical-cultural relevance. By mineralogical and petrographic analysis and other different analytical methods (SEM-EDS, LIBS, XRD) the investigations addressed to define: i) chemical and mineralogical analysis of coatings/crusts (with different composition from the unaltered stone substrate) and the salt fano- and crypto-efflorescence; ii) physical-mechanical decay and Ca-binder dissolution of bedding mortars used for the masonry stone ashlars; iii) compositional and microstratigraphic characterization of ancient treatments (*i.e.*, Ca-oxalate films) on the surface of facades; iv) chromatic modifications of surface with respect to the substrate due to the alteration processes. The results show the incidence of several factors in the alteration process, as function of the occurred time, petrophysical features and composition of geomaterials, their position in the monument structure, exposition to the weathering processes, microclimatic characteristics, environmental conditions. The presence of organic and inorganic substances frequently is observes as depositions on the surface (*e.g.*, atmospheric particles) or as ancient treatments (*i.e.*, weddellite and whevellite). These secondary crystalline phases has been find in several monuments (*e.g.*, St. Antioco di Bisarcio, San Mamiliano di Simassi, Santa Maria di Tergu, San Pantaleo di Dolianova, etc.), independently from the kind of substrate (volcanic rocks, sandstone, marble). In fact, the presence of the Ca-oxalate on the facades of ancient monuments, as noted, is a testimony of application of organic substances on the surfaces themselves, with aesthetic reason, to standardize or improve the tone colour of the stone, or conservative reason, to limit the negative effects of weathering.

Protohistoric glass from southern Italy: from Early Bronze Age to Advanced Iron Age (18^{th}-6^{th} Century BC)

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Keywords: archaeometry, glass, bronze-iron ages, trace elements, provenance.

This work reports the results of an archaeometrical investigation performed on 145 glass beads dated from the Early Bronze Age (18^{th} cent BC) to the Advanced Iron Age (6^{th} cent BC), coming from 15 southern Italian sites. A quite large amount of data is available in literature on Bronze Age glass from northern Italy (*e.g.*, Angelini et al., 2005), while very few are available for the South. The aims of the work were: to define the raw materials (vitrifying, fluxes, colorants) and the technologies employed for the glass production, to suggest hypotheses regarding the items provenance and to compare the northern and southern Italian glass supply routes. The research was carried out with a multi-technique approach: ESEM-EDS analyses for textural study; chemical analyses obtained by Electron Microprobe (EMPA) for major and minor elements, and by LA-ICPMS for trace elements; isotopic analyses for the determination of the Sr and Nd isotopic signatures. The results provided evidences of a great complexity in the chemical composition and production technologies, as enhanced by the presence of mixed alkali, plant ash and natron glass. Among the natron samples there are: classic natron glass, alumina cobalt blue glass produced with cobaltiferous alums as colorant, black glass characterised by high iron contents (10% FeO) and high-alumina glass (10% Al_2O_3). Trace and *REE*s analyses provided information on the raw materials employed: mixed alkali glass made up with purified plant/wood ashes and pure quartz sands; classic natron samples with mineralogically mature sand; black glass with Fe-Ti rich sand; alumina cobalt blue mostly influenced by the cobaltiferous alum used as colorant; plant ash glass with quartz pebbles; high-alumina glass with a clays and heavy minerals rich sand. The comparison of our trace results with those reported in literature, and the Sr-Nd isotopic signatures, allowed to conclude that: mixed alkali glass were imported from the FBA production site of Frattesina; natron, black and alumina-cobalt blue glass were produced in Egypt; plant ash glass had a Mesopotamian origin; high alumina glass are very uncommon among the contemporary glass. The comparison between northern and southern Italy, demonstrates the existence of different trade routes, most of all in the Early and Middle Bronze Age 1-2, when the North was involved in the trades with the central Europe, while the South was already inserted in the Mediterranean interactions. Data relative to the Advanced Iron Age evidenced the spread of natron glass over all the country, being this period characterised by the progressive evolution and standardisation of the natron glass production, which reached its peak in Roman times.

Angelini, I., Artioli, G., Bellintani, P., Polla, A. (2005): Protohistoric vitreous materials of Italy: from Early faience to Final Bronze Age glasses. *In*: “Annales du 16e Congrès de l’Association Internationale pour l’Histoire du verre”, Nottingham, UK, 32-36.

SEM-EDS X-ray compositional maps for minero-chemical characterization of ancient pottery: a first application on Adrano pottery (NE Sicily, Italy)

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Keywords: SEM-EDS, X-ray maps, pottery, Adrano, Sicily.

In archaeology, the classification of ceramic materials is an essential procedure. Alongside the macrosopic examination of the pottery paste, the classical archaeometric methods in order to define *fabrics* consist in the petrographic analysis performed by optical microscopy (OM), which allows to define the mineralogical composition and the morphological features of the inclusions, and in the chemical analyses of the matrix by energy dispersive spectrometry (EDS). Recently, new analytical procedures by using scanning electron microscopy (SEM) coupled with EDS have been applied to archaeometry in the fields of pottery petrography (*i.e.*, Knappett et al., 2011). Several computer controlled procedures were proposed, principally for image analysis and automated mineral analysis (Nuspl et al., 2004). Finally, specific systems (LEO, 1999) provide automatic modal analyses.

In this work new analytical SEM-EDS protocol, based on the acquisition of multi-elemental X-ray maps is presented. After thresholding, the detected particles are stacked in a data-base and processed by a dedicated software program which calculates the modal percentage of each selected phase by its chemical composition. Despite long acquisition time necessary to obtain a good spatial resolution and a good statistical precision, the dataset allows detailed description of mineralogical inclusions, their chemical composition, porosity and matrix. In this way, quantitative chemical and petrographic parameters can be obtained and used to help classifying ceramic sherds. Moreover, the amount of collected data allows to provide statistically reliable information. In addition, the developed procedure (both data acquisition and processing) is semi-automatic and therefore not depending by the operator interpretation. Finally, a comparison of chemical and petrographic data is possible, being the detected mineralogical phases expressed in compound% and represented by a modal analysis table. The procedure was tested on a set of sherds of black glaze pottery (4th to 2nd Centuries B.C.) from the site of Adrano (NE Sicily, southern Italy).

Knappett, C., Pirrie, D., Power, M.R., Nikolakopoulou, I., Hilditch, J., Rollinson, G.K. (2011): Mineralogical analysis and provenancing of ancient ceramics using automated SEM-EDS analysis (QEMSCAN): a pilot study on LB I pottery from Akrotiri, Thera. J. Archeol. Sci., 38, 219-232.

Leo Electron Microscopy Ltd. (1999): QEMSCAN: automatic mineral analyser. http://www.leo-em.co.uk/astqem.htm last update March 1999

Nuspl, M., Wegscheider, W., Angeli, J., Posch, W., Mayr, M. (2004): Qualitative and quantitative determination of micro-inclusions by automated SEM/EDX analysis. Anal. Bioanal. Chem., 379, 640-645.

Improvements of microanalytical methodologies for minero-petrologic investigation in Archaeometry

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Keywords: micro-XRF, SEM-EDS, micro-imaging, ornamental stone, ceramics.

The development and improvements of analytical investigations for the solution of minero-petrological issues is an important phase for basic and applied research. Archaeometry, which performs measures related to ancient objects, takes advantage of this know -how for the enhancement of Cultural Heritage.

Researches carried out in the stone sector of Cultural Heritage mostly use a microanalytic and multi-instrumental approaches; indeed the optical microscope, the SEM-EDS and the micro-XRF allows complete minero-chemical characterization of the raw stone materials. However, they can be used in different modes and with proper and suitable analytical conditions.

Bench-top μ-XRF is here applied as a novel surface technique for quick acquisition of elemental X-ray maps on rocks, X-ray mapping was performed with a 100 μm resolution and a 30 μm spot size over ~ 5x4 cm areas on samples of Euganean trachyte, a volcanic porphyritic rock from the Euganean Hills (NE Italy), historically used in cultural heritage. The quantified petrographic features allowed discriminating different extraction sites, suggesting an objective method for archaeometric provenance studies using μ-XRF imaging (Germinario et al., 2016). The suggested application to archaeometric provenance studies is only one of the possibilities offered by μ-XRF. This represents a novel alternative approach to classic provenance studies of stones, which are traditionally carried out based on chemical or microchemical properties, without considering texture.

Manual scanning electron microscopy (SEM) with linked energy dispersive spectrometry (EDS) is a routinely used for spot analyses.

In recent years there have been proposed a number of systems and applications for automating mineral analysis. A new analytical protocol, starting from the acquisition of multi-elemental X-ray maps by means of an SEM-EDS system, is recently presented; the method uses homogeneous composition particles obtained by map tresholding: from these we extract EDS spectra and then full quantitative analysis which are stacked in a data-base; by means of hierarchical cluster analysis we can classify the particles and calculates the modal percentage of each selected phase.

This procedure, as a result of the amount of collected data, provide statistically reliable information (modal percentage) about distribution of different phases, mineralogical inclusions, porosity and matrix in stones as well as in ceramics. The developed procedure (both data acquisition and processing) is semi-automatic and therefore not depending by the operator interpretation.

Both micro-XRF and SEM-EDS modes for micro-imaginig have saved all analytic spectra and hence the entire spectrum EDS is extracted to get a full quantitative analysis for each mineral phase or inclusions. However, with the same night acquisition time (14-16 hours) by means of SEM-EDS in order to cover the whole petrographic thin section a 5 micron resolution was used but a 2 micron one is obtainable.

Germinario, L, Cossio, R, Maritan, L, Borghi, A, Mazzoli, C. (2016): Textural and mineralogical analysis of volcanic rocks by μ-XRF Mapping. Microsc. Microanal., 22, 690-697.

Chert circulation in central-northern Apulia during Neolithic

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Keywords: chert, Neolithic, Apulia, Gargano, pXRF, petrography.

Current archaeological knowledge about the circulation of chert in central Mediterranean Sea identifies Gargano Promontory as one of the main sources. The systematic archaeological research in the area showed that mining activity coincided with the Neolithisation process of southern Italy and continued for about 800 years, until Copper Age. In addition, the Gargano is located along one of the supposed ways of the spread of the Neolithic in southern Italy, which is the “bridge” of Adriatic islands connecting the southern Croatia to the north of Apulia.

The macroscopic and chemical analysis of a selection of 243 samples of chert from mining districts and geological outcrops throughout Gargano Promontory (northern Apulia) provided a reference dataset to compare with new data obtained on flint tools and *debitage* from archaeological excavated contexts at Scaloria, Masseria Candelaro, Monte Aquilone, Ripa Tetta (Tavoliere area), Balsignano and Madonna delle Grazie (Murge area).

New petrographic, colorimetric (CIELAB) and chemical (portable XRF) data on 151 samples showed that most of the cherts from the Tavoliere settlements share the same chemical/colorimetric features, together with few samples from Murge ones. Further, the flint from Madonna delle Grazie and Balsignano show different compositional groupings not compatible with those of the mining districts of Gargano. The relatively small size of most of these artefacts points to the use of secondary flint sources, associated with the continental deposits from the Tavoliere area, not yet characterised. Such results lead to a more complex scenario of raw chert supply and circulation of finished tools.

Archaeometric characterization of prehistoric grinding tools from Milazzo Bronze Age settlement (Sicily, Italy)

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Keywords: archaeometry, Early Bronze Age, grinding tools, volcanic rock, SEM-EDX, XRF.

In this contribution we present the archeometric characterization of archaeological grinding stones, made of volcanic rocks, coming from the "Piazza XXV Aprile" archaeological site of Milazzo (Messina, Sicily). The settlement age was attributed-on the basis of archaeological remains and pottery typologies-to the Messina-Ricadi facies, dated to the end of Early Bronze Age, in the half of II millennium BC (Martinelli & Tigano, 2012).The studied objects are manual grinding tools classified as saddle-quern type and are composed by two stones: an active tool, usually called handstone/pestle, working with a linear movement of the hands on a passive surface, formed by a grinding slab or grindstone (Storck & Teague, 1952).

The archaeometric studies of prehistoric grinding tools from archaeological sites in the Mediterranean area are important for identifying the production sites and tracing the historic trade routes. To reach this objective, a multidisciplinary analytical approach, including SEM-EDX, XRPD and XRF, has been employed. The raw materials of the studied millstones are mainly volcanic rocks characterized by calcalkaline and K-alkaline affinities with volcanic arc geochemical signature. Only one sample is made by a basalt belonging to the Na-alkaline series and showing an intraplate signature. Comparison with literature data of similar rocks allowed to constrain the volcanic origin of the exploited lavas. Instead, the intraplate-type raw material came from Mt. Etna Volcano (Sicily). The arc-type volcanic rocks are mostly trachi-andesites, basaltic –andesites and one rhyolite. Although most of them came from the Aeolian Arc, a provenance of some samples from the Aegean Arc cannot be excluded. This could be the most probable provenance area for the rhyolite sample.

Overall results evidenced that Sicily, from the prehistory, provided abundant raw material for the construction of the most primitive grinding stone sand of the more technological millstones of Roman Age (*e.g.*, Di Bella et al., 2016). Our results confirm that, in the Bronze Age, the contacts between populations of eastern Sicily/Aeolian Islands and the Aegean ones were very active.

Di Bella, M., Mazzoleni, P., Russo, S., Sabatino, G., Tigano, G., Tripodo, A. (2016): Archaeometric characterization of Roman volcanic millstones from Messina territory (Sicily, Italy). Per. Mineral., 85, 69-81.

Martinelli, M.C. & Tigano, G. (2012): Un sistema di approvvigionamento idrico nell'età del Bronzo. Atti XLI Riunione Scientifica dell'Istituto Italiano di Preistoria e Protostoria "Dai Ciclopi agli Ecisti. Società e territorio nella Sicilia preistorica e protostorica", 16-19 novembre 2006, San Cipirello (PA), CD-ROM, 1301-1304.

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The archaeological site of "*Porta Mediana*" necropolis, Cuma, Italy. Geomaterials from a case-study mausoleum

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Keywords: geomaterials, mausoleum, mortars, cultural heritage.

"*Porta Mediana*" Necropolis (Cuma) consists of 70 mausoleums, dated from the 4th Century BC to the 5th AD, revealed by archeologist of the Centre Jean Berard between 2001 and present within the 'Kyme 3' project.

The site is located in the volcanic area of Campi Flegrei, a geological district that produced large volume of geomaterials, highly available and with good petrophysical features, used since ancient times in the local architecture.

This study, also conducted within the research activities of PON SINAPSIS (SIstema NAzionale Protezione SIti Sensibili), focuses on geomaterials from one of the 70 funerary monuments of the site. The mausoleum, named D46, dated between the 1st and 2nd Century BC (Brun & Munzi, 2011), seems to be particularly representative for the variety of geomaterials (both natural and artificial) identified.

The study was performed by using consolidated experimental methods, such as optical microscopy in polarized light (OM), and X-ray diffraction analysis (XRPD). The results showed presence and wide use, as building stones, of mainly local materials, belonging to Phlegrean lithotypes, such as *Tufo Giallo Napoletano* (NYT) and lava, the latter with structural function. A sedimentary lithotype, probably belonging to Sorrento peninsula's carbonatic series, is also present.

As far as artificial geomaterials are regarded, such as mortars and *cocciopesto*, use of volcanic aggregates of local origin is confirmed too. In particular, as concern mortars, the mix design is, in any case, the result of a mixture of lime and pozzolanic aggregates.

A deep knowledge of geological and petrographical features of materials used in ancient sites is the mandatory basis to allow right actions both for a conscious use and for the conservation of that invaluable cultural heritage.

Brun, J.-P. & Munzi, P. (2011): Cumes (Italie). Les fouilles du Centre Jean-Bérard 2000-2010, in Bulletin de la Société Française d'Archéologie Classique (41, 2009-2010). Rev. Archéol., 51, 147-221.

A Multi-analytical approach for the characterization of ancient Roman coins in orichalcum

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Keywords: orichalcum, coins, multi-analytical, XRF, SEM-EDS, EMPA.

A selected number of Roman orichalcum coins, from private collections, have been studied. Numismatic analysis indicates that they are asses, sestertius and dupondium, minted by Julius Caesar, Augustus and Claudius (Crawford, 1974; Sutherland, 1984). The aim of this study was to disclose the chemical composition of the orichalcum alloy, the nature of the patina and corrosion products; orichalcum is an ancient copper based alloy with a variable percentage of zinc (Craddock, 1978). With this aim a multi-analytical approach was involved, *i.e.*, X-ray fluorescence (XRF), scanning electron microscope (SEM-EDS), electron micro probe analyser (EMPA). In particular, XRF analysis was performed on different spots of coins' surfaces to have information about the chemical composition of the external layers. SEM-EDS analysis allowed to investigate alloy's microtexture (*e.g.*, segregation micro-domains) and to obtain morphological information. In addition, X-ray maps, acquired across section of coins, give information about elemental distribution inside the alloy; whereas EMPA analysis permits a quantitative chemical composition of major, minor and trace elements composing this ancient alloy. All these techniques confirmed that copper and zinc are the main components of the coins. Other metals, *i.e.*, Fe, Pb, Sn, Co, Ni, As, Sn, Sb and Bi, were also found in the alloy. These elements could provide information about sourcing raw materials sites. Si, S, Cl, K and Ca were found on the surfaces, being contaminant from the soil. Quantitative analysis with microprobe permitted to evaluate the different percentage of Cu and Zn in all the samples. The use of invasive technique (EMPA) was necessary to quantify the abundances of each elements composing the original alloy, thus eliminating soil contaminants and alteration product of the layers developed through time on surfaces. These results, could contribute to fill the lack of knowledge about the orichalcum alloy.

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Crawford, M.H. (1974): Roman Republican Coinage. Cambridge Univ. Press, Cambridge, 919 p.
Sutherland, C.H.V. (1984): The Roman Imperial Coinage: From 31 BC to AD 69. Spink, London, 304 p.

Chinese Jades from the collections of the Museum of Oriental Art of Turin: from the material characterization to the historical attribution

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Keywords: jade, nephrite, carving techniques, Raman, tool marks.

Fourteen beautiful stone artefacts are preserved in the Museum of Oriental Art of Turin, but they were not yet exposed because of some serious doubts about their origin and, in some case, their authenticity. Most considerations were made on the basis of a stylistic analysis that, nevertheless, requires the material characterization in order to be firmly verified. A preliminary petrographic analysis done by microscope investigation and Raman spectroscopy analysis allowed to identify tremolite in most objects, and to ascertain the use of nephrite jade in the object manufacture. The observation of the traces of the original tool marks by means of binocular microscope and grazing lighting allowed to distinguish the carving techniques employed, that can be usefully related to the chronology of the objects.

Phoenician Red Slip Ware from Sulcis (Italy): a preliminary report

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Keywords: Red Slip Ware marker, Phoenician pottery, optical microscopy, X-ray diffraction, scanning electron microscopy.

Phoenician expansion spread all over the Mediterranean coast and came together with the foundation of new colonies. *Red Slip Ware*, a ceramic class characterized by a shiny deep red surface, seems to be a good marker to identify and to date the early Phoenician presence on the territory. Indeed, *Red Slip Ware* is found in every Phoenician site, from the motherland to the colonies. Representative fragments of *Red Slip Ware* from the Phoenician-Punic site of Sulcis (Sant'Antioco, Sardinia) have been studied. These artifacts were unearthed in the area called Cronicario. The site has been dated employing the stratigraphy between the 750 and the 650 BC and it represents the oldest colonial settlement on the island (Campanella, 2005). The purpose of this work is to explore the technological background and the provenance of raw materials in order to discriminate imported or local ceramic productions. With this aim, X-ray powder diffraction (XRPD), optical (OM) and electron microscopy (SEM) were used. The external coating is a very thin clayish and non-vitrified layer with a very few inclusions of small size. Mineral assemblage is predominantly composed by quartz, K-feldspar and plagioclase feldspar, with minor amount of hematite, mica and rare calcite. The occurrence of hematite suggests an oxidizing firing environment. These results support the hypothesis that the samples were made with local raw materials and probably fired at temperature below 850°C (Riccardi et al., 1999) as supported by the high optical activity of the internal body. Electron microprobe analysis (EMPA) was also used to provide quantitative analysis on the outer surface, ceramic bulk and inclusions (Riccardi et al., 1999; Shoval, 2017). These Sardinian ceramics present similarities with other *Red Slip Ware* from Motya (Sicily), particularly in the external appearance and minerals assemblage. Thus, suggesting a selection of a similar raw material. Nevertheless, some peculiar differences such as the nature of accessory minerals and the content of CaO can be used to distinguish between artefacts of these two Phoenician-Punic sites (De Vito et al., 2013).

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Riccardi, M.P., Messiga, B., Duminuco, P. (1999): An approach to the dynamics of clay firing. Appl. Clay Sci., 15, 393-409.

Shoval, S. (2017): The application of LA-ICP-MS, EPMA and Raman micro-spectroscopy methods in the study of Iron Age Phoenician bichrome pottery at Tel Dor. J. Archaeol. Sci., in press, DOI: 10.1016/j.jasrep.2017.03.040.

Preliminary mineralogical, petrographic and chemical investigations on archaic clay statuettes from the first phase of the Greek sanctuary of Francavilla di Sicilia

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Keywords: votive statuettes, Francavilla, archaeology, petrography, geochemistry.

The current town of Francavilla di Sicilia (Messina) is located on the north of Mt. Etna, on the left bank of the Alcantara river. The creation of the anonymous Greek center of Francavilla is supposed to be mainly the result of a long penetration process by the Chalcis from Naxos, who were certainly looking for fertile land for cultivation in the Alcantara Valley. The numerous excavation campaigns conducted on its territory since 1979 in Via Russotti, led to the discovery of the remains of a sanctuary with its late archaic votive materials and the later votive deposit. The sanctuary is associated with the nearby dwellings, excavated as well. Among the materials found, belonged to the first phase of the sanctuary (from 2nd quarter of the 6th to the early 5th Cent. B.C.), stand out a series of votive female statuettes, seated or standing, representing bidders or goddesses. Their total number at the moment, amount to 127 specimens.

The most fascinating element is the big variety of types, with numerous variants and subgroups, that the context of Francavilla offers us. In fact there are Greek-oriental type specimens, ionic-attican type, various local types which, until now, do not find any comparisons with other Siceliots contexts, a very significant number of Corinthian or Corinthian type statuettes, a specimen of *kourotrophos* and a winged bidder, and various types still not completely defined.

From the archaeometrical point of view, 11 samples have been selected for*:* i) petrographic analysis out of thin section; ii) mineralogical analysis by XRD; iii) quantitative chemical analysis (XRF). All the samples belong to the first phase of the sanctuary, except one, belonging instead to the second phase, mainly to chronologically expand the field of investigation, in order to try to identify any elements of continuity in the use as well as in the processing of the clay techniques. Thanks to the obtained results, it was possible to confirm the great variety of Francavilla context, which therefore is not limited to the typological and iconographic aspects, but it also extends to the use of raw materials and their treatments. Furthermore, it was possible to identify 4 macro groups of fabrics, according to groundmass and inclusion features and to establish, in many cases, the firing temperatures thanks to the identification of neoformation phases. Finally, the present work allow us to formulate hypothesis about their origins thanks to the comparison with chemical data of several samples of raw materials clay outcrops in eastern Sicily.

An archaeometric study of wall paintings in St. Angelo in Criptis cave (Santeramo in Colle, southern Italy, BA): a tool for restoration and enhancement of the site

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Keywords: wall paintings, pigments, crypt-church, Raman, SEM-EDS.

The St. Angelo in Criptis cave (Santeramo in Colle, Bari) is a suggestive and still active natural karst cavity located in the National Park of Alta Murgia (Apulia, south of Italy). It belongs to a wider and more complex medieval structure, locally known as Iazzo St. Angelo, which consists of three adjacent buildings covering the entrance of the cave and, partially, the cave itself. The complex was initially used as church and after as manor farm. The cavity in the underground space was firstly probably devoted to the pre-classical "cult of water", later converted to Christianity and entitled, in the early Middle age, to St. Michael the Archangel. Some fine, stratified frescos enrich the cave. They mainly consist in three wall paintings, portraying (i) the Descent of the Holy Spirit and the Christ Pantocrator (two pictorial phases), (ii) the Virgin and Child flanked by St. John and the St. Michael (two pictorial phases), and (iii) the St. Michael Archangel slaying the dragon. Actually all the paintings are in very precarious conditions and needs urgent restoration. Attempt of dating concerns exclusively the Christ fresco, constituded by two pictorial phases, and for which the palaeographic font analysis collocated the oldest painting in the late 12th and early 13th Century and the most recent one, between the 13th and 14th Century. This study, financied by the "Fondazione Cassa di Risparmio di Puglia" with the project "La grotta di Sant'Angelo in Criptis a Santeramo in Colle (BA): studio dello stato di conservazione e valutazione della stabilità", focused on the archaeometrical investigations of paintings with the aim to characterise raw materials, palette of colours and painting technique of pictorial layers and to provide a meaningful contribute to the historical and chronological knowledge of the cave. Paint layers and theirs supports were investigated by optical microscopy, scanning electron microscopy equipped with Energy Dispersive System, Raman spectroscopy and X-ray diffraction techniques. Samples from the Virgin and from the Christ paintings confirmed the existence of the observed two different pictorial cycles, whereas only a paint layer characterised the St. Michael Archangel painting. Archaeometrical analyses allowed to recognize four different types of supports and to highlight strong analogies between the more recent cycles of both the Christ and of the Virgin paintings. All the colours present in the paintings resulted by the mixing of simple pigments like ochres (red and yellow) and carbon, which were mixed in different way to obtain pale or dark colours and/or to produce secondary hues. Interesting is the finding of the cinnabar pigment in the blue of the Pantocrator mantle belonging to the first cycle of the Christ painting. This is a very uncommon finding among pigments used in rock paintings, and could be considered indicative of a period in which the site was an important cultual centre.

TourinStone: a free mobile application for promoting geological heritage of Torino (NW Italy)

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Keywords: applied petrography, multimedia application, ornamental stones, cultural heritage, Torino.

The knowledge of stone resources (minero-petrographic features, their use and exploitation techniques from ancient times to the present) can provide a broad overview of the historical and cultural significance of such materials, highlighting the relevance of an economic activity so important for the history and traditions of the different cultures developed through the centuries all over the Mediterranean area. In every Italian region a significant historic heritage on rocks exists, which can be found in the historical buildings. The abundance of stone materials coming from Piemonte (NW Italy) employed over the centuries to realize paving, monuments and public buildings shows the close link between the city of Torino and the surrounding territory, emphasizing the role that stone has played on the culture and economic wealth of Torino during the centuries: first as capital city of Savoy kingdom, then as the Italian capital, and finally as the main center of the domestic industry. In recent decades, however, because of the economic situation, also Torino has undergone a deep transformation that has led it to become a tourist town full of cultural attractions. Its monuments and stone buildings built over the centuries represent a major excellence of the city. In this framework, the knowledge and enhancement of historic ornamental stones from Torino can lead to a new geotouristic approach for the development of urban geological heritage.

TourinStone is an application for mobile to promote, increase and enhance the urban geological heritage of Torino, thanks to which the visitor can enjoy the cultural and the scientific aspect at the same time.The application illustrates twenty-six historical sites of interest where most ornamental stones of historical and scientific interest can be observed in detail. The sites are grouped in four georeferenced thematic itineraries through which the user can discover and enjoy the city from a cultural and a geomaterial point of view.

A numbered list of the stones used in all described monuments reports the specific data of each rock. This list is divided according to the genesis of rocks: igneous intrusive, igneous effusive, metamorphic and sedimentary. The form of each rock is organized according to the following fields: scientific classification, trade name, quarrying district, simplified geological map, geological setting, macroscopic description of the rock, main uses (*i.e.*, monuments, churches or significant palaces where the rock has been employed), macroscopic photo of the rock.

The mobile application can be downloaded free from the App Store or Google Play for Apple and Android devices, respectively.

Tracking trachyte on the Roman routes: provenance study of Roman infrastructure and insights into ancient trades in northern Italy

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Keywords: volcanic rock, ancient quarries, Roman roads, trade routes, LA-ICP-MS.

Roman colonization of northern Italy during the late Republican Age brought a significant building activity in the new acquired territories, especially involving the construction of new infrastructure, which demanded huge amounts of stone. Trachyte of the Euganean Hills was one of the most used materials for building infrastructure, in particular roads, and even bridges, forum squares and aqueducts. This paper addresses the recognition of the provenance quarry of Euganean trachyte used in Roman public infrastructure in northeastern Italy, mostly built from the 1st Century BCE to the 1st Century CE. Petrographic features and major- and trace-element composition of bulk rock and phenocrysts, analyzed by XRF and LA-ICP-MS, were used as provenance tracers. The provenance determinations allow exploring the management of trachyte quarries and the development of extraction activities in the Roman times, as well as the related commercial and economic dynamics involving stone supply for public works. Moreover, indications are given with regard to the territorial organization of Roman settlements, their areas of political influence and ownership and competition of quarries. Finally, broad insights into ancient trades in northern Italy and the main routes of stone circulation are provided.

Comparative mineral-petrographic study between Neolithic *greenstone* tools and analogous pebbles from the alluvial deposits of the Lemme valley (northeastern Piemonte region, Italy): archaeometric implications

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Keywords: *HP* meta-ophiolite, greenstone, jadeitite, omphacitite, eclogite, prehistoric implement.

A great number of prehistoric stone implements (axes, chisels, hatchets and disc-rings) has been found in archaeological sites spread all over the western Europe – *i.e.*, in southern France and along a corridor running from southern Italy to Great Britain, but especially in the Po plain. These implements are made of alpine *"*greenstone*"*, rare *HP* meta-ophiolites (namely "Na-pyroxenites" and "Na-pyroxene + garnet rocks") cropping out in the western Alps as both small primary outcrops at high altitude in the Monviso or Voltri massifs and secondary deposits downhill around them.

The field occurrence of these rare lithotypes is of paramount important for archaeology, as their characterization would allow reconstructing the supply sources and the possible migratory routes or trade channels followed by our ancestors.

A certain number of "greenstone" geologic samples was retrieved from the alluvial beds of the Lemme valley streams (northeastern Piemonte region, Italy) and analyzed with a classic mineral/petrographic approach, including XRPD, polarizing microscopy and SEM-EDS. The compositional and microstructural features of these potential source rocks were compared with those of implements from archaeological sites located not too far (*i.e.*, Brignano Frascata, Momperone, Villaromagnano and Rivanazzano – few dozens of km far, as the crow flies), searching for common traits suggesting a possible univocal origin.

In addition to morpho-typological outcomes previously inferred by archaeologist, the obtained mineral-petrographic evidence (compositional and microstructural markers) points to a feasible origin of the raw materials used for the production of stone implements retrieved in close archaeological sites from the investigated conglomeratic horizons and alluvial beds. These outcomes therefore support a preferential supply of raw materials from secondary sources rather than primary outcrops, thus grabbing the best available technological material with the minimum effort – a habit consistent with the principle of the cost/benefit ratio and probably diffused during the early-to-middle Neolithic.

Archaeometric characterisation of ancient mortars from the Roman theatre of Benevento (Italy)

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Keywords: ancient mortars, Roman theatre, pozzolana, cocciopesto, building phases.

The Roman Theatre of Benevento (2nd Century AD) lays near the *cardo maximus* of the ancient Roman urban structure and represents an outstanding evidence of Roman technological expertise in the field of construction and building materials.

It showed a semi-circular shape, a cavea with a diameter of *ca*. 98 m and an outdoor with 25 arches divided in thee orders, of which today remain only those of the first order. After the advent of Christianity, the Roman theatre was abandoned and destroyed several times by earthquakes, floods and lootings, being then re-occupied by private habitations built inside it.

Nine bedding mortars were collected in the Roman theatre of Benevento and analysed by a multi-analytical approach in according to the UNI-EN 11305:2009 and UNI-EN 11176:2006 recommendations, in order to obtain information about their technology and composition.

Thin sections were observed via Light Polarised Microscope (LPM) and Scanning Electron Microscopy coupled with Energy Dispersive Spectroscopy (SEM/EDS) for the determination of mineralogical composition and textural features of collected mortars. Hydraulic classification of mortars (CO_2/H_2O ratio) was carried out with Simultaneous Thermal Analyses (TG/DSC and FTIR-EGA), whereas Fourier Transform Infrared Spectroscopy (FTIR) in trasmittance mode (KBr pellets) was adopted for the identification of newly-formed phases.

Two main groups of mortars have been preliminary distinguished in according to the type of aggregate, as well as the binder-to-aggregate ratio (B/A) and hydraulic classification. Lime binder and pozzolanic lightweight volcanic aggregate with rare cocciopesto (B/A ranging from 1.1 to 1.8) formed the first group, whereas hydraulic lime mortar mixed with silicate sands (B/A ranging from 0.7 to 1.3), which moderate contents of feldspar, quartz and lithic fragments as quartzarenite and minor limestone are observed, constituted the second one.

The features of the first group are quite consistent with the traditional technology used in the Roman period where the lightweight aggregate was used to promote a better mechanical performance after hardening as well as a rapid setting of the mortar.

The composition of the second group of mortars allows inferring a local provenance of the raw materials. Nevertheless, a different technology can be observed, inferring the several building phases that involved the Roman theatre through its history.

Finally, nitrates and sulphates were detected by means of FTIR spectroscopy, indicating the occurrence of decay and alteration pathologies.

The results could be considered as preliminary but essential information for a deeper investigation about the reconstruction of building phases of this monument.

European project NANO-CATHEDRAL: efficacy assessment of nanomaterials for conservation of natural stones

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Keywords: NANO-CATHEDRAL, consolidants, protectives, natural stones.

NANO-CATHEDRAL project, started in June 2015, develops new nano-materials, technologies and procedures for the conservation of deteriorated stones in monumental buildings, cathedrals and high value contemporary architecture. Cathedrals, distributed throughout Europe, are representative of the diversity of European cultural heritage (Lazzeri et al., 2016).

Five different cathedrals were selected as they may be considered as representative of both different exposure conditions and different types of stones: Cathedral of Pisa (Italy), Cathedral de Santa María of Vitoria-Gasteiz (Spain) as representative of south European "Mediterranean" climate in coastal and continental regions; Sint-Baafs Cathedral of Ghent (Belgium), Cathedral of St. Peter and Mary in Cologne (Germany) and St. Stephen's Cathedral, in Wien (Austria) as representative of north European climate in coastal and continental regions, respectively; the Oslo Opera House, as an example of a contemporary building coated with white Carrara marble. They also represent different lithotypes such as marble, sandstone, limestone.

During the first phase of the project, stones and their decays have been extensively studied. Based on the specific decay phenomena of the selected lithotypes, different products, namely nano-particles based consolidants and protectives exhibiting photocatalitic, anti-fouling and hydro-repellency proprieties, have been selected for laboratory testing on lithotypes.

To verify fundamental requirements for stone conservation (*e.g.*, they have to preserve the originality of the stone materials, provide high performance treatments, and provide long-term conservation), artificially decayed lithotype specimens for lab tests are prepared and a systematic testing program has been performed for consolidant and protective treatments (Ban et al., 2016). The results of the tests carried out by the laboratories have been employed to improve the products for the second phase of the project, *i.e.*, the application of consolidants and protectives on-site.

Preliminarily, products have been applied and tested on pilot areas, with the aim to develop homogeneous operational guidelines; moreover, *in situ* tests have been carried out before and after the application of the products to evaluate their efficiency and compatibility. The results will be employed to select the best products to apply on the Cathedrals.

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Effectiveness, compatibility and durability of consolidants for marble: a review of the last ten year of researches

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Keywords: consolidant, marble, cultural heritages, review.

The choice of suitable consolidant treatment for cultural stones is one of the main challenging issue for conservation and protection of ancient masonry. Among building materials, marble is one of the most used for building and sculptures. Due to its low porosity, the assessment of suitable treatment for marble consolidation is not trivial; beside, the type of product, treatment methodology (Ferreira Pinto & Delgado Rodrigues, 2012), effectiveness and compatibility investigation (Sassoni et al., 2016a) and durability monitoring (Sassoni et al., 2016b) have to be taken in great account. Recently, researchers have extensively tested and proposed new products for consolidating carbonate stones, including organic and inorganic products (Hansen et al., 2003), nanoparticles (Sierra-Fernandez et al., 2017), biological organisms (De Muynck et al., 2010). Nevertheless, no entirely satisfactory treatment is currently available for marble consolidation. At the same time, no unique evaluation criteria to use as laboratory estimators of consolidating performances have been assessed (Delgado Rodrigues, 2010). The present paper aims to carry out a review of the state of art, based on the last ten years of researches, on consolidants for marble substrate. We summarize the different type of commercial and research products proposed for marble consolidation, by comparing also effectiveness, compatibility and durability of each proposed product, in function of consolidant features (*i.e.*, product concentration, solvent type) and treatment methodology (application process, and contact time).

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Building materials and cultural models in late Roman Tuscany: archaeometric studies on stones, mortars and vitreous *tesserae* from "Villa dell'Oratorio"(Capraia e Limite, Florence)

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Keywords: stones, glass, mosaic, mortars, Tuscany, late antiquity, archaeometry.

In the framework of the archeological investigations of an outstanding Roman villa in Tuscany (Villa dell'Oratorio, in the territory of Capraia e Limite, Florence), a multi-disciplinary and multi-methodological approach has been applied to characterize building and decorative materials and retrace construction phases and manufacture technology.

The Villa, built in the middle of the 4th Century, probably belonged to the great senator Vettius Agorius Praetextatus as remembered in an inscription found in the site. The importance of this family in the Late Roman world is underlined by Macrobius, who defined the 4th Century as the *Saeculum Praetextati*. The architecture of the building reflects the relevance of his owner: in particular, it includes a hexagonal structure, about 30 meters in diameter, decorated with painted wall plasters and beautiful figurative floor mosaics. The structure is equipped with apsed rooms (at least 5), exhibiting similarity with some monumental triclinia of Constantinople.

Due to the relevance of the site, archaeometric analysis have been carried out on mortars, plasters, stones and vitreous *tesserae* with the aim to identify raw materials and support the archaeological investigation about cultural models and political-economic equilibria during Late antiquity in Tuscany.

In detail, stone *tesserae* have been analyzed by classical minero-petrographic and chemical methods (optical microscopy, XRD and XRF); the obtained results have been compared with reference decorative stones to obtain information on provenance of employed materials. Raman spectroscopy and SEM-EDS analysis have been performed on vitreous *tesserae* to obtain information on colouring and opaquening agents. Finally, mortars samples from different building units of the Villa have been studied through minero-petrographic and chemical methods.

The archaeometric analysis carried out on the building elements suggested that in spite of iconographic and architectural models proper of the great Mediterranean "urban villa", local raw materials and artisans were involved in this great construction work.

Between Archaeology and Archaeometry. Some case studies on Roman Pottery and Architecture in ancient Catania and Syracuse

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Keywords: archaeology, archaeometry, pottery, bath, mortar, clay, Sicily.

The paper deals with the theme of archeology and archaeometry through the experience of two research projects carried out in archaeological contexts of Catania and Syracuse. The first project was aimed at analyzing a group of ceramics from the Hellenistic and Roman pottery workshop area of Syracuse. The results allowed to obtain fundamental data for the characterization of the fabric and the reconstruct the cycle of ceramic production between the 2nd Century BC. and the 1st Century AD.The second project focused on the Achillian Baths in Catania, a roman-imperial bath placed in the subsoil between Piazza Duomo and the Cathedral. The analysis carried out on mortars integrated with stratigraphic elevation analysis allowed to reconstruct the phases sequence of the building. The results also provided data for a restoration project.

Archeology and experimental research

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Keywords: Lipari painter, XRF, RAMAN, cinnabar, caolinic clays, pigments.

The fundamental episode of archaeometric experiences in the area of the Strait of Messina at the beginning of the eighties was the masterful restoration of two Bronzes discovered in Riace (RC), which gave great emphasis to experimental analyzes.

Between the mid-eighties, thanks to a new way of understanding the research, the Messina Museum began to interact between geologists, physicists, and chemists at the Universities of Messina and Catania. Greek and Roman marbles, stones, metals, ceramics, terracotta artifacts and muses were studied. From so many published experiences it has emerged that research can significantly enrich our knowledge only if scientists answer questions arising from a profound knowledge of archaeological and numismatic materials. Paradigmatic is the result of the bronze coins: the recognition of recounts on Ptolemaic subtypes was confirmed by the analysis that demonstrated the compatibility of the Sextus Pompeius axes alloys with the specimens of III Century B.C. Ptolemaic Mint (Calareso et al., 2001). The acknowledgment that the sarcophagus of Luca Archimandrita of the Basilians, who died in 1149 A.C. was a proto-byzantine sarcophagus reworked in the twentieth Century was confirmed by the analysis that revealed a Proconnesio marble. The archaeometric study was fundamental in the recognition of the heaviest bronze coin of Dionysius of Syracuse, to deny that it could be considered equivalent to a drama (Mondio et al., 1998; Triscari, 1998): alloy analyzes revealed tin in percentages far below 12.5%, the minimum necessary to establish an equivalence between the bronze and the silver coin.

Another important information was derived from Syracuse's limestone (with which the temples and walls of the city are made) examination.

But probably the most important exam was performed in the recent years on data so far unknown. Studying the production of the Lipari Painter and his followers, the pigments used in a technique of overexposure after cooking pots-considered from literature as derived from local caolinic clays-have been examined. XRF and Raman surveys, conducted on many samples with portable instruments (Quartieri et al., 2015), demonstrated the use of mercury sulphide (cinnabar). This result suggests likely a relationship with the Etruscan area, apparently to be supplies from the Amiata Mountain deposits and to relocate the Lipari Painter into the experience and into the pictorial culture of the IV Century B.C.

The results achieved so far can widely be considered a happy example of interaction among different fields of investigation: historical, archaeological, physical, chemical and geological.

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Preliminary study of a "*bronze foot*" from the Lipari museum (Sicily, Italy)

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Keywords: bronze statues, X-Ray Fluorescence, SEM-EDS, Lipari Island, Aeolian Archipelago.

This study examines a foot's fragment made of bronze, with lost-wax casting, kept at the Lipari Museum, to define the elemental composition of the used metal alloy and to perform a virtual reconstruction of the original statue. The bronze fragment was discovered in a dumping ground near the harbor of the Lipari Island (Aeolian Archipelago, SE Tyrrhenian Sea) and published by Bernabò Brea (1985) in a small note. For the formal characters and for the realization technique it seems to date at classic or proto-hellenistic age, but the continuation of the study and the results of the analysis can provide a more accurate framework.

Combination of non-destructive handling X-Ray Fluorescence and micro destructive SEM-EDS analyses allowed of constraining the alloy chemical composition. XRF results indicate a slightly variable content of prevalent Pb > Cu > Sn alloy. SEM-EDS analyses evidenced heterogeneous compositions, with areas variable enriched in Cu > Sn > Pb and Pb > Cu > Sn alloys. Furthermore, 3*D* structured light-blue scanning of the bronze foot was performed to obtain a digital reconstruction usable to create a digital model of the statue with the aim to hypothesize dimensions and posture necessary for the archeological constraints.

Overall characterization of the bronze foot's fragment will further provide key information on the bronze production technology and chronology, perhaps allowing it to be inserted among other bronzes discovered in the Strait of Messina.

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Isotopic composition of lead for raw material tracing: the case of Roman lead-glazed ceramic

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Keywords: provenance, Roman glazed ceramics, lead isotope analysis, SIMS.

Numerous studies of glazed coatings on ancient ceramics aimed at understanding the ancient production process, how it changed and developed through the centuries (Tite et al., 1998; Özçatal et al., 2014). In addition, investigating the provenance of the raw materials involved in glaze production is important to reconstruct the main trade routes that disseminated this technology.

Stable lead isotope analyses, using secondary ion mass spectrometry (SIMS), was applied to trace the provenance of lead minerals involved in the production of Roman lead-glazed ceramics. The fragments analyzed here were unearthed in different archaeological contexts of ancient Rome (*Testaccio Market*, *Magna Mater* sanctuary and *Domus Tiberiana* on the Palatine Hill, *Forum of Caesar* and *Forum of Nerva)*, spanning the period from the 2nd Century AD to the Middle Age.

The ceramics analyzed clustered within the distribution patterns of several deposits including Bulgaria, Italy (Sardinia), Greece and Britain. However, the comparison with the lead isotope data of ores by statistical treatment of the data (PCA) shows that the deposits from England were important sources of lead used for the production of glazed ceramics since the second Century AD.

A comparison of our lead isotopic results obtained using SIMS with data collected from previous works by ICP-MS and TIMS (Wolf et al., 2003; Walton & Tite, 2010) shows that SIMS can be used for lead isotope provenance research. In addition, SIMS micro-analytical technique includes easy sample preparation, quick acquisition times, and is minimally destructive, which are advantages in the field of cultural heritage (Hull et al., 2014). Furthermore, the acquisition of accurate and precise isotopic measurements on a micrometer scale with the possibility to choose the location of each analysis point avoids the inclusions especially in the case of ceramic materials.

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Authentication of metallic finds at the archaeological museum of Paestum by means of non-destructive and non-invasive techniques

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Keywords: metallic objects, micro-XRF, FTIR, non-destructive analysis, Paestum.

Located on the Tyrrhenian coast of Salerno, Paestum was one of the main centres of ancient *Magna Grecia*. It was founded by Greeks around 600 B.C. as ancient *Poseidonia*, although the oldest traces of human settlements dated back to the Paleolithic. At the end of the 5th Century B.C., the Romans conquered Poseidonia and in 273 B.C. changed the name in Paestum.

Situated near the ruins of the ancient city, the National Archaeological Museum of Paestum collects since 1952 most of the archaeological finds here recovered, which testify artistic and handmade activity of the Greek city and Latin colony. The direction of the Museum promoted research activities on the scientific methodologies for the study of archaeological finds in collaboration with the *Associazione Italiana di Archeometria* (AIAr). Within such synergic collaboration, several non-destructive and non-invasive analyses were employed for the identification of the materials constituting the different typology of finds (ceramics, metals, wall paintings), currently observable in the exhibition "Possessione-Trafugamenti, furti e falsi".

Among them, some metallic objects (coins, surgical instruments, bronze head and statuette) confiscated by the police and preserved at the National Archaeological Museum of Paestum were analysed by means of micro X-ray fluorescence (micro-XRF) and Fourier Transform Infrared Spectroscopy (FT-IR), with the aim of determining their authenticity.

Among the coins, two Nero's *sestertia* (64-65 A.D.) and Minea's *semis* (1st Century B.C.) were analysed. The latter is constituted by a bronze alloy formed by copper (74.2%), tin (19.1%) and lead (6.7%), whereas the two Nero's sestertia show different composition: leaded bronze (copper 70.9%, tin 6.2% and lead 22.5%) and brass (copper 91.5% and tin 7.5%). Comparing these results with the numismatic knowledge about the *orichalcum* coined during Neronian period, we can deny the authenticity of analysed *sestertia*.

As far as the surgical instruments are concerned, they were made with brass alloys and appeared stylistically different from those known in Paestum. Furthermore, the area of origin and the reference period are unknown. Therefore, the archaeological and archaeometric results allowed supposing that these objects are not authentic.

A bronze head, dated around 5th – 4th Century B.C. is formed by 75% of copper, 14% of tin and 6% of lead and is covered by a thin layer that showed the infrared features of an acrylic resin.

The statuettes, instead, were mainly formed by copper and tin and covered by organic compounds observed on the surfaces and attributable to an artificial patina. Chemical compositions of these statuette, stylistically attributed to the Etruscan and Roman period, do not match those of the authentic analogues.

Islamic pottery production in Sicily (X-XI Centuries): technological aspects of local and imported products from Paternò (CT) on the basis of minero-petrographic and chemical characterization

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Keywords: Islamic archaeology, eastern Sicily, pottery production, glazed pottery.

Situated on a volcanic hill on the south-western slope of Mt. Etna, Paternò was an important *madīna* ("city") during the Islamic period in Sicily. Defined by the geographer al-Muqaddasī as the city lying "under the mount of the flowing fire" (Al-Muqaddasī, 1991), his historic role for these centuries still need to be cleared: nevertheless, the idea that his importance could come from the presence of a *ribāṭ* (a military-religious institution, often located on frontier zones) is getting more credits from both documental and topographical data.

These historical remarks of an Islamic *madīna* fit perfectly with the archaeological and archaeometric data obtained so far: evidences from the material culture have shown the clear presence of a local glazed pottery production – testified from the archaeometric results as well as from findings of kiln wastes and, significantly, of kiln bar fragments, attesting this particular kind of technology (Coll Conesa & García Porras, 2010) – strictly related with other kinds of products, especially the light-surface pottery.

Our research focused on a double search path: on one hand, it was necessary to clearly define the local products and to characterize them on both minero-petrological and chemical aspects; the other important aim was to start treating the technological features of ceramic bodies and glazes (glass recipes and metal-oxides used as pigments), to acknowledge the socio-economical concerns and the territorial impact of such craftsmanship.

The following archaeometric tools have been used: i) Optical Microscopy (OM); ii) X-Ray Fluorescence Wavelength-Dispersive Spectroscopy (XRF-WDS) on powdered samples; iii) X-Ray Diffraction (XRD) on powdered samples; iv) portable and non-destructive X-Ray Fluorescence Energy-Dispersive Spectrometer (XRF-EDS).

The 18 samples are distinguishable in two groups: 14 samples come from an archaeological excavation on the hilltop of Paternò, including some three kiln wastes as reference samples for local products; 4 reference samples have been chosen to link imported products to a supposed provenance (2 samples come from Palermo, the capital of Islamic Sicily; 2 samples are from late byzantine layers-IX cent. as a reference for products from north-eastern Sicily).

Both the archaeological and archaeometric researches have to continue, and also other archaeometric tools will be used as well in the future, such as Raman spectroscopy to comprehend other technological features of the glazes (Cruz Zuluaga et al., 2012). This will be a good start point for further studies, which will provide more details on different traditions in pottery making, comparing the new know-how derived from the Islamic world – and probably from the near Islamic capital of the isle, Palermo (Arcifa & Bagnera, 2014; Ardizzone et al.,2014) – with the ones more related to previous technological substrates, detectable in some products spread between eastern Sicily, Calabria and Apulia.

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Archaeometric approach to study pottery from the archaeological site of S. Omobono (Rome-Italy)

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Keywords: pottery, archaeometry, provenance, raw materials, OM, XRF, EPMA, XRPD, micro-Raman.

This work concerns the results of an archaeometric approach used for the study of pottery coming from the archaeological site of S. Omobono in Rome (Italy). The archaeological area, accidentally discovered in 1937, is located in the historical center of the town, between the "Campidoglio" and the Tevere river. It is a sanctuary that was founded in the sixth Century BC. With the beginning of the Republican age, it was completely rebuilt with the construction of two twin temples dedicated to *Fortuna* and *Mater Matuta*. At present, the visible situation shows the Republican age architecture and the imperial age phases. Above the east temple cell was later built a church which since 1575 took the name of St. Omobono's church (Brocato et al., 2012; Brocato & Terrenato, 2012; Terrenato et al., 2012; Diffendale et al., 2016). The 16 ceramic samples analyzed in this work come from different areas of the archaeological site and date back to the 7th and 6th Centuries BC. The approach used to study the samples was finalized to the petrographic, mineralogical and chemical characterization of the pottery, performed by different analytical techniques: Optical Microscopy (OM), X-Ray Powder Diffraction (XRPD), X-Ray Fluorescence (XRF), Electron Probe Micro-Analysis (EPMA) and micro-Raman Spectroscopy. The compositional data were processed by Principal Component Analysis (PCA) to better highlight similarities and differences among the samples. The combination of all data allowed us to identify several *fabrics* of pottery, characterized by different chemical, mineralogical, petrographic and textural features. At the same time, the study carried out on clinopyroxenes and rock fragments, present as non-plastic inclusions in the pottery, allowed us to make hypothesis on their provenance. In particular, the study highlighted that the mineralogical composition of the non-plastic inclusions of the pottery is compatible with the local production of the Roman Magmatic Province.

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The mosaic of the *Frigidarium* of "Villa Bonanno" in Palermo: mineralogical and petrographic analyses for *in situ* conservation and restoration interventions

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Keywords: Sicily, Roman mosaics, bedding mortars, limestone *tesserae*, restoration.

The topic of this study was the mineralogical and petrographic characterization of bedding mortars (made of different layers) and *tesserae* of Roman age (3rd Century A.D.), taken from the mosaic of the *Frigidarium* of "Villa Bonanno", brought to light by archaeological excavations conducted in the historical centre of Palermo. The collected samples have been analysed by thin-section optical microscopy (PLM), and scanning electron microscopy coupled with energy dispersive spectrometry (SEM-EDS). The study was aimed to define the "recipe" (composition of temper and binder, temper size distribution, temper/binder ratio), in order to assess the provenance of raw materials (supply site/area) and to acquire useful information in order to formulate "restoration mortars" that should be most comparable with the original ones, for replacements and/or integration. Lithotypes constituting the coloured *tesserae* were also characterized by thin-section optical microscopy. The mineralogical and petrographic investigations allowed establishing two different recipes used for the formulation of the studied mortars in terms of both compositional and textural features. The aggregate is composed by diverse proportions of detritic calcareous granules (both bioclasts and limestone fragments deriving from the local outcropping biocalcarenites and limestones), siliceous sand (monocrystalline quartz, chert and quartzarenite fragments), volcanic ash (*pozzolana*) and sometimes *cocciopesto*. The resulting hydraulic binder was the product of the 'pozzolanic reaction' between volcanic ash and the aerial lime (specifically made by the calcination of locally available magnesian limestone or dolostone). The coloured *tesserae* can be all classified as compact limestones of Mesozoic or Cenozoic age, likely of local provenance. Detailed micropaleontological analysis (nannofossils) is ongoing for a more precise stratigraphic assignment. It was found a satisfactory technological correspondence with the more or less contemporary manufactures within Palermo and western Sicily (Montana et al., 2016). Concerning the sandy aggregate, it was shown a substantial compositional and textural equivalence with the plasters used in the baroque palaces of Palermo demonstrating a remarkable continuity in the criteria of selection of raw materials, mainly dictated by the qualitative characteristics of locally available geomaterials.

Montana, G., Randazzo, L., Cerniglia, R.M., Aleo Nero, C., Spatafora, F. (2016): Production technology of Early-Hellenistic lime-based mortars originating from a Punic-Roman residential area at Palermo (Sicily). Int. J. Conserv. Sci., 7, spec. issue 2, 797-812.

Lava stone and the church of Santa Maria in Randazzo (Sicily)

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Keywords: Sicily, architecture, historical building, lava stone, quarries.

The foundation of the church of Santa Maria is linked to the legendary discovery of a painting of a Madonna in Randazzo, a city of ancient foundation at the slopes of Mount Etna. A church destined to preserve the sacred icon was built in the same place, in the 13th Century.

Two epigraphs, still preserved on the church's western facade, testify that it was built in 1239 and its interior consisted of twelve columns supporting pointed arches. In 1917, Walter Leopold (1894-1953) drew a plan of the church, excluding all the parts he considered posterior to the engraving of the epigraphs. He excluded the covering of the transept with drum and dome and the new main facade, works that had completed the construction of the church only in the mid-19th Century (Passalacqua, 2016).

But the church of Santa Maria underwent a consistent construction period in the 16th Century, when the noblewoman Giovannella De Quadris Rizzeri donated her feuds to the *fabric,* to complete it. This availability of funds allowed the start of important works that we can only read about in some accounting registers that provide new evidence of the history of the building.

From the documents, it can be supposed that the administrators of the church decided to enlarge it from the apsidal area. Many local labourers, assisted by marble workers and stone-cutters, often of Tuscan origins, who worked in Messina during the 16th Century, came to the town on Etna to work in the new construction-site.

The reconstruction model foresaw, first of all, the rebuilding of the tribune, finished off by three semi-circular apses and, after 1580, the principle nave was also rebuilt.

The new project is attributable to Andrea Calamecca (1524-1589). He was active in those years in Messina and his presence in Randazzo, although not documented, could be justified by the work realised in the *fabric* by his brother Domenico (1520-1569-72). He redesigned the building in a rigorous Renaissance style, erasing its precedent medieval character. The renovation works continued uninterruptedly until 1634, when the *fabric* administration was transferred to Palermo, causing a substantial stasis of the construction site.

Only at the end of the 18th Century did Giuseppe Venanzio Marvuglia (1729-1814) realized the dome on the transept. The building was completed in the mid-19th Century by Francesco Saverio Cavallari (1810-1896) with the reconstruction of the towered facade in new medieval form (Passalacqua, 2011).

The peculiar feature of the building, probably, since its foundation, is the use of lava stone in the interior and on all the facades, strongly characterizing the structure (Cultrone et al., 2001). Investigations on the stone material, taken from the columns separating the aisles from the nave, from the southern facade, which is presumed to have been reconstructed in the 16th Century, and the external covering of the apses (completed only in the 1630s) should confirm the hypothesis, inferred from the study of archival documents, that the building, despite being founded in the medieval period, saw various reconstructions from the early decades of the 16th Century, and was only completed in the 19th Century.

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Lumps as a key to identify the stone used for lime in historical mortars

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Keywords: lumps, mortars, material culture.

Mortars are artificial materials realized by man along the past ages and to be used in architecture with different functions. The study of their composition is therefore not only aimed at the knowledge of the components that constitute them, but also allows us to investigate the material culture that produced them. It is well-known that a mortar is constituted by binder, aggregate, water, and possible additives. As for the binder, it is important to evaluate the presence of fragments exhibiting a whitish colour and sometimes an inconsistent aspect, generally named "lumps". The presence of these fragments indicate that lime was realized according to a traditional technology with slaking of the quick lime according to the so-called "melting" method The white pasta (lime putty) is then cast (through a net that holds the bigger underburnt/overburnt lime fragments) to a pit where it is left for the aging process. The study at the optical microscope in transmitted light allows to recognize the nature of such lumps making it possible to recognize the following typologies: lumps of the binder not amalgamated into the mixture; underburnt lime fragments (burning relicts of limestone); overburnt lime fragments; overburnt lime fragments hydrated and carbonated after the setting reaction. Such petrographic approach to the study of the "lumps" is a valid tool to identify the kind of carbonatic stone used to realize the binder. We should also recall that an excess of these fragments indicates a poor production technology. In particular, the type of lumps indicates which stage of the production cycle has been less cured.

Stones of the “Terme del Sarno" façade (Pompeii, Italy)

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Keywords: lithological mapping, Pompeii, Neapolitan tuff, Campanian ignimbrite, Somma Vesuvius lavas.

This study deals with the lithological analysis of the “Terme del Sarno” façade at Pompeii (Naples, south Italy). The thermal complex is a big building located in the south-western of the ancient city walls at Pompeii, the façade of which, facing south, preserves quite completely three levels, a basement and two noble floors. The façade has a big extension, approximatively 650 m^2, with length and height of 50 m and 15 m, respectively. The architectural analysis pointed out the used of different building technique in the various portions of the façade (basement, arches, windows and recess jambs and architraves). The lithological mapping was therefore addressed to specifically define the types of stone use in all the visible blocks and ashlars. In addition to the macroscopic identification, a series of 90 samples were collected from the façade and petrographically (optical and electron microscopy) and mineralogically analysed to better constrains the lithotype. The analysis revealed the use mainly of volcanic and volcano-clastic rocks, and in particular of yellow tuffs, grey tuffs, leucite phonolitic tephrite, and of travertine. Yellow Tuffs were supplied from the Neapolitan Yellow Tuff (about 15 ky), the Grey Tuffs from the Campanian Ignimbrite (about 39 ky) and the leucite phonolitic tephrite from the lava flows of Somma Vesuvius, respectively. Travertine derives from the Sarno limestone (Calcare del Sarno). Few blocks are composed by micrite limestone, marble, mortars and fragment of masonry, clearly deriving from the recycle of ancient building materials.

The lithological mapping revealed that the basement is mainly composed of leucite phonolitic tephrite, associated to travertine and sporadically also to yellow tuff. On the first level of the façade prevails Grey Tuff interposed to bricks on the western portion, whereas on the eastern one the Yellow Tuff. The second level is instead composed mainly by Grey Tuff, with the exception of portions executed in *opus reticulatum*, composed predominantly by Yellow Tuff. Travertine in the uppermost and eastern portions of the second level represents a rebuilding made by archaeologists during the ’60s excavation and restoration. The distribution in the façade of the various lithotypes, characterised by different bulk density and mechanical properties, confirms ancient Roman builders high level knowledge of the technical features of these materials and of their structural behaviour.

Pre-consolidation of decayed Angera columns with ammonium phosphate. A pilot study in a Milanese courtyard of XVI Century

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Keywords: Angera stone, pre-consolidation, inorganic-mineral treatments, ammonium phosphate, calcium phosphates.

Angera stone is a lithotype widely employed in Lombardy (north Italy) for ornamental elements/frameworks of historical buildings. Owing to decay processes it is affected by detachments, exfoliations, pulverizations with consequent loss of material. The traditional application of synthetic organic products on the Angera surfaces had a significant role in the decay processes as well (Colombo et al., 2006). Over the last years, the boundaries of Conservation Science have been pushed toward the use of inorganic-mineral treatments that are stable, durable, highly transpirable and more compatible with the stone substrates. Ammonium phosphate [DAP, $(NH_4)HPO_4$], one of the most recent inorganic-mineral treatment, is based on the reaction between a water soluble precursor with carbonatic substrates; the newly formed crystalline phases are able to restore the lost cohesion of the microstructure. Recent studies investigated the interactions of DAP solutions with calcite of marbles and limestones (Matteini et al., 2011; Possenti et al., 2016). To the best of our knowledge, no data are available on the application of DAP to: i) the conservation of dolostones; ii) the pre-consolidation of decayed stones.

Therefore, in this study we explored the potentialities of DAP treatments as a pre-consolidating agent for white Angera stone. DAP solutions were vaporized on vertical specimens to avoid mechanical contact with decayed surfaces. The research evaluated the effects induced by the molarity and the application method (repeated applications, wetted or dry substrate, comparison with paper poultice) on the surface and the influence of pre-consolidation on the subsequent consolidation with DAP.

The formation of specific crystalline phases and their diffusion inside the first few microns of the stone matrix were investigated following a multi-analytical approach (SEM-EDS, Raman and IR spectroscopies, XRD). The research outcomes supplied outstanding indications for restoration, supporting the application of DAP pre-consolidating treatments to Angera columns strongly decayed in a Milanese courtyard of XVI Century.

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A comparative study of different formulations of poultices for soluble salts removal from experimental plasters

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Keywords: restoration, plasters, soluble salt removal, poultice products, extractive capability.

Soluble salts extractive capability of some commercial materials currently used in plaster restoration sector (Arbocel™ plus sepiolite; Arbocel™, sepiolite and sand; Westox-Cocoon®) were tested in the present study, with the aim to evaluate their efficiency, their compatibility with the substrates as well as in terms of costs and duration of intervention. The three poultice products were first characterized in terms of porosimetric distribution. The desalination tests have been performed on samples of plaster specially formulated and made at the laboratory. Experimental specimens were then brought into contact with a solution of Na_2SO_4 0.3 M. The efficiency rating of these different types of poultice products was carried out, for the whole duration of the test, by means of ion chromatography and electrical conductivity measurements performed on obtained solutions. Between the tested products, Westox-Cocoon® showed the best efficacy in terms of soluble salts extractive capability while the other two products, which were successfully used in previous experiments (Montana et al., 2014), did not have the same positive results in this case study. Furthermore, in a real system it is also necessary to take into account other factors such as easiness of application, capacity of the various poultices, compatibility with the substrate and cost/benefit ratio. Being fully aware that the proposed approach is still preliminary, this paper provides a practical example of standardizing a survey methodology for evaluating the efficiency of salt extraction methods from porous building materials.

Montana, G., Randazzo, L., Castiglia, A., La Russa, M.F., La Rocca, R., Bellomo, S. (2014): Different methods for soluble salt removal tested on Late-Roman cooking ware from a submarine excavation at the Island of Pantelleria (Sicily, Italy). J. Cult. Herit., 15, 403-413.

Determination of reactivity of volcanic aggregates in ancient mortars by using LIBS

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Keywords: LIBS, mortars, volcanic ash.

Laser-Induced Breakdown Spectroscopy (LIBS) has recently affirmed as versatile multi-element method for studying the composition of archeological materials (Gaudiuso et al., 2010; Giakoumaki et al., 2007; Pagnotta et al., 2005). Its suitability in cultural heritage studies is due to numerous advantages of the technique, being non-invasive, micro- or not destructive, requiring no sample preparation and assuring a high spatial resolution (Legnaioli et al., 2014). In mortar-based building materials studies, the opportunity to explore the chemical composition of both binder and aggregates by using LIBS represents a valuable contribute to solve archeological questions related to manufacture, processing, raw materials provenance and reconstruction of chronological phases in multi-layered structure (Sağın et al., 2012). In fact, the possibility to discriminate, on chemical base, different hydraulic features of mortar employed in a certain building can address information of the possible changes in recipes over the time and over various construction and restoration phases. Apart from binder, aggregates have a key role in determining the final proprieties of mortars; in ancient structures, the choice of a particular type of reactive aggregates were often related to aesthetical *vs.* practical utility requirements. In some recipes, volcanic sand was widely used to confer reactivity to the admixture (Rapp, 2013). Hydraulicity levels can be valued on the basis of silica and alumina *vs.* lime contents in C-S-H phases; therefore, a microchemical analysis can provide valuable data to esteem this parameter, inspecting the possible variation in reactivity conferred by reactive aggregates ranging in grain size and thickening. In this study, LIBS has been used to evaluate the level of hydraulic in mortars used as wall covering and characterized by volcanic aggregates sampled by applying a micro-stratigraphic criterion from a Norman Castle built in XI Century in Sicily and retouched more and more until XVI Century. The obtained results have been employed to (i) validate the method in mortars studies, highlighting the possible variation in reactivity levels with grain size and thickening of aggregates, and (ii) inspect the craftsmen's knowledge related to the different recipes employed over the structure, possibly related to different construction phases.

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Pagnotta, S., Grifoni, E., Legnaioli, S., Lezzerini, M., Lorenzetti, G., Palleschi, V. (2005): Comparison of brass alloys composition by laser-induced breakdown spectroscopy and self-organizing maps. Spectrochim. Acta B: Atomic Spectr., 103-104, 70-75.

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Sağın, E.U., Böke, H., Aras, N., Yalçın, Ş. (2012): Determination of $CaCO_3$ and SiO_2 content in the binders of historic lime mortars. Mater. Struct., 45, 841-849.

Villa del Capo and *Villa del Pezzolo*: Roman mortars from Sorrento Peninsula

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Keywords: ancient Roman mortars, Sorrento Peninsula, Villa del Capo, Villa del Pezzolo.

This study concern the characterization of ancient Roman mortars present in *Villa del Capo* (commonly called *Bagni della Regina Giovanna*) and *Villa del Pezzolo* in Sorrento Peninsula. Different materials (bedding, coating and floor mortars) were collected in the two villas. Mortar characterization was carried out through optical microscopy (OM) on thin sections, X-ray powder diffraction (XRPD), scanning electron microscopy analysis (SEM), energy-dispersion X-ray spectroscopy (EDS), thermal analyses (TGA-DTA) and mercury intrusion porosimetry (MIP).

Bedding mortars were realized using a mixture of slaked lime, water, fine-grained volcanic materials with addition of a coarse grained volcanic and carbonatic aggregates; as coating and floor mortars are concerned, the previous described mix design presents also fragments of (fine- and coarse-grained) ceramic materials. The provenance of lime and carbonate fragments, identified in the villas, is still unknown, probably they could have been produced on site using local raw materials, widely present in the Sorrento Peninsula. More interesting are the differences in the provenance and mixture of volcanic aggregates identified in the *Villa del Capo* and *Villa del Pezzolo* mortars.

Villa del Capo mortars show volcanic aggregates related to the Neapolitan Yellow Tuff formation, due to the peculiar mineralogical association (phillipsite > chabazite > analcime) (de Gennaro et al., 2000). Occurrence of leucite-bearing scoriae and garnet crystals, typical of volcanic deposits related to the Somma-Vesuvius activity, are also present in some samples from *Villa del Capo*.

Mortars from *Villa del Pezzolo* belong to three distinct building phases. Volcanic tuff fragments in mortars of the 1st building phase could be assigned to the Campanian Ignimbrite formation, cropping out widely in Sorrento Peninsula. This was confirmed by the presence of glassy shards, partially devitrified and replaced by authigenic feldspar, a typical feature of welded gray Campanian Ignimbrite lithofacies (WGI; Langella et al., 2013). The volcanic aggregates in samples of the 2nd and 3rd building phases show instead presence of leucite-bearing volcanic scoriae and garnet crystals, thus suggesting use of a volcanic aggregates influenced by Somma-Vesuvius eruptions.

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Chemical characterisation of ancient, medieval and modern metallurgical slags in southern Tuscany and Elba Island

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Keywords: slag, roasting, smelting, southern Tuscany, Elba Island.

The geological evolution of southern Tuscany led to the formation of several base metal deposits, which were exploited starting from Etruscan period until the 1980s. Throughout these twenty-seven centuries, the extractive metallurgy processes evolved following available techniques, nevertheless, slags were invariably produced during the process.

Slag formation enhances metal separation from the gangue, therefore they had to have a rather low melting point and a relative density lower than the metal which should be extracted from the ore. Hence, slags reflect the characteristics of the metallurgical extraction process, showing a different chemical composition related to charge, choose of flux and process efficiency. Thus, slags do not represent just a waste of the metallurgical processes, but they are important by-products, with specific characteristic that can provide significant informations. This study is focused on the slag heaps located near roasting/smelting sites on the four main districts of Elba Island, Baratti (Populonia), Campiglia Marittima and Massa Marittima.

Chemical analyses on slags were performed using a Hand-Held X-Ray Fluorescence Spectrometer (HH-XRF), that allows to perform fast and non-destructive analysis, so that a large number of different slag heaps can be quickly characterized. Moreover, it was possible to analyse materials found in Baratti archaeological site without any impact on them.

The composition of the analysed samples gives preliminary information concerning the chemical variability between slags from different sites and originating from different processes. It is possible to infer the provenance of both the ore and the material used as flux, to understand the efficiency of the metallurgical process, as well as to infer the likely age of each site's production.

These data are a useful base for further archaeometric investigations and have in the meantime a potential cultural-touristic appeal. Therefore, the collected data were used to develop a database available online that allows the visualization on a map of georeferenced information. So, essential details were shown for each site, such as photos or general data about the type and age of production, together with results for chemical composition of slags.

Traces of metallurgy in the Panormos Phoenician colony (Palermo, Italy): archaeometric characterization of iron-slags

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Keywords: Panormos Phoenician colony, iron slags, SEM-EDX, XRF, Palermo.

Archaeological works carried out in Palermo (NW Sicily) by the Archaeological Section of the Soprintendenza BB.CC.AA. of Palermo, between 2011 and 2012, revealed a settlement dating back to the Ellenic age and belonging to the Panormos Phoenician colony (Aleo Nero et al., 2016). The archaeological site brought to light fragments of potteries-Punic type amphorae-shells remanents, besides iron slags and oxidized strata connected with traces of metallurgical activity. Few information exists about Sicilian metallurgy during this age, and the iron slags connected with this activity have been little studied so far. This contribution is aimed to broaden our knowledge on this class of remains, contributing to increase the archaeological information about the Phoenician metallurgy in Sicily, and overall in southern Italy. To reach these objectives, textural, mineralogical and geochemical characterization of iron slags was carried out through a multidisciplinary analytical approach including Electron Microscopy with electron-dispersive energy (SEM-EDX), X-Ray Powder Diffraction (XRPD) and X-Ray Fluorescence (XRF).

The studied iron slags show pseudo-spherical shape, spongy appearance and rust color. SEM-EDS analyses evidenced the presence of a glassy matrix with variable amount of iron silicates and Ca-rich portions in which iron oxides are embedded with dendritic and/or globular habitus. XRPD investigations identified quartz, calcite, fayalite and hedenbergite, with wüstite, maghemite and magnetite as primary iron oxides, and lepidocrocite and goethite as secondary hydrated iron oxides. In terms of bulk composition, XRF analyses highlighted prevalent amounts of SiO_2 (13.31-46.12 wt%), FeO (37.99 – 68.76 wt%), CaO (9.22 – 19.38 wt%), Al_2O_3 (2.21 – 3.17 wt%) and P_2O_5 (0.87 – 2.26 wt%) and minor amounts (< 2%) of MgO, K_2O, SO_3, TiO_2, MnO and Na_2O.

These results indicate that the investigated samples represent metallurgical materials associated with iron smithing. Slag mineral phases include iron silicates, calcite, quartz and iron oxides as the most abundant phases. Concerning the smithing process, the significantly high amount of lime in the investigated slags leads back to the Carthaginian-type metallurgical process. The high calcium content suggests the use of a lime-based flux. This hypothesis is reinforced by the occurrence during the excavations, of recycled *Murex* shells, probably previously used to produce purple dye (Charlton et al., 2010). However, we can not exclude that the lime content could also derive by the use of local carbonatic lithologies, widely outcropping in the Palermo territory.

Aleo Nero, C., Chiovaro, M., Sabatino, G., Di Bella, M., Marcianò, G. (2016): Un esempio di attività metallurgica di età ellenistica a Panormos. In: "La città che produce. Archeologia della produzione negli spazi urbani", Giornate Gregoriane, X edizione, Agrigento, 10-11 dicembre 2016.

Charlton, M.F., Crew, P., Rehren, T., Shennan, S.J. (2010): Explaining the evolution of ironmaking recipes-an example from northwest Wales. J. Anthropol. Archaeol., 29, 352-367.

Verifying the presence of lead stannate in opaque mosaic glass tesserae (2^{nd} Cent. BC-4^{th} Cent. AD) from southern Italy

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Keywords: lead antimonate, lead stannate, yellow glass, opacifiers, SEM-EDS, LA-ICP-MS.

Lead antimonate ($Pb_2Sb_2O_7$) and lead stannate (Pb_2SnO_4) are both glass opacifiers and colorants. These compounds are dispersed in the vitreous matrix as fine particles and, due to the difference of refractive index between the crystals and the amorphous phase, prevent light from being completely transmitted, inducing the opaque aspect of the glass. Lead antimonate was used to produce opaque yellow glass from the beginning of glass production up to the Roman period. From about the 4th Century AD towards the end of the Roman period, lead stannate replaced lead antimonate in the production of opaque yellow glass artifacts (Tite et al., 2008). Only Lahil et al. (2011) reported the presence of lead stannate in glass *tesserae* dated before the 4th Century AD.

In this study we explore the presence of lead stannate in mosaic glassy *tesserae* from several archaeological sites, earlier than the 4th Century AD. The mosaic *tesserae* here studied come from Taormina (II Cent. BC), Lipari, Tusa, Piazza Armerina (III-IV Century AD), and Pompei (I Cent. BC) archaeological sites. The multidisciplinary analytical approach includes Scanning Electron Microscopy (SEM-EDX), X-Ray Diffraction (XRD), Inductively Coupled Mass Spectrometry with Laser Ablation (LA-ICP-MS). The overall results of this study extend our archaeometric knowledge of the glass mosaic *tesserae* investigating the nature and the chemical composition – including also to the trace elements – of the glass matrix, the colorants and the opacifying agents in a very wide set of samples.

Lahlil, S., Cotte, M., Biron, I., Szlachetko, J., Menguy, N. Susini, J. (2011): Synthesizing lead antimonate in ancient and modern opaque glass. J. Anal. At. Spectrom., 26, 1040-1050.

Tite, M., Pradell, T., Shortland, A. (2008): Discovery, production and use of tin based opacifiers in glasses, enamels and glazes from the Late Iron Age onwards: a reassessment. Archaeometry, 50, 67-84.

Multidisciplinary diagnostic processes aimed to treatment of stone's lacune. Analysis and restoration of the balustrade of Villa Cerami in Catania

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Keywords: interdisciplinary, pathologies, material's characterization, physical features, protective.

This paper explains as an interdisciplinary study applied by geologists, architects and restorers can be very useful to the planning and performing the conservation measures of a monument through the description of the restoration's case of Villa Cerami balustrade.

This restores carried out in 2015 and was commissioned to the University of Catania. The balustrade adorns and protects the steps of Villa Cerami, which is an example of 18th Century "urban villa" located in the historic center of Catania. Sadly, these stunning steps, whose magnificence and placement characterizes the outdoor environment of the building at present suffer from bad decorative details adorning the baluster are affected by irreversible damage.

The scientific approach, described below, was apply preliminary to the restoration and allowed to identify the materials and the type and the causes of degradation forms with the aim to plane and perform the conservation measures. In particular, the study was planned in several operating steps: i) Historical research; ii) Geometric survey (it was performed by means direct and/or instrumental methods as 3*D* laser scanner); iii) analyses of building techniques (materials, construction techniques, functional and structural performance etc.); iv) analysis of damage (it was developed by means of both traditional and no-destructive surveys and mapping) (Sanfilippo et al., 2015). Static verification was performed to choose if preserve or replace some of the more degraded balusters. In particular, the 3*D* survey has allowed a more accurate assessment of the degree of structural risk.

The petrographic features of the materials were analyzed using a Zeiss polarized optical microscope while the qualitative mineralogical composition was determined through X-ray diffraction. With the aim to investigating possible change in the physical properties of stone material due to degradation, a physical characterization using the distribution of pore access size and pore volume was determined with mercury intrusion porosimeter (MIP).

The purpose of the work was to contribute to the understanding the degradation's state of the balustrade and to the planning of the restoration and protection of the artefact aimed to decrease the water's circulation and polluting agents deposition. For this last reason was tested a polymethylsiloxane reactive oligomer with protective action (Silo 111-CTS) on the lithotype by way of efficiency and compatibility tests according to UNI 10921:2001.

Furthermore this paper provide a multidisciplinary method applicable to all severely degraded architectural elements in order to evaluate the residual cultural (aesthetic and material) and functional (degree of structural risk) content and therefore to perform the correct project choices.

Sanfilippo, G., Aquilia, E., D'Agostino, G. (2015): Scientific and interdisciplinary method us support for restoration project. The balustrade steps of Villa Cerami. Sci. Res. Inform. Technol., 5, 77-92.

Archaeometric study of a local production of "Gnathia style" ware at Pompeii

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Keywords: Pompeii, Black Glazed pottery, "Gnathia style", archaeometry.

Recent archaeometric investigations have been undertaken on a homogeneous group of pottery comprising: "Gnathia style" ware, Red figure ware and Hellenistic band-decorated ware. These ceramics, dating between the mid-4th and early-3rd Century B.C., are characterized by external surfaces often decorated with reserved bands or band-decorated external surfaces, while the interior is generally painted with uniform black "glaze". These ceramics were found in the same context with misfired sherds, abundant black glaze ware (Scarpelli et al., 2014, 2017) and numerous kiln spacers, all dating to the same chronological span. From a macroscopic point of view these ceramics seemed to have been made with a same or similar clay, forming a distinctive group/production not yet attested in the Vesuvian and nearby area. In order to define and characterize this group and its possible provenance, archaeometric analyses were undertaken including petrographic (OM-optical microscopy), mineralogical (XRD-X-ray diffraction-and Raman microscopy) and chemical analyses (XRF-X-ray fluorescence and EMPA-Electron Microprobe) on ceramic body and black glaze. This approach allowed to make a direct comparison between these classes of ceramics, proving their chemical similarity.

Scarpelli, R., Clark, R.J.H., De Francesco, A.M. (2014): Archaeometric study of black-coated pottery from Pompeii by different analytical techniques. Spectrochim. Acta A, 120, 60-66.

Scarpelli, R., Robustelli, G., Clark, R.J.H., De Francesco, A.M. (2017): Scientific investigations on the provenance of the Black Glazed pottery from Pompeii: a case study. Mediterr. Archaeol. Archaeom., 17, in press, DOI: 10.5281/zenodo.258088.

Grainsize and pore network as intrinsic factor for weathering: the *Vicenza Stone* case study

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Keywords: stone conservation, grain size, porosity, petrophysics, decay.

The textural layout of a rock, and, in particular, the grain size variation, controls the weathering dynamics under the same chemical and mineralogical composition. The addressed material was the *Pietra di Vicenza*, a bioclastic limestone, often recrystallized and cemented by micrite calcite matrix, Fe-oxides and hydroxides, with an heterogeneous texture, with variable grain size from coarse to fine, and high open porosity (22-23%). The sample sets was issued from the same quarry, where a front higher than 10 m shows fining upwards textures with different grain size. Onwards, the two sets will be analysed separately as Coarse grained (CGV) and Fine grained (FGV) *Pietra di Vicenza*.

The complete structural and textural characterization of sample sets was carried out by Optical Microscopy-OM, Scanning Electron Microscope-SEM, Image Analysis, X-ray Computed Tomography-XRCT, Mercury Intrusion Porosimetry-MIP, Hygroscopicity, Ultrasounds, Water Absorption in order to study the weathering triggered by freeze thaw ageing test and saline contamination associated with grain and pore sizes. Artificial ageing processes were induced using the UNI 11186:2008 protocol for freeze thaw testing, and the partial continuous immersion method with a Na_2SO_4 saturated saline solution for salt crystallization to compare the data on un-weathered and weathered rocks and unveil the connection between intrinsic properties and decay features.

SEM allowed identifying the on-going processes (*i.e.*, mechanical or chemical weathering) during artificial decay in the two different varieties. Freeze thaw induced in both varieties micro-cracks openings and deposition of secondary micrite. Whereas after saline solution contamination FGV showed both micro-cracks and secondary precipitation, suggesting the simultaneous occurrence of mechanical stress and chemical dissolution-precipitation processes. Conversely, CGV showed higher susceptibility to chemical processes, with a vast precipitation of secondary calcite. The petro-physical characterizations (porosimetric curve, anisotropy coefficient, water absorption and their evolution) are mutually consistent and were functional to define the extent of the induced decay, revealing that CGV is more susceptible to decay than FGV, thus highlighting the dependence of grain and pore sizes in weathering processes.

Raw materials analysis for the identification of a production site of Greek transport amphorae: the case of Corfu

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Keywords: archeometry, amphorae, Corfu and Sicily.

According to the historical sources, Corfu (ancient Kerkyra), the Greek island colonized by the Corinthians in the Ionian Sea, produced a good wine that was contained in the “corcyrean amphorae”. Modern scholars have long discussed the identification of these jars. In the Type B of her classification of the Corinthian amphorae, Koehler (1979) distinguished two forms, both attributed to Corinth, but for the older one (VI-early V Century B.C.) she also hypothesized a western-Greek workshop, whereas for the more recent one (second quarter of the V-III Century B.C) she admitted a production in Corfu, according to the results of some archaeometric analyses (Jones-Simopoulos-Kostikas in Koehler, 1979). However, other chemical investigations (Farnsworth et al., 1977) in the meantime highlighted the difficulty of distinguishing between Corinthian and Corcyrean ceramics, because of their compositional affinities. Finally, in 1983, the discovery of a workshop in Corfu confirmed the existence of a local production of the second form (Preka, 1992), but this did not solve the problem of the origin of the older one. More recently, some archaeological and archaeometric research has investigated the possibility of different western-Greek productions, probably located on the coasts of the Ionian Sea, both in Greece and in southern Italy (Spagnolo, 2002; Barone et al., 2004; Sourisseau, 2011; Gassner, 2015).

In this complicated matter, the purpose of our research is to investigate the raw materials cropping out in Corfu-also comparing them with those from Corinth-with the aim to identify the main archaeometric characteristics of island materials and to define a reference group, indispensable to resolve the open issues regarding the production of the “Corinthian B” amphorae.

Barone, G., Crupi, V., Galli, S., Longo, F., Majolino, D., Mazzoleni, P., Spagnolo, G. (2004): Archaeometric analyses on “Corinthian B” transport amphorae found in Gela (Sicily, Italy). Archaeometry, 46, 553-568.

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Gassner, V. (2015): Le anfore greco-occidentali: riconsiderando la loro evoluzione e l’identificazione dei centri di produzione. In: Roure, R (ed.), Contacts et acculturations en Méditerranée occidentale. Études Massaliètes, 12, 345-356.

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Preka Alexandri, K. (1992): A Ceramic Workshop in Figareto, Corfù. Bull. Correspond. Hellen., 23, suppl., 41-52.

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Spagnolo, G. (2002): Le anfore da trasporto arcaiche e classiche nell'Occidente greco: nuove acquisizioni da recenti rinvenimenti a Messina. In: “Da Zancle a Messina. Un percorso archeologico attraverso gli scavi, Vol. II”, G.M. Bacci & G. Tigano, eds. Sicania, Palermo, 31-46.

Non-invasive identification of organic and biomolecular components of works-of-art by spatially resolved mass spectrometry and innovative biosensors

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Keywords: AP-MALDI/MS, surface plasmon resonance, binding media.

Spatially resolved analytical methods have significantly enhanced our capacity to study ancient works-of-art by using minimally destructive approaches. In this context, great efforts have been paid to investigate with spatial resolution inorganic components of artistic and archaeological object, while only a few analytical techniques useful to investigate the organic and biomolecular components of artistic and archaeological objects have been tested so far.

New possibilities for the minimally invasive chemical characterization of organic and biomolecular components of artistic and archaeological object will be presented with specific attention to spatially resolved mass spectrometry (MS) techniques and innovative biosensing platforms.

In recent years, possibilities offered by spatially resolved MS techniques based on matrix assisted laser desorption ionization (MALDI) have been highlighted. The low-medium vacuum conditions required by MALDI-MS significantly limit potential for *in situ* analysis of large objects. Atmospheric pressure (AP) MALDI-MS has been shown to overcome the above mentioned limitations and has been proposed as a new tool for the spatially resolved and minimally invasive analysis of organic components of artistic objects. Possibilities offered by *in situ* AP-MALDI-MS in identifying organic components of ancient carbonaceous inks will be presented. In particular, AP-MALDI-MS has been used, for the first time, to identify polycyclic aromatic hydrocarbon compounds from inks used in XVII Century manuscripts. PAHs are formed as a consequence of an incomplete combustion of the organic matter. Therefore, their presence testifies that specific procedures were used in the past for the production of the carbonaceous material used as the pigment for inks. We prove that it is possible to operate at AP, applying MALDI-MS as a suitable micro-destructive diagnostic tool for analyzing samples in air, simplifying the investigation of the organic components of artistic and archaeological objects.

Biomolecular compounds have been widely used in traditional art as media, binders or glues. The simple identification of such complex systems is challenging and immunological methods have been recently applied for this purpose. Possibilities offered by Surface plasmon resonance biosensing will be briefly explained and preliminary data from the SPR imaging detection of albumin from ancient photos will be presented.

Laboratory characterization of deteriorated siloxane and epoxy resins applied for the consolidation of Venetian monumental stone surfaces in the XX Century

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Keywords: stone decay, conservation, consolidation, silicone and cycloaliphatic epoxy resins, EP2101- Sogesil XR893, laboratory characterization.

Development of techniques and research on synthetic materials used for the preservation of the immovable cultural heritage led to advances in technologies and application methods, which were also adapted for the restoration and conservation of stone materials. Restorers and conservators contributed to the spread of these treatments and application methodologies, though they were not always subjected to preliminary experimental tests to ensure their efficacy. This often led to the development of decay mechanisms, such as the generation of secondary products, due to the chemical interaction between the product applied and the stone substrate or with the environment (Antonelli et al., 2016), and later compromised the stability and the aesthetic appearance of the artefact.

In recent years, the *Laboratory for the Analysis of the Ancient Materials* at the Iuav University of Venice has undertaken a research project designed to verify the state of conservation and the morphology of the decay of consolidating and protective organic resins applied to monumental surfaces during well documented restoration works in the city of Venice (Italy) over the last 50 years. For this purpose, an experimental operating methodology was developed to evaluate the efficacy of commercial products widely used for the restoration of stone materials today as in the past, and to characterize any associated decay mechanisms.

In this context, the commercial cycloaliphatic epoxy resin *EP2101* and the siloxane compounds *Rhodorsil Consolidante RC90* and *RC80*, were carefully applied to stone specimens and tested to ascertain their chemical nature, the mechanisms involved in the polymerization reactions and their stability under oxidative stress and degradative environments.

The resins were first chemically characterized by means of GC/MS, FTIR, EDS and DTA-TG techniques (Tesser et al., 2014) then applied to laboratory samples (slides, Carrara marble, Vicenza white limestone), and finally subjected to controlled photo-oxidative, and thermo-oxidative weathering. The films morphology and the penetration depth was observed and measured by SEM-EDS determinations, while the stability of the resins was monitored by FTIR, SEM-EDX, colorimetric measurements and sponge tests. The resistance to mold growth was monitored as well.

The results obtained were compared with those obtained from a spread sampling of Venetian stone surfaces treated in the second half of the XX Century. with the same cycloaliphatic epoxy resin *EP2101* and*Sogesil XR893*, a polysiloxane no longer in the marked and today substituted with *Rhodorsil Consolidante RC90*. Chemical FTIR and µFTIR analysis, microscopic observations, SEM-EDS studies, sponge tests made it possible to characterize, compare and contrast the performance over time of two polymeric groups of consolidating resins widely used in conservation treatments on Venetian monuments in the 1960s, '70s and '80s.

The overall results prompted a number of considerations on the effects of the resins applied to stone materials and offered the authors the opportunity to make a general comment regarding treatment methods and their relative implications, making a practical contribution to the consolidated decayed crystalline marble today, which is much appreciated by the Venetian Superintendency.

Antonelli, F., Lazzarini, L., Cancelliere, S., Tesser, E. (2016): Study of the deterioration products, gilding, and polychromy of the stones of the Scuola Grande di San Marco's façade in Venice. Stud. Conserv., 61, 74-85.

Tesser, E., Antonelli, F., Sperni, L., Ganzerla, R., Maravelaki, N-P. (2014): Study of the stability of siloxane stone strengthening agents. Polym. Degrad. Stab., 110, 232-240.

On the route of lapis lazuli trade in ancient time: a multi-technique provenance study of the raw material used for carved artefacts

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Keywords: lapis lazuli, μ-XRF, μ-PIXE, trace elements, archaeometry, provenance.

Lapis lazuli is a blue semi-precious stone that has been used since Neolithic Era (VII millennium B.C.) for the manufacturing of precious carved artefacts. The possibility to associate the raw material to man-made objects could help historians and archaeologists to reconstruct trade routes especially for the ancient time when written testimonies are scanty or absent at all. Despite the Badakhshan Province (Afghanistan) remains the most plausible hypothesis for the lapis lazuli used in antiquity, alternatives proposed in literature are worth to study to confirm or disprove their historical reliability. To solve the issue we started in 2008 a long-term research, involving an interdisciplinary team, and only recently we presented a protocol for determining the provenance of lapis lazuli rocks used for carved artefacts by means of non-invasive techniques (Angelici et al., 2015; Re et al., 2015; Lo Giudice et al., 2017). Markers for the univocal attribution of the raw material to a source were identified analysing 45 rocks of known provenance from 4 quarry districts. The research has been focused in searching markers on single mineral phases using microscopic techniques, which allow to observe and to analyse single crystals. In particular it was verified that all the markers found (presence of a mineralogical phase, trace elements, luminescence bands) are simultaneously detectable by means of ion beam analysis (IBA), in particular micro-PIXE (Proton Induced X-ray Emission) and micro-IL (IonoLuminescence), or X-ray techniques, in particular micro-XRF (X-Ray Fluorescence) and XRL (X-Ray Luminescence). These techniques are non-invasive and applicable in air, allowing to analyse artworks and rocks of practically any shape and dimension without sample preparation.

The protocol was successfully applied to determine the provenance of raw material used for carved lapis lazuli artefacts kept in different museums in the northern Italy. The studied collections have a great historical value and include objects ranging from the first millennium B.C. to the XVIII Century. Following the protocol, a total of about 40 artefacts were analysed and results ascribe the raw material to the Afghan quarry district.

Angelici, D., Borghi, A., Chiarelli, F., Cossio, R., Gariani, G., Lo Giudice, A., Re, A., Pratesi, G., Vaggelli, G. (2015): μ-XRF analysis of trace elements in lapis lazuli-forming minerals for a provenance study. Microsc. Microan., 21, 526-533.

Lo Giudice, A., Angelici, D., Re, A., Gariani, G., Borghi, A., Calusi, S., Giuntini, L., Massi, M., Castelli, L., Taccetti, F., Calligaro, T., Pacheco, C., Lemasson, Q., Pichon, L., Moignard, B., Pratesi, G., Guidotti, M.C. (2017): Protocol for lapis lazuli provenance determination: evidence for an Afghan origin of the stones used for ancient carved artefacts kept at the Egyptian Museum of Florence (Italy). Archaeol. Anthropol. Sci., 9, 637-651

Re, A., Angelici, D., Lo Giudice, A., Corsi, J., Allegretti, S., Biondi, A.F., Gariani, G., Calusi, S., Gelli, N., Giuntini, L., Massi, M., Taccetti, F., La Torre, L., Rigato, V., Pratesi, G. (2015): Ion beam analysis for the provenance attribution of lapis lazuli used in glyptic art: the case of the "Collezione Medicea". Nucl. Instr. Meth. Phys. Res. B, 348, 278-284.

From the lab ot the art site: application of Raman spectroscopy for the non-destructive analysis of pigments

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Keywords: Raman spectroscopy, cultural heritage, pigment analysis, Raman mapping, *in situ* analysis.

Raman spectroscopy is becoming increasingly important as an analytical technique in conservation science. The approach has many advantageous properties, such as its non-destructive character, the ability to record molecular spectra of inorganic as well as organic particles, with a diameter down to *ca*. 1 µm, and the relatively easy interpretation of the spectra, by comparing them with reference spectra. As such, the technique can be used to study modern as well as antique art objects.

One can take full advantage of the excellent spatial resolution of the technique, by performing mapping experiments. Indeed, by recording a number of spectra of a structured array of well-defined positions, it is possible to process the spectra in such a way that an image can be obtained. This is an ideal tool to study the distribution of pigments and/or degradation products.

Moreover, recently it was also demonstrated that mobile Raman instrumentation can be used for studying art objects directly. By using mobile instrumentation, that is often equipped with a fibre optics probe head, it is possible to record Raman spectra on the art site. The main advantage of this approach is that information can be obtained without the need of sampling and thus, by virtually not damaging the artwork.

During this presentation, plenty of examples of our approaches will be given and the advantageous properties of Raman spectroscopy, in the laboratory and *in situ*, will be demonstrated.

Session S10:

Sustainability and circular economy in the production of concrete and cementitious binders

Conveners:

Luca Valentini (Univ. di Padova)
Azzurra Zucchini (Univ. di Perugia)
Cristina Leonelli (Univ. di Modena e Reggio Emilia)

Chemical activation and rheological control of alkali-activated slag binders: are we ready to give up cement-driven chemistry?

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Keywords: alkali activated cement, granulated blast furnace slag, sodium carbonate, solution chemistry.

Properly formulated, alkali activated binders made of blast-furnace slag and fly ash could reduce by 80% the CO_2 emissions associated with the manufacturing of cement (van Deventer et al., 2010). However, several technical barriers remain to be overcome before its use may become widespread. The first one is the use of liquid alkaline activators, like NaOH or waterglass, which are difficult to be dealt with in a ready-mixed concrete plant. Secondly, the hardening rate must be sufficient to comply with the requirements of present day manufacturing operations. Finally, the flow properties of the mix in its fresh state must be sufficient to ensure an adequate open workability time and the proper filling of the forms.

Sodium carbonate has been proposed as a source of dry alkali activation (Bernal et al., 2015; Bernal et al., 2016), but it is insufficient to deliver by itself mechanical strength higher than 10 MPa at 2 days curing time, as required *e.g.*, for CEM 42.5N (EN 197-1:2011). Additions capable to bind the carbonate ions are required to control the kinetics of slag reaction and to increase the *p*H of the pore solution (Ke et al., 2016).

We show the performance of an activation system based on sodium carbonate and calcium hydroxide, on a binder composed of 50% blast furnace slag and 50% class F fly ashes. We can reach 8.5 MPa at 24 hours, 17 MPa at 2 days, and 45 MPa at 28 days curing. Early hardening is enhanced by low Ca^{2+} concentration in the pore solution, increasing the slag solubility. The strength gain between 7 and 28 days is influenced by the amount of precipitated calcite. The lack of sodium silicate in the activation system enhances the flowability of the mix and no early workability loss is observed.

The low Ca^{2+} concentration in the pore solution causes the surface potential of the slag particles to be negative. Therefore, novel superplasticizers must be developed, different from those currently used in cement-based mixes.

The chemistry of such a system is distinct from the one of cement-based systems, both as reaction kinetics, setting mechanisms and surface properties. Cement-based binders and alkali activated slag binders do not show synergetic interactions.

Bernal, S.A., Provis, J.L., Myers, R.J., San Nicolas, R., van Deventer, J.S.J. (2014): Role of carbonates in the chemical evolution of sodium carbonate-activated slag binders. Mater. Struct., 48, 517-529.

Bernal, S.A., San Nicolas, R., van Deventer, J.S.J., Provis, J.L. (2016): Alkali-activated slag cements produced with a blended sodium carbonate/sodium silicate activator. Adv. Cem. Res., 28, 262-273.

Ke, X., Bernal, S.A., Provis, J.L. (2016): Controlling the reaction kinetics of sodium carbonate-activated slag cements using calcined layered double hydroxides. Cem. Concr. Res., 81, 24-37.

van Deventer, J.S.J., Provis, J.L., Duxson, P., Brice, D.G. (2010): Chemical Research and Climate Change as Drivers in the Commercial Adoption of Alkali Activated Materials. Waste Biomass Valor, 1, 145-155.

Development of compatible admixtures for low clinker cementitious materials

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Keywords: supplementary cementitious materials, activators, accelerators, superplasticizers, hydration kinetics, rheology, compressive strength, sustainability.

Nowadays, concrete is the most used material in the world and it accounts for 5-8% of CO_2 emissions. Clinker replacement by Supplementary Cementitious Materials (SCMs) is one of the most successful strategies to reduce the embodied energy and the carbon footprint of Portland cement. This substitution is limited by the lower reactivity of SCMs, that leads to lower early mechanical strength. In order to overcome this drawback, two different types of chemical admixtures can be used. Accelerators, such as moderate concentration of alkali solutions, enhance the SCMs dissolution, while the addition of comb-shaped superplasticizers decreases the water demand maintaining a high fluidity and leading to higher early mechanical strength. However, previous studies have proved the existence of strong incompatibilities between these two types of admixtures, due to the process of competitive adsorption. This can be resolved by using com-shaped polycarboxylate ether superplasticizers with a molecular structure compatible with alkalis additions (Marchon et al., 2013). Specifically, Marchon et al. (2013) developed a criterion that allows to select less competitive PCEs in alkaline conditions, according to the adsorption equilibrium constants, based on the PCE molecular architecture.

The objective of this project is the formulation of a new generation of low clinker concrete that consider the local availability of raw materials in Switzerland, leading to a more sustainable concrete. In this work, a blended cement composed by 50% of Portland cement and 50% of SCMs, such as limestone, burnt oil shale and fly ash has been studied. The limited early reactivity of the blend has been increased by the addition of accelerators, such as NaOH, Na_2SO_4 and gypsum. Three different PCEs have been added and their compatibility with these accelerators has been investigated. The rheological properties, the hydration kinetics and the mechanical strength at 24 h have been tested on pastes and mortars.

Results have proved the compatibility between these accelerators and comb-copolymers with a high adsorption equilibrium constant. In particular, in systems activated with NaOH or Na_2SO_4, the most promising PCE in terms of rheological properties, cement hydration kinetics and cumulative heat release after 24 h is PCE1, a methacrylic-based polymer. In addition, the combination of 0.17 M $Ca(NO_3)_2$ with PCEs has a positive impact on the yield stress of the pastes activated with alkalis. In the system activated with gypsum, PCE1 and PCE3, a maleic-based PCE, lead to the best properties.

Marchon, D., Sulser, U., Eberhardt, A., Flatt, R.J. (2013): Molecular design of comb-shaped polycarboxylate dispersants for environmentally friendly concrete. Soft Matter, 9, 10719-10728.

Alkali activated materials from recycled sewage sludge of Pietra Serena sandstone

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Keywords: alkali activated materials, waste, metakaolin, sewage sludge, fly ash, sustainability.

A growing interest for the themes of sustainability and reuse of waste materials has been observed in the last years. Wastes derived by various human activities, until now under-utilized or simply dismissed, start to be valorised by the alkaline activation process to produce new materials for several applications, with economic and environmental benefits (Bernal et al., 2016).

Stone cutting and processing is associated with significant production of waste materials, like the sewage sludge, which has low commercial value and needs precise requirements for suitable disposal. In this work, the possibility of reusing sewage sludge deriving from the cultivation of a sandstone known as Pietra Serena, quarried in the Firenzuola district (Florence, Italy), by the alkali activation process has been evaluated. The sludge has been used as is and after thermal treatment at 800°C.

Synergic uses of this material in binary and ternary mixtures with fly ash class F and high-quality metakaolin have been tested, with the aim to produce cementitious binders. Sodium hydroxide solutions 8 M and 12 M and sodium silicate solution have been used as activators. Characterization of products was performed by X-ray power diffraction, Fourier transform infrared spectroscopy, scanning electron microscope, colorimetry and mechanical tests.

The main product of alkali activated Pietra Serena sewage sludge was an amorphous gel in which unreacted grains can be still recognized. In blends with fly ashes and metakaolin, sewage sludge revealed double usability: they act as fine fillers, enhancing packing density and contribute to increase the mechanical strength of alkali activated materials particularly when used after the decarbonation pre-treatment, that leads to the formation of C-S-H gels.

Bernal, S.A., Rodríguez, E.D., Kirchheim, A.P., Provis, J.L. (2016): Management and valorisation of wastes through use in producing alkali-activated cement materials. J. Chem. Tech. Biotechnol., 91, 2365-2388.

Smectite-rich sediments as precursor for alkali activated binders: an alternative to kaolin?

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Keywords: alkali activated binders, smectite, calcined clays, emission reduction.

There is an urgent need for current industrial policies to be calibrated on strategies for mitigating the impact of global warming. For the cement industry, which contributes to 5-7% of the total anthropogenic CO_2 emissions (Barcelo et al., 2014), many options exist to improve energy efficiency (IPCC, 2014). However, this will not be enough to achieve significant emission reductions in the future, also because of the rise in demand for housing and infrastructures (United Nations, 2014). Alkaline-activated materials are a class of alternative binders, which, if properly formulated, could cut greenhouse gas emissions associated with the construction industry. Currently, many researchers are focussing on alkaline activation of industrial by-products, like slag and fly ash. However, the limited availability of these materials, related to isolated industrial processes, pushes research towards more readily available and cheap materials, such as calcined clays. In this framework, metakaolin has been extensively investigated (Liew et al., 2016) while limited information is available about other kind of clays for alternative binder manufacture. In the present work, we investigate the potential use of a natural smectite clay soil for the production of binders with good mechanical properties. Clays were calcined in a laboratory muffle for 3.5 hours at a temperature of 750°C, activated with an alkaline solution and cured at room temperature, until compositional, structural and mechanical analyses were performed. Also, partial replacement of calcined clay with calcium carbonate powder and addition of sodium citrate solution in the formulation were tested. From this study, smectite clay reveals to be a high potential precursor for manufacturing alternative binders, permitting to reach compressive strengths as high as 60 MPa after 20 days of curing.

Barcelo, L., Kline, J., Walenta, G., Gartner, E. (2014): Cement and carbon emissions. Mater. Struct., 47, 1055-1065.

IPCC (2014): Climate Change 2014: Synthesis Report. Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. Core Writing Team, R.K. Pachauri & L.A. Meyer, eds. IPCC, Geneva, Switzerland.

Liew, Y.-M., Heah, C.-Y., Mohd Mustafa, A.B., Kamarudina, H. (2016): Structure and properties of clay-based geopolymer cements: A review. Progr. Mater. Sci., 83, 595-629.

United Nations (2014): Department of Economic and Social Affairs, Population Division-World Urbanization Prospects: The 2014 Revision, Highlights.

One-part alkali activated slags for environmentally friendly cement-free repair mortars for conservation, restoration and retrofitting of existing concrete structures

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Keywords: Ground Granulated Blast Furnace Slag (GGBS), alkali-activated materials, alternative binders, sustainability, mortars.

Introduction. The "world of constructions" and, in particular, the cement sector, is considered one of the main natural resources-consuming industry in the world. The global production of Portland cement, in fact, contributes around 7% to greenhouse gases emissions responsible for climate change and global warming. Hence, it is evident the need in the concrete industry of a forceful turning point towards sustainable development models in economic, environmental and social terms (Damtoft et al., 2008; Coppola et al., 2015). In this view, a general replacement of Portland clinker-based cement is one of the main strategies to limit drastically the environmental impact of construction materials. This article is aimed to optimize an alkali-activated binder, based on ground granulated blast furnace slag (GGBS) as precursor, for cement-free mortars devoted to conservation, restoration and retrofitting of existing reinforced concrete and masonry structures.

Materials and Methods. The alkaline activators, in powder form, were formulated by blending sodium silicate, potassium hydroxide and sodium carbonate. Several activator/precursor ratio – between 2 and 32% by mass – were used in order to investigate the effect of activator dosage on the rheological, mechanical and physical performances of mortars. The mixing water was adjusted in order to attain the same workability at the end of the mixing procedure, equal to 160 ± 10 mm spreading on the flow table.

Results and Discussion. The experimental data show excellent rheological characteristics of different mixtures based on GGBS. Compressive strength increases with the activator/precursor ratio up to 65 MPa at 28 days. In addition, alkali-activated GGBS mortars show a Young's modulus, close to 13 GPa, significantly lower than that of a cement mortar having the same compressive strength class. As a consequence of the lower elastic modulus, alkali-activated mortars seems to be very promising in the field of conservation and repair of existing concrete structures, since the lower rigidity is responsible for a sharp reduction of stress induced by restrained thermal and hygrometric movements. However, on the other hand, shrinkage of alkali-activated GGBS mortars is significantly higher than traditional cement based mixtures. Hydraulic shrinkage values higher than 4 mm/m at 60 days were measured. This means that use of alkali activated GGBS mortars in the repair field requires some additional ingredients (expansive agents, polymeric fibers and shrinkage reducing admixture) in order to face the very high hydraulic shrinkage of these innovative materials.

Coppola, L., Coffetti, D., Lorenzi, S. (2015): For a sustainable development in construction industry: moving from the culture of "Not more than" to that of "Not less than". Structural, 200, 1-11.

Damtoft, J.S., Lukasik, J., Herfort, D., Sorrentino, D., Gartner, E.M. (2008): Sustainable development and climate change initiatives. Cement Concr. Res., 38, 115-127.

Geopolymer versus kaolin rheology

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Keywords: metakaolin-based geopolymer suspension, kaolin-based suspension, rheology.

An important group of geopolymers is obtained using metakaolin as raw material. Metakaolin is obtained by calcination at high temperature of kaolin clay (Davidovits, 2011), widely used in ceramic field. Such close correlation between these two basic components leads to the question: from a rheological point of view, is it possible to find correspondences between the geopolymeric suspensions and those with kaolin?. Rheological behaviour is important both from a technological point of view and for studying geopolymeric reactions. In general, for any material, its easy manufacturing is essential for its success (Leonelli, 2014) and the optimization of his rheology plays a very important role. Rheometric techniques are also used to study the early phases of the geopolymerisation process thanks to the great sensitivity of modern rheometers (Poulesquen, 2011). These studies show that the rheology of a geopolymer is subject to some parameters common to those that affect the kaolin-based suspensions. For example, both are subject to the solid content or temperature.

However, in the measure of rheological behaviour, the geopolymer has an additional problem that kaolin suspensions do not show: during the test the geopolymer changes its chemistry and so its rheology. This reduces the available testing-time and therefore also the ability to take long-time measurements such as frequency sweeps, ON-OFF procedures, flow curves in steady state conditions etc. Being present additional problems, compared to those observable in kaolin-based suspensions, in the measurement of the rheological properties of the geopolymer, these must be known for proper design of rheological tests and their correct analysis. The contribution will show some differences between the rheology of the geopolymer with respect to the kaolin-based suspensions in order to facilitate the design of the tests and the analysis of the results.

Davidovits, J. (2011): Geopolymer-Chemistry and Applications. 3rd edition. Geopolymer Institute, 632 p.

Leonelli, C. & Romagnoli, M. (2014): Rheology parameters of alkali-activated geopolymeric concrete binders. In: “Handbook of Alkali-Activated Cements, Mortars and Concretes”, F. Pacheco-Torgal, J. Labrincha, C. Leonelli, A. Palomo & P. Chindaprasit, eds. Woodhead, Sawston, 133-170.

Poulesquen, A., Frizon, F. & Lambertin, D. (2011): Rheological behavior of alkali-activated metakaolin during geopolymerisation. J. Non-Cryst. Solids, 357, 3565-3571.

Use of alkali-activated binders for soil stabilisation

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Keywords: alkaline activation, fly ash, soil improvement, mechanical behaviour.

The development of soil stabilisation 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; Davidovits, 1991; Xu & van Deventer, 2000; Shi et al., 2006). The recycling of waste materials such as by-product from industrial process to synthesize a new binder favours 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 stabilizing agents for soil improvement.

In the present study, an insight into the mechanical improvement induced by an alkali-activated binder based on the activation of a fly ash on a clayey soil has been presented. An experimental multiscale investigation on the chemo-physical evolution of the system and its influence on the microstructural features of the treated soil has been developed highlighting the link between the alkaline activation processes and the macroscopic evolution of soil properties. One-dimensional compression tests have been performed and interpreted taking into account the chemo-physical evolution of the system. The effects of binder content and curing time have been considered. The addition of alkali-activated binder increases the compressive strength of the treated samples since the very short term. An increase of yield stress has been also detected, whose extent depends on the curing time and on the binder content. The macroscopic behaviour has been interpreted taking account of the chemo-physical evolution of the system. Mineralogical and fabric changes induced by alkali-activated binder have been monitored over time by means of X-ray diffraction (XRD), thermogravimetric analysis, ^{29}Si NMR spectroscopy and Mercury Intrusion Porosimetry (MIP). Test results showed a high initial reactivity of the alkali activated systems to promote the formation of new mineralogical phases, 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.

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Nano-added clinkers: industrial applicability

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Keywords: X-ray computed microtomography, Portland clinker, nano-materials.

A new generation of Portland clinker, aimed to improve the sustainability of the industrial process, has been tested. The raw mixture for Portland clinker was added with a 5 wt% of nano-$Ca(OH)_2$ in order to enhance the CaO diffusion during firing. A first generation of clinkers was produced by adding lab-synthesized nano-$Ca(OH)_2$, prepared by sonochemical synthesis starting from $CaCl_2$ and NaOH. Three burning *T* were set, for clinker firing, at 1250, 1350 and 1450°C to analyse the evolution of clinker phases as alite (C_3S) and belite (C_2S) as well as free lime (CaO). The obtained clinkers were analysed by means of X-ray Powder Diffraction (XRPD) and Field Emission Scanning Electron Microscopy (FESEM). The free lime concentration was found to decreases in the nano-added portland clinkers (nPC) at each burning *T*. Thus, an enhancement on the nano-added raw mixtures cooking efficiency was deduced which reflects in a clinker burning temperature decrease of approximately 100°C. The CO_2 emissions are then expected to decrease as well together with an improvement of the plant productivity.

Moreover, nPC samples were found to have lower porosity than standard Portland clinker decreasing from 35(2)% for the latter and 26(3)% for the former.

Further experiments were then carried out devoted to the know-how transfer to the industries. That is, an industrial-made low-cost nano-CaO was selected and analysed by means of XRPD and FESEM analysis. Results showed that the mineralogical composition of the nano-material was approximately pure CaO, with just a few percentages of calcite and Portlandite. Dimensionally, the industrial nano-CaO is formed by nano-aggregates of approximately 500 nm in size, quite larger than the nano-$Ca(OH)_2$ lab-synthesized particles. A second generation of nano-added clinkers was produced and the porosity was checked by means of phase-contrast synchrotron X-ray computed microtomography at the SYRMEP beamline of the Elettra laboratory (Basovizza, Italy). Results showed that no significant differences are present on the averaged porosity between PC and nPC being, at 1250°C, 13(1)% for both clinkers, at 1350°C, 41(8)% and 34(2)% respectively, at 1450°C, 23(1)% and 26(1)% respectively. Interesting differences were observed, instead, on the dimensional distribution of pore volumes. The nPC samples fired at 1250°C and 1350°C have higher sized pores (with size of the order of 10^{-5} mm^3) with respect to PC with important effects on the energy needed for the clinker grinding process. Even though the observed differences between treatments were weak, probably due to the high dimensions of the nano-aggregates on the industrially produced nano-CaO, the nPC samples show promising results. At present, a third generation of clinker is going to be tested, produced by different nano-materials containing CaO, such as nano-$CaCO_3$, that can be industrially made in comparable size.

Session S11:

Geomaterials and their likes: from Nature to technology and manufacturing

Conveners:

Mariano Mercurio (Univ. del Sannio)

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Characterization and self-cleaning properties of N-doped TiO_2 coatings on *Perlatino* limestone

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Keywords: limestones, nanocrystalline TiO_2, photocatalysis.

Stone-based monuments, buildings and sculptures are exposed to deterioration processes having a powerful impact on their cultural, social and economic values. The effects of the atmospheric pollutants are particularly severe on limestones and calcarenites. These agents cause deposition of sulfate and nitrate species, with development of black crusts that accelerate the stone decay and produce unacceptable staining of the surface. It is therefore necessary to remove soiling material to slow down the deterioration processes and to improve the appearance and the aesthetic quality of the buildings.

Recently, much attention has been devoted to the development of *self-cleaning* and *hydrophilic* surfaces. Nanostructured TiO_2 is the most widely studied photocatalytic material and used in self-cleaning coatings for buildings and Cultural Heritage applications.

To extend the photocatalytic activity of nanocrystalline titania into the visible spectral range, doping of titania by non-metal elements is currently widely investigated. In this study, we report the results on a new self-cleaning coating for limestone materials based on nitrogen-doped TiO_2 (N-TiO_2) nanoparticles obtained by the sol-gel process, using titanium oxy-sulphate ($TiOSO_4$) as precursor and ammonium hydroxide as nitrogen source. Structural and morphological properties of synthesized N-TiO_2 nanopowders were characterized with spectroscopic and microscopic techniques. N-TiO_2 powders are mainly composed of anatase in nanocrystalline form, as highlighted by Raman and X-ray diffraction measurements. The Raman peak positions and FWHM suggest crystallite size in the 5-10 nm range, in good agreement with XRD and TEM analyses. Diffuse reflectance spectroscopy measurements show a shift in the band gap towards lower energies with respect to the undoped commercial TiO_2 (P25, Evonik). The photoinduced properties and the compatibility of the nanostructured N-TiO_2 based coating were tested, according to UNI-Normal protocol, on *Perlatino,* a limestone of *Custonaci basin*.The durability of the treatments was evaluated by resistance to crystallization of salts and by leaching tests.

The N-TiO_2 coating on limestone samples does not cause significant color changes, reduces the water capillary absorption and, under UV-VIS irradiation, increases the wettability of the surfaces.

In addition, the photocatalytic efficiency of N-TiO_2 coatings under visible light irradiation, assessed through the degradation of Rhodamine B and Methyl Orange organic dyes on stained *Perlatino* stones, is greater than that observed for P25 commercial product.

High temperature viscosity of porcelain stoneware bodies

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Keywords: porcelain stoneware, viscosity, liquid phase, crystals.

The viscosity of porcelain stoneware at high temperatures is crucial to understand the vitrification path, the viscous flow sintering kinetics and the pyroplastic deformation of this material. For the determination of the porcelain stoneware final viscosity is necessary to consider both the viscosity of the liquid phase formed by the melting of feldspars – and other minerals – and the viscosity of the body made up of a suspension of crystals dispersed in the melt. Fundamental theoretical background exists with semi-empirical constitutive laws of viscous flow sintering and glass densification as well as high viscosity liquids and melts (Prado et al., 2001). Since different approaches are needed to measure/estimate the two viscosities, the best model for ceramic tiles has been defined by contrasting experimental data with calculated viscosities within the IPERCER project. It worth be noticed that the parameterization depends on the chemical composition of the liquid phase and the persistence of crystals in the melt (related to the solubility of solids into liquid). Further variables, such as porosity, particles size and shape, play a significant role. Existing models for high temperature viscosities of glasses and melts present some limits that will be overviewed. In particular, the well-known model proposed by Fluegel (2007) takes into account a large number of oxides, allowing its application to melts characterized by wide ranges of composition. On the other hand, the maximum concentration of alumina expected by the model is too low for the systems here in study, generating a significant error between the calculated and the measured viscosities. The more recent model proposed by Giordano et al. (2008) is based on a lower number of oxides, but the alumina levels are more compatible whit those of the systems of interest.

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Effect of the activator concentration on the reaction products and properties of alkali activated Ca-rich clays

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Keywords: Ca-rich illitic clay; alkali activated.

The interest of several studies dealing with the long term stability of ancient cements found a reasonable explanation of their durability in the co-concurrence of alkaline aluminosilicate hydrate phases with the principal hydration product of Ordinary Portland Cements.

Different studies demonstrated that activator alkalinity is one of the most important factor influencing the kind of reaction products obtainable (the typical N-A-S-H geopolymeric gel, a C-A-S-H gel or a mixture of them) in alkali activated Ca-rich aluminosilicates systems. However, also the availability, the mineralogical and textural properties of the Ca-bearing sources (*e.g.*, crystallinity and particle size) can affect reaction products, by varing the Ca solubility in the alkaline medium.

On that basis, the present study aims to deepen the knowledge of the influence of the activator alkalinity and of the mineralogical properties of mechanically and thermally treated Ca-rich illitic clays on the nature and mechanical performances of the derived reaction products.

The activation of the carbonate-rich illitic clay was performed by high energy grinding and subsequent thermal treatments at 700°C. The effects exerted by the clay activation method on the clay properties were investigated through particle grain size analysis, XRPD, FTIR and selective attack in acidic and basic media, both to evaluate variations in mineralogical properties and in the solubility behaviour of the treated sample.

The alkali activated pastes were prepared by the employment of 4 M, 6 M and 8 M NaOH solutions. An alkaline solution/binder ratio = 0.55 (by weight) was adopted to achieve a satisfactory workability of the pastes, which were poured in prismatic moulds (1 x 1 x 6 cm^3) and cured at ambient temperature and relative humidity above 90%. FTIR, XRPD, SEM analysis, compressive and flexural strength test were performed on the specimens after 2 and 28 days of curing.

The results showed that when the activator is 4 M NaOH precipitate of Ca-rich phases chemically compatible with a C-A-S-H gel. An increase in the NaOH concentration was responsible for an higher extent of geopolymeric gel formation, due to an increased amount of dissolved species. In particular, 6 M and 8 M NaOH solutions brougth the pastes to show a better reacted and compacted matrix, based on the predominance of a calcium enriched (N,C)-A-S-H geopolymeric gel. Moreover, compressive test results showed that a NaOH concentration of 6 M is sufficient to achieve a satisfactory strength of treated Ca-rich illitic clay.

Effects of mechanical and thermal activation on reactivity of carbonate-rich clays

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Keywords: illite/smectite carbonate-rich clay, mechanical and thermal activation, clay reactivity, geopolymers.

The present study focuses on the assessment of the effects of mechanical and thermal activation on reactivity of carbonate-rich clays, aimed to understand the mineralogical differences originated and to exploit such information for technological transferability to industry.

Illite/smectite carbonate-rich clay samples were subjected to the following activation methods: (a) thermal activation in red or ox atmosphere and soaking temperatures between 400 and 900°C; (b) mechanical activation (milling for 5, 10 and 15 minutes); (c) a combination of such treatments. Mineralogical and textural changes in the activated samples were evaluated through X-ray powder diffraction (XRPD), Fourier transform infrared spectroscopy (FTIR) and thermal analysis (DTA/TG) techniques.

For each treatment, samples showing the highest extend of dehydroxylation of clay minerals (highest amorphous content) with minor recrystallisation phenomena, were selected to evaluate solubility under NaOH solution (3 M) by means of coupled plasma-mass spectrometry (ICP-MS). The application of the three processing routines, yielded three types of activated clays with different leaching modes of Si, Al, K and Ca: (1) thermal heating at 800°C relatively increases the Si/Al ratio (up to 1.7), but their absolute concentrations are equal or lower than those obtained from ground clays. The relatively high leaching of Ca is influenced by the formation of non-stoichiometric and poorly crystalline Ca-silicates and -aluminosilicates; (2) high energy grinding preferentially delaminates clay minerals and reduces the grain size of calcite. Ca solubility is inversely correlated with that of Si and Al. K leaching reaches the highest values; (3) high energy grinding combined with heat treating yields an extended amorphisation, mainly at the expense of clay minerals, with the highest leaching of Si and Al, and the lowest of Ca. New formed K-feldspars inhibit the concentration of K in alkaline solution.

The mineralogical differences observed demonstrate the versatility of carbonate-rich clays as raw materials for traditional and innovative applications, especially as a precursor for geopolymers.

Incorporation of Zn into complex quaternary sulfide structure through a solvothermal approach: a difficult task

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Keywords: kësterite, nanorparticles, XRD, EPR, XAS, DRS.

Kësterite–based solar cells represent one of the most promising candidate technology for the development of sustainable solar cells owing to their low toxicity and to the Earth-abundance of the constituent elements (Cu_2ZnSnS_4/CZTS, $Cu_2ZnSnSe_4$/CZTSe, $Cu_2ZnSn(S,Se)_4$/CZTSSe).

In this study, we reconsidered the state-of-the-art of the solvothermal syntheses of kësterite, and proposed a novel approach, based on the use of thioureate intermediates. Sulfide nanoparticles were, in fact, obtained through two different solvothermal methods, sharing the common strategy of the use of thiourea (TU) as a homogenous source of S^{2-} during the synthesis. Samples were characterized by a thorough multianalytical approach, including XRD, SEM micromorphology and microanalysis, Diffuse Reflectance Spectroscopy, Electron Paramagnetic Resonance and SQUID magnetometry and X-ray Absorption Spectroscopy.

The main result of the present study is the achievement of $Cu_{2.5}Zn_{0.5}SnS_4$ kësterite nanoparticles, obtained through a procedure which minimises energy consumption and environmental costs. The uptake of Zn by the sulphide structure was verified by both XRD and XAS spectroscopies, and the valence states of the metal cations were determined as Cu(I), Zn(II) and Sn(IV) by the combination of the EPR, XAS and SQUID techniques. Moreover, the band gap of the obtained products resulted 1.6 *e*V, full in line with the data reported for natural and synthetic kësterite.

A further consideration concerns with the lack of a stoichiometric uptake of Zn. The present study, in fact, suggests that both thermodynamic and kinetic controls may be operative during the reactive process in solution. The use of the thioureate intermediates increases the amount of Zn taken up by the nanoparticles, and appears as a good way to modify the reaction path, enhancing the coprecipitation of Cu- and Zn-bearing sulphides. Nevertheless, the solvothermal process for obtaining kësterite nanoparticles from a simple, scalable, energy saving, environmentally friendly approach is not straightforward, and further investigations are needed to assess the best conditions to undergo the complete control of the chemical composition of the precipitate.

Lightweight aggregates from glass recycling: high efficiency concretes manufacturing

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Keywords: glass, recycling, waste management, lightweight aggregates, thermal insulation, concrete.

Lightweight Aggregates (LWA) are natural or artificial cohesionless materials constituted by elements with different grain size and specific characteristics, according to EN 13055-1 specification. Reference parameters, necessary to achieve an expansion for artificial ones, are a suitable chemical composition (*e.g.*, Fe_2O_3:Al_2O_3 ratio and fluxing oxides) along with the occurrence of gas developing substances (Dondi et al., 2016). Recent investigations demonstrate that it is possible to produce LWA by using other natural materials such as volcanic tuffs, ignimbrites and zeolitized epiclastites as well as industrial wastes and recycled materials (Kazantseva et al., 1997; de Gennaro et al., 2004, 2008, 2009). Promising results were obtained with porcelain stoneware and ornamental stone polishing muds, which contain small amounts of abrasive (max 3 wt% SiC) that is the expanding agent necessary for bloating. Good results were obtained also by mixing these muds with zeolite-rich rocks: obtained LWAs show similar or even better features that those currently marketed and provide a good prospect for the production of lightweight structural concretes. The experimental case, here reported, demonstrates that glass can be used with profit for the production of expanded aggregates with good technical properties in the cement industry (Ducman et al., 2002; Lebullenger et al., 2010). Two different kinds of glass were used: 1. Bottle glass (Na-Ca recycled glass); 2. PC and TV screen glass, rich in Ba-Sr (Dondi et al., 2009). By mixing screen glass powders with porcelain stoneware polishing mud, it was possible to exploit (when the batch is heated at high temperatures) the expanding action of SiC, which is the abrasive agent occurring in mud. By this way, it is possible to obtain LWA with controlled physical properties to be used in the concretes industry. A laboratory pilot production of LWA was performed in order to manufacture two different kinds of concrete: 1. A structural lightweight concrete (SLC); 2. A cellular lightweight concrete (CLC). Test results evidenced that glass-bearing LWA can be used in structural lightweight concretes manufacturing obtaining concrete's density between 1400 and 2000 kg/m^3 and compressive strength higher than 20 MPa. The use of the same type of LWA for the realization of CLC, moreover, definitely improve thermal features of these concretes, making the product even more competitive whenever compared to traditional materials used for thermal insulation.

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Mechanical improvement and micro evolution of a zeolite-rich lime treated pyroclastic soil

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Keywords: pyroclastic soils, zeolite, lime treatment.

Soils represent some of the most diffused building materials as they are needed for the construction of embankments and earthworks in many fields of civil engineering.

Many soils are unsuitable for construction purposes in their natural state. Among these, clayey soils are inappropriate because of compressibility, shrinkage and swelling characteristics; pyroclastic soils have marginal applications in earthworks field due to their complexity in terms of nature, heterogeneity, microstructure features and unsaturated hydro-mechanical behavior. Lime treatment is commonly used to overcome the problems typical of fine grained soils, so that the use of lime treated clayey soils for earthwork construction is rather common. On the contrary, despite of the well known high reactivity of pyroclastic soils with lime, just recently the research focused on the possible use of lime treatment for the mechanical improvement of these materials (Cecconi et al., 2010; Russo et al., 2016; Guidobaldi et al., 2017).

This study is aimed to investigate the effects of lime treatment on a zeolite rich pyroclastic soil, coming from Monti Vulsini Volcanic Complex (Gentili et al., 2014). The studied soil was treated with 5% of $Ca(OH)_2$, cured until 28 days and mechanically tested by means of unconfined compression and oedometer tests. Mechanical tests proved that the treatment induces remarkable improvements on the soil geotechnical features.

These improvements have been related with the chemo-mineralogical and microstructural evolution of the treated material over time. X-Ray Diffraction (XRD) Thermo-gravimetric analyses (TGA), Scanning Electron Microscope (SEM) and Mercury Intrusion Porosimetry (MIP) were performed on the treated soils in order to detect the mineralogical and microstructural modifications associated to mechanical improvements.

XRD and TGA revealed the high reactivity of the system at micro level, with the occurrence of pozzolanic reactions since the very short time after the addition of lime. Chabazite and the amorphous phase are the main phases involved in pozzolanic reactions and the recognized secondary phases are mainly C-A-S-H.

MIP showed that lime treatment induces a deep microstructural and porosimetric re-organization, with the extinction of the pore population corresponding to the mesoporosity (3-0.3 μm) and a marked increase of both macro and micro porosity (typical of silica gel). These indications are perfectly consistent with the SEM analyses, which clearly show the presence of three different classes of porosity and their evolution over time.

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Technological performance of surface modified natural zeolite (SMNZ) for *in vitro* loading/release of ibuprofen sodium salt: new insights on chabazite-rich tuff

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Keywords: chabazite, surfactant modified natural zeolite, Campanian Ignimbrite, etylpyridinium, belzalkonium, ibuprofen, Toth, Sips, Weibull, kinetic, isotherm, non-linear regression, AIC, BIC.

Recently, natural zeolites and their surface modified forms have been widely used in several applications, thanks above all to their peculiar properties: high specific surface area and Cation Exchange Capacity (CEC). It is well know that CEC can be changed in Anion Exchange Capacity (AEC) by using cationic surfactants. This approach shed new light in pharmaceutical sector in order to use SMNZ for non-steroidal antiflammatory drugs delivery.

In this frame, a chabazite-rich tuff (CHA) from a deposit in San Mango sul Calore (Italy), belonging to the Campanian Ignimbrite formation, was functionalised with cetylpyridinum chloride (CP) and benzalkonium chloride (BC) in order to test its pharmaceutical performance in loading and release of ibuprofen sodium salt (IBU).

Equilibrium sorption isotherms and *in vitro* loading/release tests, performed according to de Gennaro et al. (2015), were fit by linear and non-linear regression, whereas the goodness-of-fit of the different mathematical models employed was evaluated by means of the coefficient of determination (R^2) and other more appropriate statistical methods as Akaike Information Criterion (AIC) and Bayesian Information Criterion (BIC).

These preliminary results indicated that the best-fit for isotherms was attained implementing Toth equation (R^2 = 0.985, AIC = 27.26, BIC = 27.10 for CHA+CP; R^2 = 0.998, AIC = 6.05, BIC = 5.88 for CHA+BC), although good results were also obtained for Sips equation (R^2 = 0.979, AIC = 29.39, BIC = 29.23 for CHA+CP; R^2 = 0.998, AIC = 8.23, BIC = 8.07 for CHA+BC). This behaviour could be attributed to the high heterogeneity of sorption processes with predominance of anion exchange.

Additionally, the equilibrium IBU sorption concentrations estimated by Toth model account with the maximum sorption capacities found in loading kinetic runs (24.51 mg/g for CHA+CP; 13.46 mg/g for CHA+BC) modelled with a pseudo-second order equation (R^2 = 0.993, AIC = 23.77, BIC = 24.57 for CHA+CP; R^2 = 0.981, AIC = 21.38, BIC = 22.18 for CHA+BC). IBU loading was very rapid both for CHA+CP and CHA+BC , as well as for its release profiles that occurred quite completely within the first hour. Lastly, drug dissolution profile were modelled with a three-parameters Weibull equation (R^2= 0.998, AIC = 11.90, BIC = 13.10 for CHA+CP; R^2 = 0.996, AIC = 6.09, BIC = 7.28 for CHA+BC), usually used for matrix type drug deliver.

As a matter of fact, although the high promptness of IBU release, chabazite-rich Campanian Ignimbrite tuff seems to be more suitable for the IBU delivery, at least for the CHA+CP composite and to a lesser extent for CHA+BC.

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From Nature to materials science: $(Cs,K)Al_4Be_5B_{11}O_{28}$ (londonite) as a super-hard material

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Keywords: londonite, cesium, boron, hard materials.

Londonite is a rare Cs-bearing mineral with ideal chemical formula $(Cs,K)Al_4Be_4(B,Be)_{12}O_{28}$ (with Cs > K). The building block units of the structure of londonite are represented by clusters of four edge-sharing Al-octahedra linked to B- and Be-tetrahedra. Gatta et al. (2011) investigated the phase stability and the elastic behavior of londonite up to 4.85(5) GPa (at room-*T*) and up to 1000°C (at room-*P*) by *in situ* X-ray powder diffraction data, but no structure refinements were possible. Whether no phase transition was observed within the pressure-range investigated, londonite proved to have an extremely high bulk modulus: $K_{P0} = 280(12)$ GPa, similar to those of carbides (*e.g.*, B_4C with $K_{P0} \sim$ 245-306 GPa; Lazzari et al., 1999; Fujii et al., 2010). Considering the thermo-elastic properties and the significantly high fraction of boron ($B_2O_3 \sim 50$ wt%), the synthetic counterparts of londonite could be considered a potential inorganic host for ^{10}B in composite neutron-absorbing materials. Furthermore the high content of Cs makes londonite-type materials potential host for nuclear waste. However, to date, because of the absence of structural data at high pressure and to the modest *P*-range investigated by Gatta et al. (2011), a comprehensive description of the *P*-induced deformation mechanisms at the atomic scale is still missing. In this study, the isothermal compressional behaviour of londonite is studied by *in situ* single-crystal synchrotron X-ray diffraction experiment with a diamond anvil cell up to 25 GPa. The compressional behavior and the deformation mechanisms at the atomic scale are described. Londonite does not experience any phase transition or change of the compressional behavior within the *P*-range investigated.

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Influence of the raw materials on the mineralogy and microstructure of fired sanitary-ware vitreous body by synchrotron X-Ray computed microtomography

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Keywords: sanitary-ware ceramic, industrial clays, microstructure, X-ray powder diffraction, synchrotron X-ray computed microtomography.

China whiteware products represent a large part of ceramic materials and cover a wide range of applications like tile, dinnerware and sanitary-ware. They are mainly formed by a vitreous body which comes from heating above 1100 °C a mixture of clays, fluxing agents (typically feldspar) and fillers (typically quartz), after previous processing like, for example, aging, drying and body preparation (Carty & Senapati, 1998). Phase composition of vitreous body has been widely studied in past and is characterized by a glassy matrix with some crystalline phases like mullite, which forms upon heating, and residual filler (Martin-Marquez et al., 2009). Additionally, a well-developed porosity can be present, with consequent implication on some technological properties of the materials like mechanical strength (Braganca & Bergman, 2003).

Four different industrial sanitary-ware compositions were prepared by fixing the "hard" compound (21% feldspar, 19% quartz and 6% China whiteware waste) and by varying the "plastic" compound with four different industrial clay components (one per sample). After casting procedure, half of each sample was saved to investigate the packing of the green body whilst the other half was fired in a muffle furnace at the peak temperature of 1200°C to investigate the porosity of the fired product, for a total of eight samples.

All the samples, after previous XRPD characterization, have been investigated by synchrotron X-ray computed microtomography at the SYRMEP beamline (Elettra, Trieste) in phase contrast modality.

Data reconstruction have been performed and the microstructure have been evaluated by processing slices with a Matlab written code. In particular, it was possible to focus on voids but also on zircon crystals that come from the 6% of China whiteware waste, due to their "transmitted" signals which differ from the ones of the other phases (*i.e.*, quartz, mullite and glass).

For each sample, it was possible to characterize the volume of voids and zircon in terms of total volume and size distribution in the 10-1000 μm range; moreover, Higgins sphericity index and Flynn diagrams have been determined.

The results have been also compared with mercury porosimeter measurements.

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The commercial varieties of marbles cropping out in Massa inland (Apuan Alps)

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Keywords: marble, Apuan Alps, commercial varieties.

The marbles of the Apuan Alps are considered among the most popular stone materials in the world and they are used by designers and artists to decorate the most famous art heritage cities. Quarrying activity is characterized by secular history and by yields of many marble types which is unequaled elsewhere. Mining activity has a great impact on the environment which is currently affected by more than 130 active quarries, 15 of which are active in the Massa inland marble basins. The Massa basins involve different tectonic Units (Massa and Apuan Units) and some geological structures like southern Carrara syncline, Orto di Donna syncline and minor plicative structure named Madielle and Capraia syncline. There are numerous commercial varieties extracted belonging to the Marble Fm. and Seravezza Breccias Fm., whose geological and commercial characteristics depend on the original stratigraphic environment and on their structural and deformation setting developed during the metamorphic conditions. In accord with Carmignani et al. (2007) we consider a commercial variety of marble as an "informal lithostratigraphic unit"; a commercial variety of marble can be comprehensively described and separated from adjacent ones by features that are either just lithological (metalimestone, metabreccia, calcschist, etc.) or properly commercial and aesthetic (*e.g.*, color and design), regardless of its stratigraphic-structural levels. In this way we have identified nine informal lithostratigraphic units, divided into four main groups (White, Veined, Gray and Brecciated), which represent the different product varieties cropping out in the marble quarries. In each quarry of the Massa inland the commercial variety of marbles exploited were recognized and, on the basis of the geological structures, the volumes available for each variety of marble were estimated too. Moreover the percentages of squared blocks and shapeless block removable during excavation were estimated. The goals of this research are the increasing in knowledge of the localization of commercial variety of marbles in the Apuan Alps and the highlight of the potential and limits of the Massa inland marbles, allowing a better medium- and long-term planning of mining activities.

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Forensic mineralogy: the case study of the ENFSI-APST collaborative exercise “Soil 2017”

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Keywords: forensic geoscience, applied mineralogy, soils, ENFSI, APST, TG-EGA, FTIR.

Lately, the European Network of Forensic Science Institutes (ENFSI) organised ring tests involving the Animal, Plant and Soil Traces (APST) working group. In this frame, we joined the collaborative exercise Soil 2017 aimed to solve a forensic case by means of several analytical conventional techniques widely used in forensic sciences: stereomicroscopy (SM), polarised light microscopy, X-ray powder diffraction (XRD), Fourier-Transform Infrared spectroscopy (FTIR), grain size distribution measurements (GSD). We also employed a non-conventional technique: the simultaneous thermal analyses coupled to FTIR-Evolved Gas Analysis (EGA).

Collaborative exercise Soil 2017 was articulated in two parts: a former one consisting in a complete characterization of a soil (Sample A) providing information on the rock type and on the typical geological region where it could crop out; the second part concerned a comparison of three soils (Sample 1, Sample 2 and Sample 3), coming from three different places, with a trace sample (Sample 4) collected from the wheels of a vehicle, in order to identify the place of possible contamination.

As far as Sample A is concerned, it was described as a brown soil (7.5 YR 4/3) formed by highly vesicular rough textured sub-angular granules showing a GSD ranging from silt to pebble with the highest density in the range of the very coarse sand. Furthermore, rare frustules and crystals (mainly pyroxene, olivine and feldspar) were observed.

Additionally, TG curve shows a total weight loss of ~ 4 wt%, mainly observed below 600°C, attributable to dehydration (~ 105°C) and combustion/decomposition of organic matter (~ 416°C with emission of carbon dioxide). Main FTIR absorption bands were located at 3392 cm^{-1}, 1630 cm^{-1}, 1007 cm^{-1}, 809 cm^{-1}, 683 cm^{-1}, 524 cm^{-1}, 465 cm^{-1} and 414 cm^{-1}.

All these features are generally attributable to a high amount of amorphous and/or low-order phases, as confirmed by XRD analysis where minor clinopyroxene and phyllosilicate were also detected. Finally, this sample could be ascribed to a pyroclastic rock typically outcropping in volcanic regions.

Regarding the second part, Sample 1 and Sample 4 show an extremely strong comparability. In fact, both the samples are described as greyish brown soils (10 YR 5/2) formed by friable granules showing a GSD ranging from silt to pebble with the highest density in the ranges of the coarse and very coarse sand. Another distinctive feature is related to the presence in both soils of abundant scattered single crystals of quartz, metamorphic lithics and charcoal fragments. The high correspondence between them is also clearly observed comparing the TG curves and FTIR spectra. On the other hand, no comparability was found between Sample 4 and the remaining soils.

As a matter of fact, the combined use of non-conventional and conventional analytical techniques employed in applied mineralogy, provided a very useful tool for investigative purposes.

Lastly, a prompt response was obtained by FTIR spectroscopy and thermal analysis (TG), although this latter technique was not considered as a basic analytical approach by the APST answer sheets.

Synthesis and characterization of $KAlSiO_4$-O1 using a diatomite precursor

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Keywords: kalsilite, diatomitic rock, calcination treatment.

In this study, we detail the synthesis and characterization of $KAlSiO_4$-O1, a kalsilite polymorph, which for years has been considered a material of technological interest (Cook et al., 1977). It is successfully used in the preparation of high thermal expansion and in the context of high-temperature technologies, such as in blast-furnace linings, magnetohydrodynamic generators and hazardous waste incinerator clinkers.

$KAlSiO_4$-O1 has been synthesized in previous studies either by a solid state method (Gregorkiewitz et al., 2008) or a flux technique (Kremenović et al., 2013). The first aim of this work is to develop a new experimental protocol for the synthesis of $KAlSiO_4$-O1, which follows a two-step process: first, the preparation of a hydrothermally-derived precursor (at 150°C) and then the calcination of the precursor at high temperature (1000°C). The precursor is prepared starting from a silica source, potassium hydroxide and aluminum hydroxide. A novel starting material used as the silica source is tested, *i.e.*, a naturally derived amorphous silica (a diatomitic rock from Crotone, southern Italy).

Abundant $KAlSiO_4$-O1 phase was observed after 2 hours of the calcination treatment and its maximum abundance is observed at around 5 hours; coexistence with leucite is attested during the time interval 6-100h.

The sample recovered after 5h was fully characterised by powder X-ray diffraction, inductively coupled plasma optical emission spectrometry, infrared spectroscopy and ^{29}Si magic angle spinning nuclear magnetic resonance. The amorphous phase in the synthesis powders was estimated with quantitative phase analysis using the combined Rietveld and reference intensity ratio methods. Determination of cell parameters and density of $KAlSiO_4$-O1 were also achieved allowing us to compare their values with other studies. Our results suggest that this method could be a more cost effective means of producing $KAlSiO_4$-O1 without compromising its physical properties.

Cook, L.P., Roth, R.S., Parker, H.S, Negas, T. (1977): The system K_2O-Al_2O_3-SiO_2. Part 1. Phases on the $KAlSiO_4$-$KAlO_2$ join. Am. Mineral., 62, 1180-90.

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Construction and Demolition Waste (CDW) for eco-innovative building product

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Keywords: waste, geomaterials, LCA, CDW, XRD.

A recent review (Jamshidi et al., 2016) explored the effect of adding waste glass (WG) in the manufacture of urban stepping surfaces concluding that the use of WG can improve various phases of pavement life and structure by enhancing the structural performance, durability, environmental friendliness, and aesthetic features. In this study we extend this knowledge also to cement-based interior design tiles.

In detail this work aims to evaluate the technical performances of aesthetically appealing fully recycled (over 70%) pre-casted cement based products (Terrazzo tiles) manufactured by using GW and construction and demolition waste material (CDW).

Three representative ECO TILES mixtures were selected and characterized by means of XRD and SEM imaging in order to study the effect of the different binding materials (limestone powder, quartz powder and fine grinded WG powder) on coarse grained WG granulates. A fourth additional mixture of Portland cement and CDW material was characterized.

Preliminary results on X-ray diffraction patterns show that during manufacture curing time there is no newly formed phases, potentially affecting the physical and technical properties. High magnification SEM imaging further confirmed this observation also highlighting the good binding performances of a mixture composed by the 78% of recycled WG.

An additional goal of this study is to demonstrate the possibility to minimize carbon dioxide emissions during the production of ECO TILES and reduce the environmental impact up to -20% than for the traditional tiles. For this purpose power consumption and gas emission of the production activities during a traditional tile manufacture cycle has been measured and compared to the manufacturing cycle for the ECO TILES production, by carrying out a full Life Cycle Assessment (LCA), in order to demonstrate the lower environmental impact of these eco-sustainable products.

The reuse of waste for new eco-innovative products, together with the reduction of the environmental footprint associated with industrial process, strongly contributes to the achievement of EU 2020 goals on waste reducing resource efficiency.

Jamshidi, A., Kurumisawa, K., Nawa, T., Igarashi, T. (2016): Performance of pavements incorporating waste glass: The current state of the art. Renew. Sustain. Energy Rev., 64, 211-236.

Application of ammonium phosphate to marble. Investigation of newly-formed calcium phosphates with synchrotron light and high lateral resolution FTIR microspectroscopy

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Keywords: Carrara marble, inorganic-mineral treatments, ammonium phosphate, calcium phosphates.

Inorganic-mineral treatments exhibit great potentialities for the consolidation of stone materials due to their high compatibility with the substrate. Their reaction mechanism is based on the diffusion, inside weathered stone matrixes, of water soluble precursors that, reacting with the substrate, supply a crystal network able to reconnect detached grain boundaries. The newly-formed crystalline phases are stable and due to their low solubility provide a passivating action toward atmospheric agents even in acid environment. Diammonium hydrogen phosphate [DAP, $(NH_4)_2HPO_4$] has been recently suggested for the treatment of sedimentary and metamorphic carbonatic decayed stones. The reaction of DAP with calcite of the substrate involves a pseudomorphic replacement and favours the growth of calcium phosphates inside the porosity. Preliminary studies (Matteini et al., 2013; Possenti et al., 2016) show that the reaction at room temperature is non-stoichiometric and induces the formation of hydroxyapatite [HAP, $Ca_5(PO_4)_3(OH)$] (Ni & Ratner, 2003) and other metastable phases.

In this pilot study we characterized the complex assemblages of calcium phosphates formed after DAP treatments on Carrara marble specimens with a multi-analytical approach (scanning electron microscopy, vibrational spectroscopies and powder X-ray diffraction). A set of quarried and thermally decayed samples were treated by poultice and capillarity using DAP solutions at different molarities. Ground-breaking techniques such as X-ray diffraction with synchrotron light in transmitting geometry and high lateral resolution FTIR microspectroscopy were employed to overcome some of the analytical limits of conventional approach, assessing the overall composition of main and trace phases as well as their arrangement on the substrate.

Preliminary findings show the formation of a shell-like layer around the calcite grains, composed by a mixture of crystalline and amorphous calcium phosphates; the formation of specific phases, their morphologies and the relative amount depend on the solution molarity and the treatment duration. Moreover, our data show a correlation between the kind of crystalline phase and its morphology and position within the shell structure.

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A bridge between past and future concrete: Al-tobermorite in ancient Roman mortars

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Keywords: Al-tobermorite, Campi Flegrei, Roman technologies.

Roman mortars and concretes responded to subaerial weathering and submarine mechanical action of waves and seawater chemical interactions for > 2000 years. They provide an example of longevity and environmental sustainability for concretes formulated with lime and pyroclastic rock aggregates. Studies of marine concrete drill cores show that an unusual, calcium-silicate-hydrate mineral with cation-exchange properties, Al-tobermorite $\{[Ca_4(Si_{5.5}Al_{0.5}O_{17}H_2)]Ca_{0.2}Na_{0.1}\cdot 4H_2O\}$, crystallizes through pozzolanic processes in lime clasts and through post-pozzolanic processes in diverse components of the mortar fabric: pumice clasts, dissolved feldspar, and relict voids (Jackson et al., 2017). Although Al-tobermorite has never been observed in conventional, cement-based concretes, it occurs in ancient Roman concrete harbor structures, in the hydrothermally altered basalt of Surtsey volcano, Iceland, and as an alteration product at the cement-rock interface in nuclear waste repositories. Al-tobermorite mineral cements have been recognized in I Century A.D. subaerial mortars of the *Piscina Mirabilis*, a vast cistern used for storing fresh water in Baia. Petrographic, XRD, SEM-EDS investigations indicate that pozzolanic aggregate comes from *Campi Flegrei* deposits. In Roman marine concretes, lime mortars produced with weakly zeolitized *Campi Flegrei pozzolana* and seawater created a highly alkaline, but relatively short–lived pozzolanic system buffered by calcium hydroxide, which produced C-A-S-H cementing binder and Al-tobermorite at < 95°C. Post-pozzolanic Al-tobermorite and zeolite crystallization occurred at low temperatures, in association with clasts of *Campi Flegrei* Neapolitan Yellow Tuff and *pozzolana*. Post-eruptive, syn-depositional hydrolysis and dissolution of trachytic glass generated alkaline fluids, from which zeolites, mainly phillipsite, originated (de' Gennaro et al., 2000). After lime was consumed, renewed dissolution in the massive seawater structures produced alkaline fluids and new zeolitic cements-like those in the eruptive deposits, but with distinctive chemical variations. The *in situ* phillipsite reacted to produce additional Al-tobermorite at ambient seawater temperatures. In subaerial mortars, carbonation of *Campi Flegrei* zeolite within pumice apparently released alkaline earth elements, which also produced Al-tobermorite. Further investigations of Al-tobermorite formation in Roman mortars and concretes are very important since the crystals: a) form at lower temperatures than in laboratory syntheses, b) apparently crystallize through *in situ* release of alkaline cations from volcanic glass and crystals, and c) represent a beneficial alkali-silica reaction, which produces new cements that reinforce cohesion of the concrete and potentially enhance fracture toughness. Most remarkably, the application of ancient Roman technologies to innovative pyroclastic concretes could represent a new state-of-the-art in modern construction materials.

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New insights on the consolidation of mud bricks

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Keywords: mud brick, consolidation, alkaline solutions, ethyl silicate.

The consolidation and protection of mud bricks is a challenge in the field of conservation of archaeological sites. One of the solution is represented by the coverage of the entire excavation, that assures a protection against mud dissolution. Unfortunately this is not always feasible, both for economical and practical issues. For this reasons an alternative solution is needed. An experimentation has been carried out in order to test the efficacy of some products to slowdown the dissolution process and increase the brick toughness. Three typologies of raw materials have been used to made mud brick specimens. As consolidating agents, alkaline solutions (NaOH and KOH), silicate consolidants and nanometric lime have been used. After the treatments, several investigations have been performed to check the consolidation features of each treatment, as well as the chemical and mineralogical interaction of the products with the substrates. Results suggested that the efficacy of each treatment depends on the nature of the raw material used for the mud bricks. However nanometric lime and NaOH solution showed very poor performance, while ethyl silicate and KOH are very promising compounds for successful conservation.

Syenites from ring complexes in the eastern desert (Egypt) as fluxes for porcelain stoneware tiles

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Keywords: Abu Khuruq, technological behavior, porcelain stoneware tiles, syenites, syenoids.

The progressive depletion of the main feldspathic flux deposits in the World (pegmatites, aplites and albitites) is forcing the ceramic industry to search for suitable substitutes. The aim of this study is to assess the potential of some feldspar sources in the Egyptian Eastern Desert, where thirteen ring complexes outcrop on a 500 km-long strip (22-28°N, 33-35°E). The age of their emplacement ranges from 90 MA to 350-400 MA, with intermediate episodes around 140 MA and 230 MA (El Ramly & Hussein, 1983). They are constituted by syenoids (ranging from quartz-syenites to alkali-syenites and nepheline-syenites) associated to gabbros, essexites, alkaligranites and foidites plus extrusive lithotypes (basalt, trachyte and rhyolite). The outcrop extension and the ratios among the different lithologies vary upon the complex, as accessibility and distance from infrastructures. The most promising ring complex is the Abu Khuruq (Obeid & Lalond, 2013) taking into account geological, petrographic and logistical issues, including the occurrence of nepheline syenites. Seven samples of syenoids were collected and characterized from the chemical, mineralogical, petrographic and fusibility viewpoints. Three samples were selected for lab-scale mineralurgical treatments (comminution and magnetic separation). Beneficiated samples were tested into porcelain stoneware batches (from 10 to 30 wt% in replacement of sodic and sodic-potassic feldspars) and compared with a reference body. Simulation of the industrial processing was carried out at the laboratory scale by wet milling; slip drying and deagglomeration (< 500μm); granulation (< 2 mm, water 8 wt%); pressing (40 MPa); drying in oven (100°C overnight); fast firing (max temperature from 1160 to 1220°C; 60 min cold-to-cold). Fusibility is high (beneficiated syenites) to very high for raw samples (due to the iron oxide content in the 4-6% range). Technological behavior of unfired tiles does not exhibit any significant effects of the replacements. Syenite-bearing batches show a faster densification kinetics, with slightly decreasing water adsorption, even though the best firing range tends to narrow while increasing syenoids contents. In conclusion, syenites can be used as effective fluxes, without technological hindrances, to manufacture porcelain stoneware tiles. The firing behavior of syenite-bearing batches reasonably can be adjusted by setting key parameters (*e.g.*, the feldspar amount and the Na/K ratio). Color of fired bodies requires a tailored mineralurgical treatment to further lower the iron oxide amount.

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Exploring waste-based body formulations for ceramic tiles and clay bricks

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Keywords: ceramic tiles, clay bricks, waste recycling.

Waste recycling in vitrified ceramic bodies is getting a growing concern in the literature, where a wide range of residues have been proposed as raw materials for porcelain stoneware tiles, with promising results in terms of base properties (Andreola et al., 2016). However, drawbacks arose about technological behavior of waste-bearing bodies and actual cases of transfer to the tile-making industry seem to be limited to cannibalization of residues of the ceramic process itself (Andreola et al., 2008; Bernardo et al., 2008; Guzmán et al., 2013; Guzmán et al., 2016). The target of introducing high amounts of end-of-life residues is particularly challenging because of the fast innovation rate in the tile industry, that is shifting current expectations towards large ceramic slabs. The present contribution relates preliminary results of the MATER_SOS project (POR-FESR, 2014-2020) which is aimed at testing the chances for an actual industrial symbiosis involving the recycling chain in the Emilia-Romagna region, Italy, where the Sassuolo-Scandiano ceramic district is situated. The analysis of regional waste flows led to select various typologies of wastes which for characteristics and amounts appear to be potentially suitable as ceramic raw materials, mostly glasses, ashes and sludges, some well-known (*e.g.*, soda-lime glasses, rice husk ash) and others less investigated (*e.g.*, wood combustion ash). A dozen samples of residues were characterized (chemical and phase composition, particle size distribution, thermal properties) and used as fluxes in replacement of feldspathic raw materials (from 20% to 60%) in a standard porcelain stoneware batch. Bodies underwent a laboratory simulation of the industrial tile-making processing in order to test their technological behavior in milling, pressing and firing stages. Every waste has been classified through a technological profile summarizing compositional features and effects on grindability, compressibility and sintering by means of variation indexes based on particle size distribution, bulk density, firing shrinkage and water absorption. The main advantages achievable with waste-bearing batches is about the temperature of maximum densification that can be reduced of tenths degrees depending on the residue. General drawbacks are the tendency to have lower bulk density (symptom of close porosity) and a darker color after firing. Deviation from the tolerable range in the industrial practice may occur in specific cases (*e.g.*, excessive slip viscosity with combustion ashes). Nevertheless, technological properties usually do not scale linearly with the waste percentage and frequently escape from the additivity rule, thus making every waste type a case-study and suggesting caution in batch design.

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Guzmán, Á., Gordillo, M., Delvasto, S., Quereda, A., Sánchez, V. (2016): Optimization of the technological properties of porcelain tile bodies containing rice straw ash using the design of experiments methodology. Ceram. Int., 42, 15383-15396.

POR-FESR (2014-2020): MATER_SOS, Sustainable materials for restoration and construction of new buildings. www.matersos.it.

Mechanical properties of hexagonal hydroxylapatite (*P*6_3)

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Keywords: hydroxylapatite, thermomechanical properties, equation of state, elastic constants.

In this work, the mechanical properties of hexagonal hydroxylapatite (44 atoms in the unit cell, *P*6_3 space group), a crystalline ionic system that is very important for biotechnological applications, were investigated by *ab initio* quantum mechanics techniques. This material represents the main component of the mineral phase of bone tissues and, for this reason, it is very relevant for the development of prosthetic implants and coatings.

Few data are present in literature about the second order elastic constants (SOECs) of hydroxylapatite, both on the experimental (Gardner et al., 1992; Katz & Ukraincik, 1971) and theoretical sides (Ching et al., 2009; Menendez-Proupin et al., 2011; Slepko & Demkov, 2011). However, there are no data available in literature on the equation of state of this mineral. In the present study, we show the thermo-chemical and thermo-physical properties of the hydroxylapatite in the 0 – 10 GPa and 0 – 1000 K ranges. The hybrid DFT/B3LYP density functional in conjunction with Gaussian-type orbitals basis set were adopted, adding a correction for dispersive forces and employing the quasi-harmonic approximation. The zero-pressure bulk modulus of hydroxylapatite, calculated using a 3rd-order Birch-Murnaghan equation of state, was 115.9 GPa in athermal conditions (0 K) and 109.5 GPa at 300 K. In addition, we provided the second order elastic constants (SOECs) of this mineral phase in athermal conditions. The calculated bulk modulus from SOECs was 116.6 GPa, in good agreement with the results from the equation of state. These data could be helpful for experimental researchers involved in mechanical analysis this kind of materials at physical conditions that are difficult to obtain during experimental procedures, and for guiding researchers interested in quantum mechanical modelling of hydroxylapatite.

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Characterization of a Cambrian-Ordovician limestone (Kazakhstan) for the industrial production of quicklime and hydrated lime products

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Keywords: Kazakhstan limestone, Cambrian-Ordovician, quicklime, hydrated lime, silica content.

A Cambrian-Ordovician limestone succession from a virgin deposit in Kazakhstan is going to be quarried for feeding a Twin Shaft Regenerative (TSR) kiln and a three-stage Cim-Hydrax-4G hydrator plant, recently commissioned by a local client. The essential technical requirement is the low silica content (SiO_2 = 1.0%). From the petrographic point of view dominant facies are represented by coated grain peloidal grainstone to packstone with sparse millimetre size micritic rectangular intraclasts and flat pebble rudstone to packstone/grainstone. Burial diagenetic features include sparite blocky and poikilotopic cements, dolomite and silica replacements. The silicification occurs either in the form of replacive microquartz and chalcedony, or in the form of euhedral bipyramidal crystals with size of 90-200 µm. Thermal analysis (TG-DTG) shows a good burnability with no significant differences in calcination velocity along the core. Burning tests at 1050°C allow to simulate the calcination process occurring in a TSR kiln firing natural gas. The lime mechanical degradation is low, so the cracking tendency and the dust formation are acceptable. The slaking reactivity, according to EN 459-2, is high (t_{60} = 1.6min., T_{max} = 71°C). Subsequently, hydration tests simulate the industrial process within a three-stage hydrator plant. Physical characterization of hydrate includes residual moisture determination and sieving with air jet technology for dispersion and desagglomeration of fine powders. The quality control of the final product has been performed by X-ray diffraction analysis with the Rietveld method. In particular, the quantitative phase analysis (XRD-QPA) on dry slaked lime permits to evaluate the conversion rate of the hydration process ($CaO + H_2O = Ca(OH)_2$). The Rietveld analysis on coarse (200 µm) and fine (80 µm) fractions shows agglomerates of unreacted lime (CaO) and residual quartz (SiO_2) crystals can be effectively removed using an industrial separator. Conversely, it is more difficult, or impossible, to remove impurity as periclase (MgO) and other unreacted cementitious phases, *i.e.*, merwinite, larnite and hatrurite, which are mainly concentrated within fine powders. Finally, this study confirms that a multidisciplinary analytical approach is essential for predicting technological properties of different lime products, designing tailor-made industrial plants and helping the company in formulating the best warranty.

Session S12:

Mineral and biosphere interfaces: focus on environmental processes and technologies

Conveners:

Giovanni De Giudici (Univ. di Cagliari)
Laura Gaggero (Univ. di Genova)
Valentina Rimondi (Univ. di Firenze)
Valerio Funari (Univ. di Bologna)

Differences in composition of shallow water benthic communities associated with two ophiolitic rock substrata

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Keywords: hard bottoms, ophiolitic rocks, benthic communities, inhibition/facilitation processes, biomineralogy, Mediterranean.

The role of geology on ecosystems, even anthropic, is an assessed paradigm. On marine rocky shores, physical, chemical and biological processes operate to maintain the benthic assemblages' heterogeneity, but among the abiotic factors, the composition and texture of the rocky substrata have been only sporadically considered. However, biomineralogical studies have demonstrated an unsuspected ability of the benthic organisms to interact at different levels with rocky substrata. So, under similar environmental exposure, the mineralogy and fabric of the substratum can affect the structure of the benthic communities. The macrobenthic assemblages developed on two different ophiolitic rocks (serpentinites and metagabbros) in contact at a restricted stretch of the western Ligurian Riviera (western Mediterranean), with identical environmental and climatic conditions, were analysed. The samples were investigated at four levels of the shore (i) 1 m above the mean sea level (supralittoral zone), (ii) at the mean sea level (midlittoral zone), (iii) at 1 m depth (upper sublittoral zone), and (iv) at 3 m depth (sublittoral zone), evidencing differences in terms of species distribution and percentage coverage. Contrarily to terrestrial biotic record on the same lithotypes, algal communities growing on metagabbros were poorer in species richness and showed a much simpler structure, when compared to those occurring on the serpentinites. The most diffused animal organism, the barnacle *Chthamalus stellatus,* was exclusive on serpentinites, and absent on metagabbros. On average, the serpentinites hosted a higher number of OTUs (Operational Taxonomic Unit), ranging from a maximum of 12.2 ± 3.1 in the midlittoral zone, to a minimum of 6.3 ± 3.6 in the supralittoral one. On metagabbros, the highest number of recorded OTUs was 6.2 ± 0.9 in the midlittoral zone, and the lowest was 3.3 ± 1 in both sublittoral zones.

Our results suggest a complex pattern of interactions between lithology and benthic organisms that operate through processes of inhibition/facilitation related to some mineral properties.

In conclusion, the processes linked to the biomineralogy, although poorly known, appear very significant in marine ecology and need a deeper insight, because influence the dynamics and persistence of spatially structured benthic populations, and seem to be essential in favouring the generational change, through the supply side recruitment (Underwood & Fairweather, 1989) and the species connectivity (Burgess et al., 2014).

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Underwood, A.J. & Fairweather, P.G. (1989): Supply-side ecology and benthic marine assemblages. Trends Ecol. Evol., 4, 16-20.

Concentrations of metals and metalloids in wild asparagus: comparison between uncontaminated environments and sites contaminated by past mining in Sardinia (Italy)

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Keywords: *Asparagus acutifolius* L., metals, metalloids, past mining.

Wild edible plants are considered more healthy than crops because unaffected by the use of fertilizers, herbicides and pesticides. However, the occurrence of potentially toxic elements in wild plants is poorly known so far. Metals and metalloids occur as natural constituents dispersed in the Earth and can be mobilized by natural and anthropogenic means, including weathering, agriculture, urbanization and industrialization. Metals and metalloids usually occur at relatively high concentrations in areas hosting ore deposits. The potential for contamination is increased when mining operations expose mineralized materials and wastes to weathering processes. The dispersion of contaminants often extends over areas larger than the exploitation site and may persist for long time from the mine closure.

Among wild plants distributed in the Mediterranean environment, the *Asparagus* genus includes over 250 species used traditionally for domestic dishes and medical applications, especially in rural communities. In this study, 22 elements were determined by ICP-MS in wild asparagus (*Asparagus acutifolius* L.) of Sardinia (Italy) collected in uncontaminated environments and areas contaminated by past mining.

Among the considered elements in wild asparagus, Be, Bi, Te, Tl and U were undetected (< 0.03 µg/g); B, Cu, Fe, Mn, Rb and Zn were the most abundant (median: 10 to 58 µg/g); Ag, As, Co, Cd, Li and Sb were less abundant (median: 0.01 to 0.05 µg/g) and Ba, Mo, Ni, Pb and Sr showed large variations (median: 0.4, 0.3, 3, 0.1 and 0.5 µg/g, respectively). Median values of Ag, B, Ba, Co, Cu, Fe, Li, Mn, Mo, Ni, Rb, Sr and Zn in asparagus were similar either in uncontaminated or mining-related areas in Sardinia. Elements Cd, As and Sb in asparagus were clearly dependent on corresponding amounts in the bedrock at past mining sites. The uptake of Cd in asparagus was higher than that of other toxic elements. High values of the estimated daily intake were obtained for Cd in all mining-related areas, and for As and Sb at specific mining-related sites, respectively of Baccu Locci (As mine) and Su Suergiu (Sb mine).

Considering the widely diffused consumption of wild plants in rural areas, results of this study indicate health hazard to residents living nearby mines due to chronic dietary exposure to Cd and Sb in asparagus. Moreover, the assumption of crops grown on the locally contaminated soils would increase health hazards. Results of this study indicate that abandoned mine sites and mine related-areas need effective measures to reduce environmental contamination (Biddau & Cidu, 2017).

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Microorganism-silica mineral interaction in a pristine quartz-sandstone cave environment (Venezuela): first observations

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Keywords: cave minerals, bacteria, fungi, speleogenesis, Tepui.

Caves carved in Tepui quartz-sandstone table mountains (Venezuela) are among the most unexplored and untouched places on Earth. For example, the ~ 20 km-long Imawarì Yeuta cave has been discovered and explored only in 2013. Hosted in the Precambrian rocks of the Auyan Tepui massif, it is now considered one of the longest quartz-sandstone cave systems in the world (Sauro et al., 2013). It follows that this cave, along with other caves in the area, represents a unique natural laboratory where to study new mineral forms (Galli et al., 2013) and unique minerogenetic processes (Sauro et al., 2014), water geochemistry (Mecchia et al., 2014) and speleogenesis (Sauro, 2014) in Si-rich environments. Additionally, this isolated environment might potentially be a niche-like habitat for microbial communities genetically different from the normal surface and subsurface microorganisms, having silicon instead of carbon at the base of their life cycle. This might potentially procure new information on the origin and evolution of life on Earth and other planets. In this preliminary work, we present SEM-FESEM analyses on representative silica samples from Tepui caves reporting numerous microbial aggregates, many of which were never previously recognized in non-hydrothermal silica environments. Results suggest a key role of microbial organic activity in Si-rich mineral disintegration, which could have important implications in understanding the driving processes ruling silica weathering. In particular we observed silicified bacteria and microfungi that interact with amorphous silica, quartz and kaolinite minerals. The role of silica dissolution in cave formation is still debated among geologists (Sauro, 2014, and references therein). Microbially-mediated dissolution of quartz might explain why such extensive karst systems are "easily" excavated in one of the hardest rocks on Earth.

Galli, E., Brigatti, M.F., Malferrari, D., Sauro, F., De Waele, J. (2013): Rossiantonite, $Al_3(PO_4)(SO_4)_2(OH)_2(H_2O)_{10}\times4H_2O$, a new hydrated aluminum phosphate-sulfate mineral from Chimanta massif, Venezuela: description and crystal structure. Am. Mineral., 98, 1906-1913.

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Mercury speciation in *Pinus nigra* barks from Monte Amiata (Italy): an X-ray absorption spectroscopy study

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Keywords: mercury, tree bark, Monte Amiata, X-ray absorption spectroscopy.

This study determined, by means of X-ray absorption near-edge structure (XANES) spectroscopy, the speciation of mercury (Hg) in black pine (*Pinus nigra*) barks from Monte Amiata, that were previously shown to contain exceptionally high (up to some mg kg^{-1}) Hg contents because of the proximity to the former Hg mines and roasting plants.

Linear fit combination (LCF) analysis of the experimental spectra compared to a large set of reference compounds showed that all spectra can be fitted by only four species: β-HgS (metacinnabar), Hg-cysteine, Hg bound to tannic acid, and Hg(0). The first two are more widespread, whereas the last two occur in one sample only; the contribution of organic species is higher in deeper layers of barks than in the outermost ones.

We interpret these results to suggest that, during interaction of barks with airborne Hg, the metal is initially mechanically captured at the bark surface as particulate, or physically adsorbed as gaseous species, but eventually a stable chemical bond is established with organic ligands of the substrate. As a consequence, we suggest that deep bark Hg may be a good proxy for long term time-integrated exposure, while surface bark Hg is more important for recording short term events near Hg point sources.

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Metal recovery from MSWI fly ash and bottom ash by bioleaching and ion-exchange resin

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Keywords: Municipal Solid Waste Incineration (MSWI), fly ash and bottom ash, natural bacteria strains, *At. thiooxidans*, *At. ferrooxidans*, bioleaching, ion exchange resin, metal recovery.

Waste incineration is commonly seen as a good option for reducing waste volume and recovering its energy. Unfortunately, there is the production of huge amounts of solid incineration end-products, *i.e.*, fly ash (FA) and bottom ash (BA). BA and FA contain many hazardous and marketable metals. The FA and BA safe disposal combines with the extraction of metals as secondary raw material. Establishing an efficient technology that fulfils environmental and industrial requirements is a prerequisite to starting a factual rollout. We present an eco-friendly and cost-effective method (1) to recover valuable metals like Zn from BA and FA, and (2) to improve BA and FA safe disposal. The leaching of metals from the bulk materials was investigated in a controlled lab environment using a natural mixed culture where *Acidothiobacillus thiooxidans* and *Acidothiobacillus ferrooxidans* are the dominant strains. The bio-assisted leaching provided good yields of metal extraction exploiting the bacterial catalytic production of sulphuric acid. We assessed different experimental setups and the use of a regenerating ion-exchange resin to improve the purity of the recovered metals. The potentially recoverable metals by this two-step process and the environmental stability of the final residues will be discussed.

Bottom and fly ashes from municipal solid waste incinerators: more hazardous than has been revealed?

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Keywords: Municipal Solid Waste Incineration (MSWI), fly ash and bottom ash, environmental magnetism, iron oxides, superparamagnetic (SP) nanoparticles, anthropogenic pollution.

During their production, management, and landfilling, bottom (BA) and fly (FA) ashes from municipal solid waste incineration may liberate Fe-bearing, ultrafine particles and easily enter different environmental sinks of the biosphere. We aim to explore a collection of BA and FA samples from Italian incinerators to probe magnetic mineralogy and the fraction of harmful superparamagnetic (SP) nanoparticles (d < 30 nm). Temperature- and frequency-dependent magnetometry, Mössbauer analysis, X-ray diffraction, and electron microscopy observation are performed. The integration of information from our rock magnetic and nonmagnetic techniques leads us to conclude that the dominant magnetic carrier in our samples is magnetite and its intermediate/impure forms, while sulphides (*i.e.*, monoclinic pyrrhotite) are important ancillary magnetic phases. The SP fraction fluxing from the BA and FA outputs of a single incinerator is acknowledged for the first time and estimated in 10^3 ton/year (*i.e.*, the same order of magnitude of FA yearly production). The inhalable risk inherent to primary and secondary pollution by SP grains originated from waste incineration is logical. Although new studies are wanted to substantiate these observations, this work stresses the need to calibrate the current technologies towards a safer management of combustion ashes and certainly to inform the environmental impact assessment by using a combination of different methods.

Sulfur isotope signature in the Volcanogenic Massive Sulfide (VMS) deposits of the Italian northern Apennine

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Keywords: sulfur isotope, VMS deposits, Jurassic ophiolites, Ligurian Tethys, northern Apennine, Italy.

Volcanogenic Massive Sulfide (VMS) deposits occur in the Jurassic Tethyan ophiolites of the Italian northern Apennine, in the regions of Liguria and Emilia Romagna. They have been known as an economic source of copper since the Bronze Age, possibly representing the earliest copper mines to be discovered in western Europe so far. From 1850 to 1910, a number of new deposits were discovered and intensively mined. After, mining activities started again during "Autarky" and lasted until the early Seventies. The northern Apennine deposits represent a rare example of seafloor-stratiform, stratabound, and sub-seafloor stockwork hydrothermal vein ore-bodies associated with both the ultramafic basement and the basalt volcanic cover in one single ophiolite sequence. Because of the lack of a significant metamorphic overprint, they yielded a unique opportunity to investigate how and to what extent the different depositional settings (seafloor *vs.* sub-seafloor) and host rocks (basalt *vs.* serpentinite) have influenced the primary mineralogy, the composition of the sulfide ore and the the sulfur isotopic signature. Here we report the results of a systematic study of sulfur isotopes in sulfide minerals from selected VMS deposits of the northern Apennine, considered as resentatives of the various depositional settings described. The mineralization consists of pyrite-chalcopyrite-sphalerite with or without pyrrhotite, galena and magnetite. Quartz, calcite and chlorite are major gangue minerals. Sulfur isotopes analyses were performed on single sulfides: pyrite, chalcopyrite, sphalerite and pyrrhotite. The average $\delta^{34}S$ value is +5.2‰ in pyrite, +6.7‰ in chalcopyrite, +6.1‰ in sphalerite and 4.6‰ in pyrrhotite. The overall average $\delta^{34}S$ of +5.9‰ is comparable with data from other sulfide deposits of the eastern Mediterranean Tethys. However, the Apennine ores display a distinctive range from +11.4‰ to the negative field (min. -2.9). The highest $\delta^{34}S$‰ values are found in stockwork veins crosscutting basalt and gabbro, and in stratabound ores within basalt (av., +8.9‰). The $\delta^{34}S$ decreases in serpentinite-hosted stockwork veins (av., +5.8‰) and in stratiform deposits lying on ancient seafloors (av., +2.5‰), in which the negative values were detected. With some exception, inorganic reduction of seawater sulfate is considered to be the primary source of sulfur in the deposits. The low $\delta^{34}S$ values of serpentinite-hosted veins suggest mixing with sulfur derived from the leaching of magmatic sulfides (av., $\delta^{34}S$ = +0.8‰). The negative values detected in seafloor-stratiform ores correlate with sulfide textures indicative of the activity of sulfate-reducing bacteria causing preferential fractionation of the light sulfur isotope. The sulfur isotope variations observed in the northern Apennine VMS deposits reflect the influence of the different environments of sulfide deposition (seafloor *vs.* subseafloor) and different lithologies of the host rocks (basalt *vs.* serpentinite).

Management of highly alkaline steel slag leachate: impact of biofilm and hydraulic configuration on neutralisation

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Keywords: alkaline drainage, biofilm, mesocosm, neutralisation.

The management of alkaline (*p*H 11-12.5) leachate is an important issue associated with the conditioning, afteruse or disposal of steel slags, a major by-product of the steel industry. Global steel slag production ranges from 170 to 250 million tons annually (USGS, 2015), and there is a need to develop low cost treatments for the alkaline leachates it generates. Passive in-gassing of atmospheric CO_2 is an option for reducing alkalinity, as $Ca(OH)_2$ is neutralised by carbonic acid to produce $CaCO_3$. The relative effectiveness of such treatment can be affected by both the hydraulic configuration (*i.e.*, stepped cascades versus settlement ponds) and the presence of biofilm.

The adjustment of the carbonate system to CO_2 gas exchange has long been considered a critical process within tufa and travertine systems, and the role of biofilms is often assumed to reflect primarily consumption of CO_2 during photosynthesis. At high *p*H, such as is found associated with sites affected by alkaline leachates from alkaline wastes (*e.g.*, cementitious waste, fly ash, bauxite residue or steel slag), atmospheric $CO_{2(g)}$ converts directly to $CO_3^{2-}{}_{(aq)}$. This newly formed carbonate will combine with calcium to form calcite until an equilibrium is reached by balancing falling $Ca^{2+}{}_{(aq)}$, falling $HCO_3^-{}_{(aq)}$ and lowering *p*H. Carbonate ions are exclusively provided by air – water gas exchange, which should enhance neutralisation.

Mesocosm experiments run over periods of 20 days showed that, due to more water mixing and enhanced CO_2 dissolution at the weirs, the cascade systems are more effective than settlement ponds for lowering leachate alkalinity in all the tested conditions. The presence of an active microbial biofilm resulted in significantly more *p*H reduction in ponds, but had a small impact on the cascade systems. The *p*H variation in biofilm colonized systems shows a diurnal cycle of 1 to 1.5 *p*H units due to CO_2 uptake and release associated with respiration and photosynthesis.

Biofilms slightly improve the *p*H reduction in cascade systems and significantly improve the *p*H reduction in pond systems, but result in slightly less Ca^{2+} removal from solution in both systems. Also, when biofilm are present, both the *p*H value and calcium concentration exhibit a diurnal variation due to photosynthesis and respiration, with maximum *p*H reduction occurred during the night, but maximum calcite precipitation occurred during the day.

In the sterilised conditions, calcium loss from solution in the cascades was enhanced by ~ 28% compared to the ponds, and despite significant variability in both the systems performed significantly differently ($p = 0.004$). This effect disappears when the reservoirs are colonized by biofilms. Both ponds and cascades exhibit lower calcium loss from solution within the reservoir, higher variability, and no significant difference exist between cascades and ponds.

The results demonstrate that, where gradient permits, aeration via stepped cascades are the best option for neutralisation of steel slag leachates, and where feasible, the development of biofilm communities can also help reduce alkalinity.

USGS (2015): Iron and Steel Slag Statistics and Information. Minerals Information. U.S. Department of the Interior. U.S. Geological Survey, 2015

Manganese concretions and coatings on pebbles in a Messinian alluvial conglomerate: the role of bacterial catalysts

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Keywords: manganese ox/redox-bacteria, rock varnish, Sardinia.

Manganese is Earth's second most abundant transition metal and particularly in the reduced form its behavior mirrors that of iron. In the critical zone, these two elements are essential micronutrients for most chemosynthetic microrganisms and occur in multiple valence states in the environment, depending on *E*h and *p*H conditions. In detail, manganese occurs in three oxidation states: Mn^{2+}, which is soluble under reducing and acidic conditions; Mn^{3+} and Mn^{4+}, which are less soluble and are stable under relatively oxidizing and alkaline conditions.

In northern Sardinia (western Italy) Mn oxides concentrations were found into Messinian alluvial conglomerates and residual clayey deposits. They occur as Mn-oxides and oxi-hydroxides forming concretions and coatings on the conglomerate clasts, centimeter-size nodules scattered in the clays, and the matrix of conglomerates.

The preliminary data on mineralogical, chemical and textural composition of Mn-oxides coatings from the alluvial deposit of Scala Erre area provided useful clues to decipher their genesis and the environmental conditions that favored their formation.

XRPD analysis showed that the main Mn phase is lithiophorite. Birnessite and hollandite also occur in most samples. Quartz, illite and scarce Fe-oxides and hydroxides (hematite and goethite) complete the mineralogical association. ICP-MS and INAA analyses were performed on all samples showing a strong enrichment in transition metals, such as Co, Ni, and Zn, a moderate enrichment in Cu, Ba, Y, U, Pb and weak depletion in the other trace elements, compared to the GLOSS. Regarding the *REE* chondrite-normalised distribution patterns, the Mn-oxides coatings show a wide range of Σ*REE* contents (varying from 2025 to 5464 ppm); a significant *LREE*/*HREE* fractionation ($6.41 < (La/Yb)_{ch} < 20.46$); both positive and negative Ce anomalies ($0.74 < Ce/Ce^* < 3.27$). Ba is in the range of 1 wt% both hosted in the hollandite and occasionally as baryte micronodules. SEM/EDS analyses revealed an accretionary nature of the coating with thickness varying from some tens to five hundreds µm. Noticeably, the different concentric coats exhibit different content in transition metals and manganese as well. The occurrence of grape-like aggregates of 1 µm sized cocci points to the bacterial precipitation of Mn-oxide phases with a mechanism similarly to that of the "rock varnish" (Dorn, 2007). The barite micronodules resembling *Mixococcus xantus* testify for the sulphobacterial activity.

Dorn, R.I. (2007): Rock varnish. In: "Geochemical Sediments and Landscapes", D.J. Nash & S.J. McLaren, eds. Blackwell, London, 246-297.

Mineralogical investigation on bottom and fly ashes from Parma incineration plant

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Keywords: fly ash, bottom ash, SEM-EDS, XRD, MSWI.

The solid residues produced after the thermal process of the municipal solid wastes incinerator is an important part of the waste management system. In literature many work concerned the incinerator product but usually for a re-use in concrete or glassy materials (Andreola et al., 2008; Zacco et al., 2014). This study is focused on the mineralogical characterization of the phases found in a bottom ash and three fly ashes samples coming from Parma modern municipal solid waste combustor to understand both the environmental impact and a feasible recycle of the ashes. The samples were observed using optical and electronical microscopy (MO, SEM-EDS) and the powders were analysed by means of X-ray diffraction.

Bottom ash are the main part of the non-combustible residue of combustion and have a strong heterogeneous morphology: at a macroscopic view, clast of different colour and hardness are mixed with slivers of glass and fine dust. At MO clasts seem to be refractory waste and melt products, together with aggregates of soil and sand. At a microscopic analysis (SEM-EDS) the melt products consist mainly of amorphous silica glass, but many rock and ceramic fragments are equally present. At higher enlargement, small rounded and great amount of elongated fibrous crystals with a diameter of about 100-500 nm are clearly visible. Chemical analysis show the presence of many Ca-rich mineralogical phases and in minor amount iron oxides. The XRD analysis confirm the presence of a large amount of amorphous material (about 50% in weight) and, among crystalline phases quartz, calcite, hydroxyapatite, gehlenite, plagioclase, pyroxenes and iron oxides.

The fly ashes are the finest part driven out during the gas combustion. In this work the samples analysed are: non-treated FA (CV), treated with CaO (PCR) and with $NaHCO_3$ (PSR). The morphological aspect of the three samples is similar: small rounded crystals with a size of lower than microns together with few perfect sphere little bigger (at about 5 mm). The XRD shows that they are formed at 20% in weight of amorphous material. Among the crystalline part, the phase composition is different in the three samples. Non-treated fly ashes (CV) shows large presence of calcium sulphates like anhydrite, bassanite and gypsum, calcite, gehlenite, and chlorides like sylvite and halite. Small amount of quartz is found. In the PCR the addition of CaO produces large quantity of portlandite ($Ca(OH)_2$) reducing the presence of carbonates and sulphates while in the PSR the addition of $NaHCO_3$ develop new Na-rich phases like thermonatrite, hannebachite e nahcolite.

Andreola, F., Barbieri, L., Hreglich, S., Lancellotti, I., Morselli, L., Passarini, F., Vassura, I. (2008): Reuse of incinerator bottom and fly ashes to obtain glassy materials. J. Hazard. Mater., 153, 1270-1274.

Zacco, A., Borgese, L., Gianoncelli, A., Strui, R.P., Depero, L.E., Bontempi, E. (2014): Review of fly ash inertisation treatments and recycling. Environ. Chem. Letters,12, 153-175.

Magnetic measurement on minerals of PM_{10} filters and leaves: a new tool in airborne monitoring?

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Keywords: magnetic minerals, particulate matters, bio-monitoring.

Environmental contamination and human exposure with respect to dust or PM pollution have dramatically increased during the past 30 years and it is estimated that millions of tons of toxic pollutants are released into the air each year (WHO, 2016). The increasing demand for a regular monitoring of air quality has developed many works on magnetic measurements done on particulate airborne and on biological species as a complementary or an alternative method to traditional PM monitoring (Maher et al., 2008; Sagnotti et al., 2009).

In this work, both PM10 filters and leaves have been collected, daily, over a period of five months; filters are taken from an air-quality monitoring station run by ARPA-Emilia Romagna and leaves from a *Tilia cordata* tree, both located near the railway station of Parma. On these samples, magnetic measurements (IRM, SIRM and susceptibility), and SEM-EDS analysis has been performed and the results are then compared to the data of several pollutants of anthropogenic origin (PM_{10}, $PM_{2.5}$, O_3, NO_2, C_6H_6, CO), taken from ARPAE (Agenzia Regionale per la Protezione Ambientale dell'Emilia Romagna).

The measurements of saturation isothermal magnetic remanence (SIRM) show that for both filters and leaves the magnetic fraction mainly consists of a low coercivity, magnetite-like phase; this is confirmed also by SEM-EDS analysis, in which rounded small micrometre particles of iron oxides associated with clay minerals and calcite are clearly visible. The isothermal remanent magnetization (IRM) measurements performed at liquid nitrogen temperature (77 K) and room temperature (298 K) give an estimate of the particles grain-size distribution: the most part of the magnetic contribution, about 90%, can be attributed to single domain (SD) and superparamagnetic (SP) particles, *i.e.*, those with grain size substantially below one micrometre. This kind of particles are present in both filters and leaves.

Statistical analysis show a positive correlation between the main pollutants and the magnetic values of filters and leaves and especially between magnetic values of SD and MD particles and C_6H_6, CO and NO_2 pollutants, less with SP particles. The PM_{10} show a feeble relation with both filters and leaves magnetic signal, indicating that PM_{10} represents the entire value of the airborne particles including pollens, soils, fine dust of various type and not only magnetic materials.

Magnetic susceptibility measurements performed on filters during the period July-December shows a strong increase in value ascribable to the fall-winter period together with the value of C_6H_6, CO and NO_2 pollutants, confirming that the magnetic minerals are strictly connected with vehicle traffic of which these three parameters are indicative.

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Sagnotti, L., Taddeucci, J., Winkler, A., Cavallo, A. (2009): Compositional, morphological, and hysteresis characterization of magnetic airborne particulate matter in Rome, Italy. Geochem. Geophys. Geosyst.,10, Q08Z06.

Interactions between microfungi and pyrite mineralizations

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Keywords: acid mine drainage, pyrite mineralization, microfungi, mycoremediation.

Interactions between fungi and minerals are reported from several environments and geological materials. Recent researches have highlighted the important contribution played by fungi in sulfide rocks and mineral bioweathering, in particular in active and abandoned sulfide mines affected by Acid Mine Drainage (AMD) processes.

This work presents two experiments aimed at studying the role of native microfungal strains in the minerogenetic processes, including mineral bioweathering and biomineralization. The achieved results are shown and discussed.

The first experiment was carried out on pyrite-rich hardpans, sampled in a small waste rock dump from the abandoned Libiola mine (NW Italy), and it was devoted to study a *Trichoderma harzianum* Rifai strain as concerns its possible capability of biomineralization.

The results evidenced that *T. harzianum* was able to grow and cover most of the hardpan grains on all the autoclaved samples during a two-months incubation; in this period, it produced submillimetric thick biofilm containing significant concentrations of sulfur (most likely sulfate-S) and the fungal mycelium developed a close linkage to the mineral grains and rock fragments. At the end of the experiment, acicular and elongated prisms of gypsum crystals occurred within the fungal biofilm; they formed radiating aggregates centered on subspherical amorphous masses, most likely represented by mixtures of mycelium and cryptocrystalline or amorphous minerals, which presumably acted as nucleation centers for gypsum crystals growth. Gypsum formation may be either the consequence of an active fungal biomineralization or the result of a biologically-induced indirect mineralization, where secretion of acids and secondary metabolic products by fungal mycelium may trigger chemical reactions, induce chemical gradients, and create preferential nucleation sites.

The second experiment was carried out on almost pure and unaltered pyrite mineralization. It was aimed at evaluating the potential role played by microfungi in the weathering of sulfides. Three fungal species (*Penicillium brevicompactum* Dierckx, *P. glandicola* (Oudem.) Seifert & Samson, and *T. harzianum)* were used for the bioalteration tests. After one week, the pyrite grains were almost completely covered by mycelia and after six weeks the surface of pyrite crystals appeared pitted and pocked, showing signatures of fungal attack. Corrosion patterns were not related to specific crystallographic planes or weakness but they were randomly distributed in correspondence of the fungal hyphae attachment and dimensionally corresponded to fungal structures such as conidia (~ 3 µm).

Both the experimental results highlight the paramount role of microfungi in biomineralization and bioweathering of sulfide-bearing materials. Understanding these ecosystems and processes can increase the knowledge of these extreme habitats with environmental issues and can also yield useful applications for mycoremediation and mycomining.

Supergene non-sulfide Zn deposits: could hemimorphite have a biological origin?

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Keywords: hemimorphite, non-sulfide Zn deposit, Zn silicate, solubility constant, stability, biomineral, bacteria.

Hemimorphite, $Zn_4Si_2O_7(OH)_2 \cdot H_2O$, is one of the most common minerals in non-sulfide Zn deposits, together with hydrozincite and smithsonite. Precipitation of hemimorphite during the supergene evolution of non-sulfide Zn deposits is a debated issue (Choulet et al., 2014; McPhail et al., 2003) in which the scientific community has given till now a traditional inorganic geochemical explanation and, despite their importance for the development of ore genesis and metal dispersion models, the stability properties of hemimorphite are poorly known. Our research is right addressed to understanding the hemimorphite stability performing solubility experiments in free-drift batch reactors on inorganic hemimorphite, from a supergene non-sulfide Zn deposit, and biological hemimorphite precipitated by bacterial activity. Solid samples were characterized, before and after the solubility experiments, exploiting laboratory and synchrotron radiation based multi-technique approach that combines X-ray powder diffraction (XRPD), Scanning Electron Microscopy (SEM), and X-ray Absorption Spectroscopy (XAS). The calculated solubility product constants ($\log K_s$) are similar for both "geological" ($\log K_s = 30.3 \pm 0.4$) and biogenic hemimorphite ($\log K_s = 30.5 \pm 0.1$). We demonstrate that the solubility experiments trigger an amorphous to crystalline phase transition of biological hemimorphite, while mineralized bacterial sheaths and organic filaments, that allowed us to demonstrate its biological origin, were dissolved and no longer recognizable by Scanning Electron Microscopy.

This study provides new thermodynamic data on hemimorphite allowing us to present improved predominance diagrams ($P\text{CO}_2$ *vs.* $p\text{H}$) for the chemical system Zn – O – H – C – Si, which may be useful for developing genetic models of ore deposits, for predicting mineral dissolution/precipitation reactions and for investigating metal dispersion processes. The amorphous to crystalline state transition of bio-hemimorphite associated to the obliteration of its bio-morphological features, open up the question if bacteria could have played a role in the formation of hemimorphite deposits. Such interaction between biosphere and geosphere raises an important question about the possibility of using endemic bacteria to develop more sustainable technologies for Zn abatement and recovery in abandoned mine systems.

Choulet, F., Charles, N., Barbanson, L., Branquet, Y., Sizaret, S., Ennaciri, A., Badra, L., Chen, Y. (2014): Non-sulfide zinc deposits of the Moroccan High Atlas: Multi-scale characterization and origin. Ore Geol. Rev., 56, 115-140.

McPhail, D.C., Summerhayes, E., Welch, S., Brugger, J. (2003): The geochemistry of zinc in the regolith. In: "Advances in Regolith", I.C. Roach, ed. CRC for Landscape Environments and Mineral Exploration, 287-291.

Nanoscale distribution of Zn in foraminifera shell: a multi-scale/multi-technique investigation

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Keywords: foraminifera, zinc biogeochemical cycling, metal detoxification, multi-scale characterization.

Foraminifera are unicellular organisms widespread in marine ecosystems that, building Ca-carbonate shells, may incorporate trace metals present in the ocean waters because of natural or anthropogenic supply. The distribution and chemical speciation of these elements across the foraminifera shell is a research topic relevant for defining proxies in ocean and environmental sciences. Here we focus on Zn, being an abundant trace element in contaminated as well as clean waters. We reveal peculiar differences in Zn concentration and chemical speciation at the micro and nanometric scale with the formation of independent mineral phases, in particular hydrozincite and sphalerite. These differences appear to be related to the cellular mechanisms involved in the calcite shell biosynthesis: the Ca-carbonate synthesis in foraminifera can be either in extracellular or intracellular space, implying some diversity in physiology and cation transport process. Independent mineral phases of Zn dispersed in biogenic calcite material are likely due to an unravelled detoxification mechanism. Their formation is shown to be species dependent and is a tool for a deeper understanding of environmental processes, past ocean circulation and biogeochemical cycling. Combined use of state of art complementary probes (synchrotron radiation and laboratory set up) was crucial to achieve a reliable detailed multi-scale characterization.

Natural biogeochemical barriers in a stream affected by mine drainage

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Keywords: mine wastes, water pollution, hydrologic tracer, hyporheic zone, biogeochemical barriers.

Rio San Giorgio (Iglesiente, Sardinia, Italy), a stream affected by abandoned mine wastes, is characterized by dense vegetation in the streambed, mainly comprised of *Phragmites australis* and *Juncus acutus*. This vegetation creates natural biogeochemical barriers that drive mineralization processes and attenuate metals load in the stream. Several techniques, covering scales from micrometres to kilometres, were applied to investigate the biogeochemical processes: water chemistry, injected hydrologic tracer, mineralogy, microscopic investigation and X-ray spectroscopy. From this multiscale and multimethod approach, we recognized two predominant sets of biogeochemical processes: microbially driven metal sulphide precipitation, mainly resulting in pyrite formation; and plant uptake of metals that leads to formation of iron oxide-hydroxide and incorporation of Zn within the roots and aerial part (stem and leaves). The dense vegetation in the Rio San Giorgio streambed controls its morphology, velocity of streamflow, and, as reflected by observed bromide-tracer loss, enhanced water exchange between the streambed and the hyporheic zone. The combined effect of these vegetative controls is to establish biogeochemical barriers that greatly retard trace-metal mobility in the hyporheic zone. We estimated this effect can led to an apparent decrease in Zn load up to 60%.

Arsenic in travertine soils near Viterbo, central Italy: mobility, bioaccessibility, health risks

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Keywords: arsenic, Viterbo, thermal springs, SBET.

It is long established that the occurrence of a wide natural ("geogenic") arsenic (As) anomaly in northern Latium causes elevated As contents in local groundwaters (Angelone et al., 2009), and crops (Cubadda et al., 2010), with consequent health risk for residents (D'Ippoliti et al., 2015).

Since 2010, our group investigates the occurrence of As in local soils, mostly in association with thermal springs and travertine deposits (Ciardi et al., 2010; Sacco, 2015; Pacini, 2017; Del Soldato, 2017).

Travertine deposits associated with the thermal springs at Bullicame and Terme di Bagnaccio may contain as much as 200 mg/kg As; even higher contents (up to 500 mg/kg) may be observed in soils developed onto this travertine substrate. Sequential extraction procedures suggest that in travertine As is mostly associated to the carbonate fraction, indicating that the metalloid is mainly hosted by calcite (cf, Costagliola et al., 2013) whereas in agricultural soils the Fe oxy-hydroxides contain the highest fraction of As.

The thermal springs are the center of a recreational area that is often visited by local residents and tourists. A bioaccessibility test (SBET, Simple Bioaccessibility Extraction Test, Oomen et al., 2002) was conducted to estimate the potential intake of As by visitors through accidental ingestion of soil. The As bioaccessible fraction of soil ranges from about 90% in travertine samples to about 10% in agricultural soils. Given the amount of soil that is likely to be ingested, the health risk (both of acute toxicity and possible carcinogenic effects) for occasional visitors is low; it may become slightly higher (but still below the commonly accepted thresholds) for children accessing the area on a daily routine.

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Sacco, A. (2015): Analisi per la determinazione delle concentrazioni di Arsenico e Mercurio nei suoli della provincia di Viterbo. Tesi di Laurea Magistrale in Scienze e Tecnologie Geologiche, Università di Firenze, 147 p.

Session S13:

Elements at the edge of life: minerals and mineralization processes in present and past organisms

Conveners:

Alberto Collareta (Univ. di Pisa)

Karen Gariboldi (Univ. di Pisa)

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A complex diagenetic history for the Miocene invertebrates of the East Pisco Basin (Peru)

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Keywords: invertebrates, mollusks, diagenesis, dolomite, Pisco Basin, taphonomy.

The Miocene marine sediments of the East Pisco Basin (southern Peru) are well-known for their extraordinary concentration of exceptionally well-preserved fossils of marine vertebrates together with invertebrate remains (Di Celma et al., 2017).

In the western Ica Valley, the late Oligocene-early Miocene Chilcatay Formation consists of sandstones and siltstones interbedded with layers of cobbles and overlaid by clinoformed coarse-grained biocalcarenites. Fossil invertebrates are common and well-preserved, but the assemblage is characterized by low biodiversity, with only few species of barnacles, echinoids, tube worms and bivalves (mainly pectinids and oysters). Overall, biogenic Ca-carbonates are present and well-preserved.

In the same region, the late Miocene Pisco Formation consists of three unconformity-bounded depositional sequences (Di Celma et al., 2017), made of sandstone at the base and diatomaceous siltstones at the top. It shows mollusk-rich layers characterized by low biodiversity and high dominance (DeVries, 1988; Di Celma et al., 2017). Mollusks are commonly preserved only as gypsum casts or dolomite/gypsum molds. Pristine mollusk shells are rare and pure Ca-carbonates are only occasionally observed.

With the aim of reconstructing the diagenetic histories of both formations, mollusk and barnacle samples have been first analyzed under the optical microscope and SEM-EDS, and then analyzed via Raman spectroscopy (to recognize mineral phases) and cathodoluminescence (to discriminate pristine carbonates and different cement generations). The results of mineralogical and geochemical analyses, integrated with taphonomic observations, enabled us to reconstruct the sequence of the diagenetic processes; for example, Sr-isotope ratios measured on mollusk samples from the Pisco Formation proved that dolomite precipitation occurred during the early diagenesis as recently proposed (Gariboldi et al., 2015). These analytical results will allow to reconstruct the still rather neglected but remarkably complex diagenetic history of the Miocene invertebrates of the East Pisco Basin.

DeVries, T.J. (1988): Mollusks of the Pisco Basin. Pisco Basin Guidebook. In: "Cenozoic Geology of the Pisco Basin", R.B. Dunbar & P.A: Baker, eds. International Geological Correlation Programme 156, 127-134.

Di Celma, C., Malinverno, E., Bosio, G., Collareta, A., Gariboldi, K., Gioncada, A., Molli, G., Basso, D., Varas-Malca, R., Pierantoni, P.P., Villa, I.M., Lambert, O., Landini, W., Sarti, G., Cantalamessa, G., Urbina, M., Bianucci, G (2017): Sequence stratigraphy and paleontology of the upper Miocene Pisco Formation along the western side of the lower Ica Valley (Ica Desert, Peru). Riv. Ital. Paleont. Stratigr., 123, 255-273.

Gariboldi, K., Gioncada, A., Bosio, G., Malinverno, E., Di Celma, C., Tinelli, C., Cantalamessa, G., Urbina, M., Landini, W., Bianucci, G. (2015) The dolomite nodules enclosing fossil marine vertebrates in the East Pisco Basin, Peru: field and petrographic insights into the Lagerstätte formation. Palaeogeogr. Palaeoclimat. Palaeoecol., 438, 81-95.

Authigenic phosphorus minerals as a proxy for paleo-nutrient levels in Miocene carbonate factories

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Keywords: authigenic minerals, phosphorus, coralline algae, bryozoans, Miocene.

Phosphorus is an essential element for all life forms, it enters the biological cycle through photosynthesis and it is then transferred to the higher level of the food chain. In marine environment P represents the ultimate limiting nutrient, whose rate of supply regulates primary production over long timescales (Tyrrell, 1999). Primary production has a strong impact on carbonate-producing organisms and on the resulting skeletal assemblage. High production promotes the dominance of heterotrophs suspension-feeders (favored by food abundance), over autotroph and symbiont-bearing mixotrophs (hindered by the reduced light availability caused by the large amounts of plankton in the water; Hallock, 1988). Therefore, P availability can be used to interpret facies variations in carbonate systems. However, there are very few reliable instruments to track phosphorus in the fossil record. Phosphorus is present in marine sediments in various forms: organic P, loosely-bound P, Fe-oxyhydroxides-bound P, authigenic and biogenic Ca-P minerals and detrital apatite. Except detrital apatite, all of them are sinks for the reactive P present in the water (Ruttenberg, 1992) and thus their abundance is related to P availability and to primary-production. XRF or natural gamma radiation techniques cannot separate these authigenic P-mineral from detrital apatite of igneous and metamorphic origin, preventing an accurate reconstruction of paleo-nutrient levels. To overcome this limitation we have applied SEDEX sequential extraction, a methodology devised to separate and quantify the P-minerals of modern marine sediments (Ruttenberg, 1992), to different Miocene limestones. A coralline-algal dominated carbonate succession, a bryozoan-dominated one and a coral-reef limestone have been analyzed. The results from SEDEX have been compared with those of XRD analyses and with those of the paleoecology of the fossil assemblages, to provide evidences, from independent methodologies, of nutrient influence on the investigated carbonate systems. As expected on the basis of the comparison with modern systems, nutrient levels were higher in the bryozoan-dominated succession than in the coralline dominated one. Both systems where characterized by higher concentration of P when compared to the coral-reef limestone. These results strongly support SEDEX extraction as a viable technique to quantify authigenic P-minerals of limestones and therefore to investigate nutrient abundance in the geological record.

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Tyrrell, T. (1999): The relative influence of nitrogen and phosphorous on ocean primary production. Nature, 400, 525-531.

Fossil baleen under the microscope: seeking the key for fine-scale preservation of soft tissues

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Keywords: baleen, biomineralization, dolomite, exceptional preservation, taphonomy, soft-tissue fossilization.

Instead of teeth, modern baleen whales bear comb-like, hair-fringed baleen plates that enable bulk-filter feeding on vast amounts of small prey. Baleen is a horny material, being only moderately mineralized by crystallites of hydroxyapatite interspersed within an easily degradable keratinous matrix. Thus, baleen rarely fossilizes, making our knowledge of its evolutionary history highly speculative. Fossil baleen structures have been reported only from a few Neogene localities worldwide, and especially from the late Miocene strata of the Pisco Formation of Peru.

We undertook a scanning electron microscopy, microanalytical (EDS, EPMA) and mineralogical (XRD) study of fossil baleen structures from the Pisco Fm. Three specimens have been investigated to date (Gioncada et al., 2016; Marx et al., 2017; this work), all showing evidence of fine-scale preservation of baleen tissues. The first two consist of articulated skeletons, referred to as Balaenopteroidea indet. (rorquals and relatives), from the sites of Cerro Colorado and Cerro La Bruja. Both specimens exhibit baleen racks enclosed in dolomite concretions. Fossilization types include molding of plates or tubules and very fine-scale phosphatization of the latter (comprising their free terminations, *i.e.*, baleen bristles). We argue that both whales foundered in a soft, organic-rich sediment representing an environment chemically prone to rapid nucleation of dolomite, thus allowing the preservation of delicate soft structures as molds. Bio-mediated precipitation of dolomite due to sulphate-reducing bacteria is testified by the observation of ghosts of iron sulphide framboids within the matrix enclosing the baleen. Found at the site of Cerro Ballena, the third studied specimen consists of an articulated skeleton of a diminutive mysticete identified as belonging to the cetotheriid species *Piscobalaena nana*. This finding represents the first fossil baleen apparatus of an entirely extinct mysticete morphotype, showing an exceptional degree of preservation thanks to phosphatization of the baleen plates, in the absence of a dolomite concretion. The lack of an insulating concretion possibly allowed the development of quite large (1-10 μm-sized) crystals of fluorapatite.

This ongoing research indicates that (1) the early formation of dolomite around whale carcasses is a prominent, but not necessary, process inducing exceptional baleen preservation, and (2) calcification of soft tissues such as baleen is favoured by the presence of Ca-phosphate crystallites.

Gioncada, A., Collareta, A., Gariboldi, K., Lambert, O., Di Celma, C., Bonaccorsi, E., Urbina, M., Bianucci, G. (2016): Inside baleen: Exceptional microstructure preservation in a late Miocene whale skeleton from Peru. Geology, 44, 839-842.

Marx, F.G., Collareta, A., Gioncada, A., Post, K., Lambert, O., Bonaccorsi, E., Urbina, M., Bianucci, G. (2017): How whales used to filter: exceptionally preserved baleen in a Miocene cetotheriid. J. Anat., in press, DOI: 10.1111/joa.12622.

Secondary mineralization during diagenesis in ammonites: a helpful tool for stratigraphic survey

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Keywords: ammonites, diagenesis, secondary mineralization.

Ammonites (Mollusca: Cephalopoda: Ammonoidea) are a large group of extinct ectocochleate cephalopods that populated the oceans worldwide between the Devonian and Cretaceous periods. Their maximum expansion was during the Jurassic and Cretaceous periods, an interval in which they represent the preferred biostratigraphic marker for dating marine sedimentary rocks. Ammonites are especially useful for dating rocks because their shells are frequently found as fossils due to their morphological features and great abundance.

Ammonites were nectonic animals which inhabited the water column. After death, following the rules of taphonomy, currently fossilized ammonoid shells started a long journey before being ultimately found by a paleontologist. During this travel, they underwent several transformations which allowed to preserve or lose anatomical features and help in the purpose of using ammonites not only as biostratigraphic markers, but also as purely stratigraphic ones. What a paleontologist often (but not always) finds is a "pseudo-shell" composed by mineral phases which reflect the composition of interstitial water during transformation. The results of these processes are often spectacular, realizing real pieces of jewellery (Di Cencio et al., 2017). A thorough study of mineralization and diagenetic transformations of ammonites allows to understand what happened to them after burial and how the embedding sediments have been modified by orogenesis, tectonics, and even surface processes. Starting with the presence or absence of crystals in the cavity of ammonoid pseudo-shells, the geological evolution of a country can be written based on evidences of secondary mineralization.

Di Cencio, A., Rakotonimanana Rivoniaina, M., Randrianaly, H.N., Rakotondramasy Andriamahery, H., Raharimahefa, T. (2017): Valorisation and protection of Early Cretaceous (Albian) paleontological sites in the Mahajanga basin, north western Madagascar. XVII Edizione delle Giornate di Paleontologia, Anagni, 24-26 maggio 2017, abstr.

Amazing diatom preservation within dolomitised sediments of the late Neogene Pisco Formation, Peru

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Keywords: Pisco Formation, diatom frustules, diatom ultrastructure, dolomite, preservation.

The late Neogene Pisco Formation of southern Peru is considered a Fossil-Lagerstätte (Seilacher, 1970) due to the abundance and beautiful preservation state of its fossil marine vertebrates (*e.g.*, Esperante et al., 2015). However, the Pisco Formation strongly deserves the attribute of Fossil-Lagerstätte also for the amazing preservation state of several diatom specimens.

Early diagenetic dolomite and associated minerals (*i.e.*, Mn oxides) occasionally precipitated within the diatomaceous sediments characterising this formation (Gariboldi et al., 2015; Gioncada et al., 2016). In these instances, the filling of the diatom frustules by means of both micritic and drusy dolomite prevented them from being compressed by the sedimentary load. Thus, by means of SEM-SE images, beautifully preserved ultrastructures can be observed three-dimensionally.

Furthermore, in those cases where silica has been dissolved, highly-detailed moulds let us have a glimpse of the diatom ultrastructures.

Esperante, R., Brand, L.R., Chadwick, A.V., Poma, O. (2015): Taphonomy and paleoenvironmental conditions of deposition of fossil whales in the diatomaceous sediments of the Miocene/Pliocene Pisco Formation, southern Peru-A new fossil-lagerstätte. Palaeogeogr. Palaeoclim. Palaeoecol., 417, 337-370.

Gariboldi, K., Gioncada, A., Bosio, G., Malinverno, E., Di Celma, C., Tinelli, C., Cantalamessa, G., Urbina, M., Landini, W., Bianucci, G. (2015): The dolomite nodules enclosing fossil marine vertebrates in the East Pisco Basin, Peru: field and petrographic insights into the Lagerstätte formation. Palaeogeogr. Palaeoclim. Palaeoecol., 438, 81-95.

Gioncada, A., Collareta, A., Gariboldi, K., Lambert, O., Di Celma, C., Bonaccorsi, E., Urbina, M., Bianucci, G. (2016): Inside baleen: Exceptional microstructure preservation in a late Miocene whale skeleton from Peru. Geology, 44, 839-842.

Seilacher, A. (1970): Begriff und bedeutung der Fossil-Lagerstätten. N. Jb. Geol. Paläont. Abh., 1, 34-39.

Selective zircon accumulation in a new benthic foraminifer, *Psammophaga zirconia*, sp. nov.

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Keywords: foraminifera, early organisms, zircon, heavy minerals.

Benthic foraminifera are single-celled eukaryotes that make a protective organic, agglutinated or calcareous test. Some agglutinated, single-chambered taxa, including *Psammophaga* Arnold, 1982, retain mineral particles in their cytoplasm, but the selective mechanism of accumulation is not clear. Here, we report the ability of a foraminiferal species to select and accumulate zircons and other heavy minerals in their cytoplasm. In particular, the use of Scanning Electron Microscope coupled with an Energy Dispersive X-ray microanalysis system (SEM–EDS) enabled a representative overview of the mineral diversity and showed that the analysed *Psammophaga zirconia* sp. nov. individuals contained dominantly crystals of zircon (51%), titanium oxides (27%), and ilmenite (11%) along with minor magnetite and other minerals. The studied specimens occur in the shallow central Adriatic Sea where the sediment has a content of zircon below 1% and of other heavy minerals below 4%. For that reason, we suggest that: (i) *P. zirconia* may be able to chemically select minerals, specifically zircon and rutile; (ii) the chemical mechanism allowing the selection is based on electrostatic interaction, and it could work also for agglutinated foraminifera. In particular, this aptitude for high preferential uptake and differential ingestion or retention of zircon is reported here for the first time, together with the selection of other heavy minerals already described in members of the genus *Psammophaga*. They are generally counted among early foraminifera, constructing a morphologically simple test with a single chamber. Our molecular phylogenetic study confirms that *P. zirconia* is a new species, genetically distinctive from other *Psammophaga*, and occurs in the Adriatic as well as in the Black Sea. Finally, the presence of eukaryotic soft-walled monothalamous microfossils, capable of building a fine aluminosilicate case, in the Precambrian geological record, makes them useful as a valuable record of the early evolution of foraminifera, suggesting that biological agglutination was already present in this group. *P. zirconia* is a new documented example among foraminifera capable of highly intriguing preferential mineral uptake, showing that this behavior could have emerged very early in their evolution.

The first appearance of monothalamous foraminifera and the molecular clock, state of the art

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Keywords: early foraminifera, evolution, agglutinated test.

When did foraminifera appear in the geological record? The traditional paleontological approach put the first occurrence of Foraminifera in the Paleozoic, however the architectural complexity and design displayed by Lower Cambrian foraminiferal assemblages joint to the low fossilization potential of soft-walled taxa, indicate that the fossil record should not be interpreted so literally (Langer, 1999). In literature interpretations based on molecular sequencing data (molecular clock), which use the genetic distance to estimate divergence times between lineages, suggest that the initial appearance of foraminifera should date back to 1.1 billion years (Pawlowski et al., 2003). Finally recent paleontological data have found also several evidence of taxa similar to soft walled saccamminids back in the post Sturtian deposits of Namibia and Mongolia (Bosak et al., 2012). Other similar putatively organic structured organisms are described in many other articles (Marti Mus & Moczydlowska, 2000; Porter et al., 2003; Maloof et al., 2010) and also Late Ediacaran Agglutinated foraminifera have been found by Pazio (2012) in northern Norway, evidencing that this topic deserve to be approached deeply, joining all the efforts in order to find new sites and fossils. Aim of this presentation is to point out recent findings of organic walled forms which prove that a different approach in the preparation of samples and the study of this early forms needs to be adopted.

Bosak, T., Lahr, D.J.G., Pruss, S.B., Macdonald, F.A., Gooday, A.J., Dalton, L., Matys, E.D. (2012): Possible early foraminiferans in post-Sturtian (716-635 Ma) cap carbonates. Geology, 40, 67-70.

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Maloof, A.C., Rose, C.V., Beach, R., Samuels, B.M., Calmet, C.C., Erwin, D.H., Poirier, G.R., Yao, N., Simons, F.J. (2010): Possible animal-body fossils in pre-Marinoan limestones from South Australia. Nature Geosci., 3, 653-659.

Marti Mus, M. & Moczydlowska, M. (2000): Intemal morphology and taphonomic history of the Neoproterozoic vase-shaped microfossils from the Visingso Group, Sweden. Norsk Geol. Tidsskrift, 80, 2-13.

Pawlowski, J., Holzmann, M., Berney, C., Fahrni, J., Gooday, A.J., Cedhagen, T., Habura, A., Bowser S.S. (2003): The evolution of early foraminifera. Proc. Nat. Acad. Sci., 30, 11494-11498.

Pazio, M. (2012): The late Ediacaran Agglutinated Foraminifera from Finnmark, Northern Norway. Uppsala universitet, Institutionen för geovetenskaper Kandidatexamen i Geovetenskap, Självständigt arbete Nr 43.

Porter, S.M., Meisterfeld, R., Knoll, A.H. (2003): Vase-shaped microfossils from the Neoproterozoic Chuar Group, Grand Canyon: a classification guided by modern testate amoebae. J. Paleont., 77, 409-429.

The fossil vulture (*Gyps fulvus* Hablizi, 1783) from the Late Pleistocene volcanic deposits of Alban Hills (Latium, central Italy)

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Keywords: Alban Hills, feathers, fossilization, sof tissue preservation, taphonomy, vertebrate palaeontology.

In 1889 Romolo Meli, geologist, paleontologist, and engineer, reported to the Società Geologica Italiana the discovery of a Late Pleistocene fossil vulture found in a pyroclastic deposit known as "peperino", from the area of Alban Hills, south-east of Rome, dated at 30 ka (De Rita et al., 1995; Voltaggio & Barbieri, 1995; Giordano et al., 2002). The specimen was classified as *Gyps fulvus* Hablizi, 1783, and it is preserved into some grey blocks of peperino with a yellow-reddish coat corresponding to some anatomical portions of the animal. The fossil was stored in Meli's scientific cabinet, that since decades has become part of the Secondary School "Leonardo Da Vinci" in Rome. In a recent study, the peperino block containing the natural cast of the head was analyzed by means of CT-based techniques and it showed the extraordinary preservation of some non-mineralized anatomical portions, like the vulture's tongue (Iurino et al., 2014).

The other blocks were only described by Meli in 1889. The feathers on them, which represent at least in part a portion of the vulture's wing, have recently been analyzed, and here we present some preliminary data.

The fossil shows an extremely detailed preservation of each anatomical element of the feathers; the casts of the rachids allow to discriminate the ventral and dorsal feather leaves (Lingham-Soliar, 2015); the morphological and dimensional analysis of each feather allows to recognize its type and anatomical position.

The peculiar lithological heterogeneity of the peperino blocks allows to arrange them in the original outcrop, which is no longer visible, thus leading to the reconstruction of the entire animal.

The preservation of degradable elements such as feathers and other organic portions leads to interesting taphonomic inferences related to the characteristics of the volcanic event and, above all, provides constraints about the temperature of pyroclastic deposits.

De Rita, D., Faccenna, C., Funiciello, R., Rosa, C. (1995): Stratigraphy and volcano-tectonics. In: "The Volcano of the Alban Hills", R. Trigila, ed, SGS, Roma, 33-71.

Giordano, G., De Rita, D., Cas, R., Rodani, S. (2002): Valley pond and ignimbrite veneer deposits in the small-volume phreatomagmatic 'Peperino Albano' basic ignimbrite, Lago Albano maar, Colli Albani volcano, Italy: influence of topography. J. Volcanol. Geotherm. Res., 118, 131-144.

Iurino, D.A., Bellucci, L., Schreve, D., Sardella, R. (2014): Exceptional soft tissue fossilization of a Pleistocene vulture (Gyps fulvus): new evidence for emplacement temperatures of pyroclastic flow deposits. Quatern. Sci. Rev., 96, 180-187.

Lingham-Soliar, T. (2015): The Vertebrate Integument, Volume 2-Structure, Design and Function. Springer, Berlin-Heidelberg, 348 p.

Meli, R. (1889): Sopra i resti fossili di un grande avvoltoio (Gyps) racchiuso nei peperini laziali. Boll. Soc. Geol. It., 8, 490-544.

Voltaggio, M. & Barbieri, M. (1995): Geochronology. In: "The Volcano of the Alban Hills", R. Trigila, ed, SGS, Roma, 167-192.

Session S14:

Modern and fossil oceanic lithosphere revisited: from field to laboratory

Conveners:

Alessio Sanfilippo (Univ. di Pavia)

Emilio Saccani (Univ. di Ferrara)

Luca Pandolfi (Univ. di Pisa)

Role of the intra-oceanic tectono-sedimentary architecture in the Alpine tectonic evolution of the Monviso meta-ophiolite Complex (western Alps)

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Keywords: western Alps, Monviso ophiolite, structural inheritance, oceanic core complex, Alpine tectonics.

The eclogite-facies Monviso meta-ophiolite Complex (MO) in the western Alps represents a fragment of oceanic lithosphere which recorded the evolution of an oceanic core complex formed by mantle exhumation along an intra-oceanic detachment fault (*i.e.*, the Baracun Shear Zone, BSZ; Festa et al., 2015), related to the Jurassic extensional tectonics and opening of the Ligurian-Piedmont oceanic basin (Alpine Tethys). This detachment fault, which consists of mylonitic serpentinite and talcschist embedding blocks of metagabbro, juxtaposes massive serpentinite with bodies of metagabbro, and syn-extensional metasediments (*i.e.*, calcschist with levels of mafic metasandstone and metabreccia) and metabasalt in its footwall and hanging wall, respectively (Balestro et al., 2015a). Both the BSZ and its footwall and hanging wall were unconformably sealed by Lower Cretaceous post-extensional metasediments (*i.e.*, calcschist with levels of marble and quartz schist). These tectono-stratigraphic relationships are now deformed by large-scale folding with a significant component of shearing, occurred during the long lived Alpine tectonic evolution of the MO, resulting from (i) the Late Cretaceous to Middle Eocene subduction, (ii) the Late Eocene-Early Oligocene collision and W-verging accretion, and (iii) the Late Oligocene to Neogene westward tilting driven by deep crust/mantle indentation (Balestro et al., 2015b, and reference therein). Our findings show that the Alpine-related deformation and final MO architecture were strongly controlled by the characteristics of the inherited tectono-sedimentary architecture such as (i) lateral and vertical variations of facies and thickness of metasediments, (ii) intra-oceanic fault-rock assemblage, which acted later as weak horizons in concentrating deformation, and (iii) occurrence of remnants of a volcanic ridge segment. Our results show that the recognition of the tectono-stratigraphic architecture of the pre-collisional (Jurassic) geodynamic setting represents an important step in better reconstructing the tectonic evolution of meta-ophiolite units in orogenic belts.

Balestro, G., Festa, A., Dilek, Y., Tartarotti, P. (2015a): Pre-Alpine extensional tectonics of a peridotite-localized oceanic core complex in the late Jurassic, high-pressure Monviso ophiolite (Western Alps). Episodes, 38, 266-282.

Balestro, G., Festa, A., Tartarotti, P. (2015b): Tectonic significance of different block-in matrix structures in exhumed converget plate margins: examples from oceanic and continental HP rocks in Inner Western Alps (northwest Italy). Int. Geol. Rev., 57, 581-605.

Festa, A., Balestro, G., Dilek, Y., Tartarotti, P. (2015): A Jurassic oceanic core complex in the high-pressure Monviso ophiolite (western Alps, NW Italy). Lithosphere, 7, 646-652.

Multi-stage melt-rock interactions in the Monte Maggiore peridotitic body: textural, structural, and chemical evolution from peridotite to hybrid troctolite

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Keywords: dunite, troctolite, melt-rock interaction, olivine trace elements.

Many recent studies investigate the formation of hybrid troctolites after melt-rock interactions and impregnation of a dunitic matrix (Sanfilippo et al., 2015). They infer the reactive percolation of a melt in a dunite, dissolving olivine and crystallizing interstitial plagioclase ± clinopyroxene, leading to the dismembering of mantle olivines and variations in the olivine crystal number, size and shape. Although being often invoked, such an hybrid origin of troctolites is however rarely documented in a field-controlled geological setting allowing the observation of a gradient of the amount of melt impregnation in mantle dunites. In this study, we combined EBSD analysis and *in situ* mineral geochemistry on the Monte Maggiore (Corsica, France) peridotites and associated dunites and troctolites. This peridotitic body preserves a multi-stage melt-rock reaction decompressional evolution (Rampone et al*., 2008*), marked by a first olivine-crystallizing, pyroxene-dissolving reactive percolation at spinel-facies, leading to the formation of replacive spinel dunite. A second diffuse melt impregnation in the spinel peridotites and dunites dissolved olivine and crystallized interstitial plagioclase + opx ± cpx at plagioclase-facies conditions. This increasing modal proportion in interstitial phases led to the replacive formation of plagioclase peridotites, plagioclase dunites and hybrid troctolites. These lithological variations allow investigation of the progressive structural and chemical evolution of the olivine matrix. A structural change of the olivine CPO is observed during the reactive melt percolation forming the dunites, from an axial-[100] CPO in the peridotites, to an axial-[010] CPO in the dunites and troctolites. These structural changes during dunitization are accompanied by *REE* enrichment in olivine. Geochemical modelling shows that changes in melt composition induced by the reactive percolation account for the observed variations in olivine *REE* composition from spinel peridotite to spinel dunite. EBSD analyses allowed to perform a textural quantification of the olivine matrix during the evolution from spinel dunite to hybrid troctolite. Melt impregnation ultimately leads to the disruption of coarse mantle olivines into smaller rounded grains. Accordingly, we observe a decrease in the Grain Surface, Shape Factor and Aspect Ratio of olivine grains with progressive impregnation. This study confirms the possible hybrid origin of troctolites associated to mantle peridotites, and shows that the textural, structural and chemical features observed in the troctolite are inherited from both the spinel- and plagioclase-facies melt-rock interaction stages.

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.

Sanfilippo, A., Morishita, T., Kumagai, H., Nakamura, K., Okino, K., Hara, K., Tamura, A., Arai, S. (2015): Hybrid troctolites from mid-ocean ridges: inherited mantle in the lower crust. Lithos, 232, 124-130.

Reactive melt migration controls the trace element budget of the lower oceanic crust: counterintuitive trace element compositions of minerals from the deepest portion of the Pineto gabbroic sequence (Corsica, France)

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Keywords: Pineto, ophiolite, melt-rock reaction, olivine-rich troctolites, troctolites, Corsica.

The Pineto gabbroic sequence is a ~1.5 km-thick lower crustal section formed in the Jurassic during the opening of the Liguria Piedmontese basin. This ophiolite is situated at the top of the Alpine Corsica and was essentially unaffected by the Alpine metamorphism. Previous structural and geochemical studies of the Pineto ophiolite document that it exposes a lower crustal section similar to those forming the gabbroic oceanic core complexes from Mid-Atlantic and the Southwest Indian Ridges. The Pineto sequence is subdivided into two portions displaying different bulk composition. The northern sector mostly consists of clinopyroxene-rich gabbros to gabbronorites, displaying a weak grain-size layering and in places crosscut by basalts dykes and amphibole veins. The southern portion exposes a deep lower crustal sequence mainly made up of troctolites, with minor olivine-gabbro and sparse olivine-rich troctolite intercalations.

Previous work indicated that reactive flow (melt migration and melt-rock reaction) was the major evolution process active in this southern portion, producing lithological variations classically attributed to fractional crystallization process (Sanfilippo et al., 2015). This study aims to verify the hypothesis that this melt-rock reaction process control the chemical budget of this lowermost sector of the Jurassic oceanic crust. We carried out a throughout characterization of the major and trace element whole rock and mineral compositions. Selected samples ranged from olivine-rich (Ol > 80 wt%) troctolites, to troctolites and olivine gabbros. We showed that the whole rock composition is mainly controlled by the modal abundance of the mineral phases, although the variability of some minor elements (*i.e.*, Cr) can also be relevant to define open-system crystallization. Despite the incompatible element compositions of the clinopyroxene cores from the different rock types are almost undistinguishable, important variability characterizes the trace element compositions of olivine and plagioclase. In particular, most incompatible elements (Ti, Zr, Y, *REE*) are higher in olivine and plagioclase from the (Ol-rich) troctolites compared to those in the Ol-gabbros, despite the latter has a more evolved whole rock composition and lower forsterite in olivine and anorthite in plagioclase. This chemical variability is counterintuitive and suggests that fractional crystallization cannot have constrained the composition of these rocks only by itself. This contribution discusses the processes that led to the distribution of trace elements among olivine, plagioclase and clinopyroxene suggesting that reactive melt migration is a major, if not the main, evolutionary process active in the deepest oceanic crust.

Sanfilippo, A., Tribuzio, R., Tiepolo, M., Berno, D. (2015): Reactive flow as dominant evolution process in the lowermost oceanic crust: evidence from olivine of the Pineto ophiolite (Corsica). Contrib. Mineral. Petrol., 170, 1-12.

Interaction between mantle peridotite and pyroxenite-derived melts: experimental investigations at 2 GPa

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Keywords: pyroxenite, peridotite, mantle heterogeneity, piston cylinder experiments, melt-rock reaction.

Melt-peridotite reaction is one of the most important process in modifying the mineralogy and chemistry of the upper mantle. Interaction between peridotites and pyroxenite (or eclogite)-derived melts at deep mantle level is thought to enhance mantle heterogeneity creating hybrid rocks, such as refertilized peridotites and secondary-type pyroxenites. Recent models have proposed that the resulting veined mantle likely represents the source of oceanic basalts (Mallik & Dasgupta, 2012; Lambart et al., 2012).

We are carrying out a series of piston cylinder experiments at 2 GPa and temperature ranging 1200-1400°C. We aim to investigate the role of melt composition, and the initial temperature of peridotite matrix (subsolidus *vs.* partial molten), in high-pressure melt-peridotite interaction charges. The compositions of starting reactive melts are selected among those produced in partial melting experiments on eclogite, eclogite-peridotite mixed source and a model secondary pyroxenite. They are let to react with a fertile lherzolite gel previously synthesized at the same pressure and temperature conditions.

A first set of experiments has been dedicated to the melting behavior at 2 GPa of the secondary pyroxenite PX-1 (Sobolev et al., 2007), in order to derive the composition of partial melts to be used in melt-rock reaction experiments. At 1300°C, low fraction of an andesitic melt coexists with orthopyroxene, clinopyroxene and garnet. At 1330°C, garnet is completely exhausted by melting reaction. At 1350°C, this pyroxenite encounters relatively high degree of melting (around 50 wt%) producing andesitic basalt in equilibrium with residual orthopyroxene.

Melt-rock reaction experiments have been performed by juxtaposing pyroxenite PX-1 on a pre-synthesized fertile lherzolite layer. At 1300°C, partially molten pyroxenite interacts with lherzolite producing an orthopyroxene-rich reaction zone at the pyroxenite-peridotite interface. X_{Mg} of pyroxenes decreases from 0.90 to 0.86 across the pyroxenite-peridotite boundary showing intermediate values in the orthopyroxene-rich zone (0.87-0.88). The pyroxenite layer does not contain residual garnet as found in the melting experiments, in which pyroxenes have lower X_{Mg} (0.84-0.85). This suggests an extensive Fe-Mg exchange with the lherzolite. Remarkably, in the lherzolite layer the spinel X_{Cr} value decreases toward the interface with molten pyroxenite, as observed in some natural pyroxenite-peridotite sequences.

Lambart, S., Laporte, D., Provost, A., Schiano, P. (2012): Fate of pyroxenite-derived melts in the peridotite mantle: thermodynamic and experimental constraints. J. Petrol., 53, 451-476.

Mallik, A. & Dasgupta, R. (2012): Reaction between MORB-eclogite derived melts and fertile peridotite and generation of ocean island basalts. Earth Planet Sci. Letters, 329-330, 97-108.

Sobolev, A.V., Hofmann, A.W., Kuzmin, D.V., Yaxley, G.M., Arndt, N.T., Chung, S.-L., Danyushevsky, L.V., Elliott, T., Frey, F.A., Garcia, M.O., Gurenko, A.A., Kamenetsky, V.S., Kerr, A.C., Krivolutskaya, N.A., Matvienkov, V.V., Nikogosian, I.K., Rocholl, A., Sigurdsson, I.A., Sushchevskaya, M.N., Teklay, M. (2007): The amount of recycled crust in sources of mantle-derived melts. Science, 316, 412-417.

The significance of the ultramafic rocks from the Sila unit, northern Calabria

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Keywords: Sila Unit, peridotite, melt-rock interaction.

Ultramafic rocks occur in the northern Calabria-Peloritani Arc. They can be interpreted as deepest portions of the Sila Unit that represent a continuous section of continental lithosphere. The main lithologies consist of serpentinites after peridotites and subordinate pyroxenites. Serpentinites formed after Amph-peridotites and have the mineral assemblage Ol + Opx ± Amph ± Spl. Pyroxenites are distinguished into: (i) tectonitic, and (ii) undeformed pyroxenites. The first occur as centimetric to metric layers deformed along the main mantle foliation and show porphyroclastic textures. The mineral assemblage is given by Opx ± Cpx ± Amph ± Ol ± Spl. Undeformed pyroxenites have medium grain size and occur as centimetric to decimetric dykes cutting the main mantle foliation. The mineral assemblage is given by Opx ± Cpx ± Amph ± Spl. The subsolidus evolution of the Sila Unit ultramafic rocks can be described by four main stages. Mineral assemblages in peridotites as well as temperatures estimated using the Opx-Cpx convetional geothermometer in tectonitic pyroxenites (*i.e.*, *ca*. 820°C) suggest a first equilibration in the Spl-lherzolite facies. The transition to the Amph-lherzolite facies is documented by crystallization of amphibole, spinel, and olivine at the expenses of pyroxenes. A third equilibration in the Chl-lherzolite facies (T < 770°C) is documented by formation of chlorite after spinel. Lastly, late serpentine veins suggest hydration at T < 500°C. This later event occurred during extensional tectonics. These features suggest gradual decompression and cooling of upper mantle rocks related to lithospheric thinning associated with Permo-Triassic gabbroic magmatism (Liberi et al., 2011). Gabbros can be observed either as concordant volumes at the crust-mantle rocks boundary or as centimetric to metric dykes within ultramafic rocks. Petrographic analyses allowed to identify melt-rock interaction textures in ultramafic rocks mainly related to gabbroic melts. Melt-rock interaction processes determined locally the transformation of amphibole-peridotites into hercynite-bearing peridotites as well as of tectonitic pyroxenites into websterites. Gabbroic magmatism occurred at $P \approx 0.55$ GPa (Liberi et al., 2011), while ultramafic rocks were equilibrating in the Amph-lherzolite facies. Therefore, ultramafic rocks in northern Calabria are fragments of subcontinental mantle mainly exhumed during the Permo-Triassic rifting responsible for the breakup of Pangaea, and they record subsolidus equilibration as well as evidences for melt-rock interaction processes.

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When recent discoveries from oceanic scientific drilling help to interpret the message of ophiolites, and conversely

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Keywords: ophiolites, oceanic litosphere, drilling projects.

Observations in ophiolites have been-and are still-fundamental for our understanding of the genesis of the oceanic lithosphere at oceanic spreading centers. Unfortunately, ophiolites have experienced a complex, and generally poorly understood polygenic history. As a consequence, the numerous structural, magmatic and alteration features present in ophiolites that do not fit the canonic "Penrose" model are frequently attributed to "late complexities" related, among others, to intra-oceanic thrusting and obduction on the continent rather than to oceanic spreading processes.

A few recent IODP (International Ocean Discovery Program) expeditions have successfully sampled by drilling significant sections of the lower oceanic crust in both fast and slow spreading ridge settings. This "ground truth" has triggered the emergence of new concepts about the way the oceanic spreading center factory actually works. More specifically, the classical scenario where igneous, tectonic and hydrothermal processes contribute in a sequential way to the construction, destruction and alteration of the oceanic crust are more and more superseded by scenarios where all these processes act together at the same place and at the same time. The resulting complex feedbacks lead to the generation of magma types and of their crystallization products whose existence was never envisioned in a spreading center setting. As a consequence, several petrological and geochemical "evidence" for a supra-subduction zone origin of ophiolites become obsolete. By the same way, it is now widely accepted that deformation and hydrothermal circulation operate at mid-ocean ridges in a much larger temperature range and at greater depths than previously expected and may contribute to the construction of new lithosphere, not only to its destruction and alteration.

The IODP cores bring a unique but, by nature, patchy set of information. Observations in ophiolites remain essential to widen the field of view, *i.e.*, to apprehend the spatial distribution and mutual relationships of lithologies and structures documented in a restricted amount of drill holes in the present-day oceans.

During this talk, I will give a few examples of tectonic, magmatic and hydrothermal features exposed in the Oman ophiolite that were previously attributed to post-accretion processes and that we should re-interpret in the light of recent IODP discoveries. Cross fertilization between the two approaches will, ideally, lead to some changes of paradigms concerning the mid-oceanic ridge factory.

Sr-He-O isotopes in mafic phenocrysts from products of the Neapolitan volcanoes (southern Italy): constraints on the geochemical features of the mantle sources

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Keywords: Neapolitan volcanoes, radiogenic and stable isotopes, fluid inclusion..

An investigation through Sr-He-O isotopes and major oxides was carried out on Mg-rich olivine and clinopyroxene phenocrysts from a selection of volcanic rocks of the Neapolitan Volcanoes (southern Italy), which include Somma-Vesuvius, Phlegraean Fields, and the islands of Ischia and Procida. The data produced in the present work extend the Sr-He-O dataset available for the Neapolitan volcanic districts (*e.g.*, Graham et al., 1993; Martelli et al., 2004; Di Renzo et al., 2011; D'Antonio et al., 2013; Iovine et al., 2017), improving the knowledge especially on helium isotopic compositions of the Mt. Somma rocks, never analysed before. $^3He/^4He$ ratios (2.60-5.12 R/RA) of the investigated Mg-rich phenocrysts are markedly lower than those measured at most volcanic arcs worldwide, and are among the lowest measured in subduction zones. This range of $^3He/^4He$ is coupled with quite large ranges of $^{87}Sr/^{86}Sr$ (0.704882 – 0.708480) and $\delta^{18}O$ (4.85 – 6.70‰) measured in the same mafic minerals. The $^3He/^4He$ values, and the lowest measured Sr- and O-isotope ratios, do not suggest significant crustal or fluid contamination occurred during magmatic evolution, and they should reflect the composition of the metasomatized mantle beneath the Neapolitan region. Moreover, these values display a clear geographic trend, with radiogenic ^4He-^{87}Sr, and ^{18}O generally increasing in on-lands districts. The results of these investigations are expected to allow us to better understand the original characteristics of the mantle source(s), and to define those of other components, likely originated in the continental crust, that were involved in the genesis of the primitive magmas feeding the Neapolitan volcanoes.

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Experimental constraints on the origin of olivine-rich troctolites by melt-rock reactions

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Keywords: melt-rock reactions, olivine-rich troctolite, reactive dissolution-recrystallization.

Studies on oceanic lithosphere suggest that melt-rock reactions play a key role in the origin of olivine-rich troctolites. We performed reactive dissolution and crystallization experiments in a piston-cylinder. Experimental charges consist of three layers: (1) basalt glass powder, (2) fine powder of San Carlos olivine (Fo_{90}) mixed with 9% of basalt, and (3) carbon spheres used as melt trap. We used 3 synthetic MORB-type glasses (X_{Mg} = Mg/(Mg+Fe) = 0.74, 0.62 and 0.58). Experiments have been conducted at 0.5 and 0.7 GPa, following an isobaric step-cooled temperature path from 1300 to 1150°C, to induce reactive dissolution of olivine and *in situ* crystallization of interstitial phases from the reacted melt. Isothermal time-solved experiments have been additionally performed at 0.5 GPa, 1300 and 1250°C, from 0.3 to 60 h. The effect of pressure and run time on melt-rock reaction are evaluated by textural observations (*i.e.*, grain size, shape factor, grain orientation), mineral chemistry, and phase abundance. At this purpose EMP analysis and EBSD mapping are used.

Step-cooled experiments show a layered lithological sequence from basal olivine-gabbro, to olivine-rich troctolite and dunite. Troctolite is the result of crystallization of reacted melts and show poikilitic textures, with plagioclase and clinopyroxene including both small rounded and euhedral olivines. Evidence of disequilibrium relations are testified by the occurrence of resorbed embayed olivines consistent with dissolution processes. Isothermal experiments consist entirely of olivine and glass with similar euhedral and resorbed olivine textures.

Mineral chemistry significantly varies along the experimental charge. Olivine ranges from Fo_{82} at the olivine-gabbro/olivine-rich troctolite interface to Fo_{90} in the olivine-rich troctolite layer. The same trend is observed in clinopyroxenes showing X_{Mg} increasing from 63 to 90. Fe-Mg partitioning between olivine and clinopyroxene is close to equilibrium. Plagioclase composition varies from An_{50} to An_{75} along the charge. As expected, large anorthite variations are coupled with rather constant forsterite values, deviating from fractional crystallization paths.

In the troctolite and dunite layers, higher abundance of interstitial phases are observed at lower pressure suggesting higher dissolution of olivine and therefore enhanced melt-olivine reaction. On the other hand, at higher pressure, early crystallization of interstitial reacted melts, due to stability of clinopyroxene and plagioclase at higher *T*, inhibits the reaction.

EBSD suggests a correlation of olivine textural parameters: an increase in grain misorientation (*i.e.*, of deformation) corresponds to an increase of shape factor suggesting that the most deformed olivines are more likely resorbed by reaction with the melt.

Experiments are texturally and chemically comparable with natural olivine troctolites reported as derived by melt-rock reactions, giving constraints on their origin.

The Cotoncello Shear Zone (Elba Island, Italy): the deep root of a fossil oceanic detachment fault in the Ligurian ophiolites

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Keywords: oceanic core complexes, slow-spreading ridge, brittle-plastic transition, northern Apennines ophiolites.

The ophiolite sequences in the western Elba Island are classically interpreted as a well-exposed ocean-floor section emplaced during the Apennines orogeny at the top of the tectonic nappe-stack (Decandia & Elter, 1972). Stratigraphic association along with petrographic and geochemical features indicate that these ophiolite sequences are remnants of slow- ultraslow spreading oceanic lithosphere analogous to the present-day Mid-Atlantic Ridge and Southwest Indian Ridge (Marroni & Pandolfi, 2007; Sanfilippo & Tribuzio, 2011).

Within the oceanward section of Tethyan lithosphere exposed in the Elba Island, we investigated for the first time a decameter-thick structure, the Cotoncello Shear Zone (CSZ) that records high-temperature ductile deformation analogous to what documented in the modern Kane OCC, in the Mid-Atlantic Ridge (MAR) by Hansen et al. (2013). We used a multidisciplinary approach to document the tectono-metamorphic evolution of the shear zone and zircon U-Pb ages to date the emplacement of a plagiogranite vein. Our results indicate that the CSZ rooted below the brittle-ductile transition at temperature above 800°C. An high-temperature ductile fabric was overprinted by fabrics recorded during progressive exhumation up to shallower levels under temperature < 500°C. We suggest that the CSZ may represent the deep root of a detachment fault that accomplished exhumation of an ancient oceanic core complex (OCC) in between two stages of magmatic accretion.

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The obduction process: what extent? What timing? What cause(s)? The study of the northern branch of Neotethys in Anatolia and the Lesser Caucasus (Turkey and Armenia)

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Keywords: obduction, ophiolites, Lesser Caucasus, NE Anatolia, numerical modelling, thermal rejuvenation, mantle thinning.

Worldwide within mountain ranges the presence of slivers of preserved oceanic lithosphere known as ophiolites evidence a tectonic process responsible for their emplacement on top of the continental crust called obduction. The first order anomaly inherent to this phenomenon is that dense rocks ($\rho > 3$ g/cm^3) end up on top of less dense rocks ($\rho \approx 2.7$ g/cm^3). The driving forces responsible and consequent/accompanying processes for such a tectonic oddity remain uncertain. The ophiolites of the Lesser Caucasus and NE Anatolia are prime examples of this phenomenon with tectonic transport (> 150 km) of fragments of oceanic lithosphere towards the south on top of the South Armenian Block-Taurude-Anatolide Platform along the entire continental marge (> 1000 km). The multidisciplinary approach used throughout the study of these ophiolites yielded clues specifying the evolution of the northern Neotethys Ocean before and around the time of ophiolite emplacement (90 Ma), consequently the obduction event. Our findings strongly suggest common emplacement of all the ophiolites of the study area as a thrust sheet of Middle Jurassic oceanic lithosphere, 70~80 Ma old at obduction onset. This would be one of the biggest preserved ophiolite nappe complexes in the world (outcropping in a mountain range).

Numerical modelling validated, firstly, the hypothesis that emplacement of such an ophiolitic nappe is due to particular thermal conditions. For old oceanic lithosphere to obduct it needs to be in a thermal state close to that of young oceanic lithosphere (0-40 km thick). Secondly, numerical modelling showed that the progression of obduction over a great distance and current position of the ophiolites far over the continental margin could be explained by post-compression extension. This switch in tectonic regime is responsible for the thinning of the ophiolitic nappe, underplating of underthrusted continental lithosphere and exhumation of continental crust.

Thermal rejuvenation is supposed for the ophiolites of the Caucasus *s.l.* argued by alkaline lavas emplaced on the sea floor prior to the obduction event during the Late Cretaceous (117 Ma). The resulting seamounts and/or oceanic plateaus of this magmatism would then have blocked the north-dipping subduction zone father north under Eurasia upon their entree and this until the end of the obduction event. The obduction event on the South Armenian Block-Taurude-Anatolide Platform is synchronous with the gap in volcanic activity along the Eurasian margin. Reactivation of the north-dipping subduction zone under Eurasia is compatible with traction on the obducted oceanic lithosphere responsible for its mantle thinning, continental lithospheric underplating and continental crust exhumation. Thus the propagation of thin obductions according to the 'flake tectonics' concept over an eclogite-free underthrusted continental margin can result from a combination of reheating of the oceanic lithosphere and far-field plate kinematics.

The oceanic units of the Sorkhband area (north Makran, Iran): evidence of an association of MORB and SSZ ophiolites at the top of the Coloured Mélange Complex

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Keywords: ophiolite, gabbro, harzburgite, geochemistry, Sorkhband, Makran, Iran.

In the Makran region (SE Iran) one of the largest worldwide accretionary wedges is exposed. This E-W trending accretionary wedge resulted since the Eocene from the northward subduction of the oceanic lithosphere of the Oman Sea beneath the Lut and Afghan continental blocks (*e.g.*, Burg et al., 2013). The backstop of this accretionary wedge consists of a pre-Eocene imbricate stack of continental and oceanic units, referred as to the North Makran domain. Among them, two slices of ophiolites located at the top of the Coloured Mélange Complex and at the base the Bajgan Complex have been identified in the Sorkhband area (Delavari et al., 2016). The upper tectonic slice consists of gabbros, whereas the lower tectonic slice consists of mantle peridotites associated with dunites and chromitite ore deposits.

Petrography and geochemistry of gabbros clearly indicate an N-MORB type affinity suggesting that they were generated at mid-ocean ridge setting. Their chondrite-normalized *REE* patterns indeed show the typical N-MORB trend with flat medium *MREE*-*HREE* coupled with *LREE* depletion (La_N/Yb_N = 0.44-0.62). Consistently with petrographic analyses, they display Eu positive anomalies, which is consistent with early crystallization of plagioclase.

Mantle peridotites consist of harzburgites and depleted harzburgites, both showing marked depletion in incompatible elements and *REE*. Harzburgites are characterized by severe depletion in *LREE* compared to *MREE* and *HREE*. In contrast, depleted harzburgites show comparatively lower absolute concentrations of *HREE* and *LREE*/*MREE* enrichment (*i.e.*, U-shaped *REE* patterns). Both major element and *REE* compositions are compatible with the compositions of mantle residua after high degrees (>20%) of partial melting of a depleted mantle source. The *REE* composition of depleted harzburgites is compatibile with the composition of mantle residua after boninitic melt extraction. Moreover, the *LREE*/*MREE* enrichment observed in the depleted harzburgites can be explained by mantle metasomatism by slab-derived fluids in SSZ setting following an earlier depletion event. All these features point out for a genesis in a SSZ setting.

These new data indicate that the slices of ophiolites from Sorkhband area derived from two different oceanic tectonic settings. This occurrence provides new evidence that the boundary between the Coloured Mélange and the Bajgan Complexes represents a first-order tectonic structure that played an important role in the geodynamic evolution of the Makran area.

Burg, J.-P., Dolati, A., Bernoulli, D., Smit, J. (2013): Structural style of the Makran tertiary accretionary complex in SE Iran. In: "Litosphere Dynamics and Sedimentary Basins: The Arabian Plate and Analogues", K. Al Hosani, F. Roure, R. Ellison & S. Lokier, eds..Springer, Berlin-Heidelberg, 239-259.

Delavari, M., Dolati, A., Marroni, M., Pandolfi, L., Saccani, E. (2016): Association of MORB and SSZ ophiolites along the shear zone between Coloured Mélange and Bajgan Complexes (North Makran, Iran): evidence from the Sorkhband area. Ofioliti, 41, 21-34.

The Matchless Amphibolite of the Damara Belt, Namibia: peculiar preservation of a Late Neoproterozoic ophiolitic suture

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Keywords: ophiolitic suture, ridge subduction, Damara Belt, Namibia.

As for younger, Meso-Cenozoic belts, the evolution of Proterozoic-Paleozoic supercontinents during their assembly and amalgamation can be punctuated by events of accretion of slivers of ophiolitic sequences, but they are less reported in literature and the geodynamic processes responsible for ophiolite emplacement less understood.

The Pan-African Kaoko, Damara and Gariep belts of southwestern Africa are well-studied Paleozoic complexes, for which have been proposed a tectonic and geodynamic evolution in terms of subduction tectonics during the assembly of the Gondwana supercontinent. The Damara belt of Namibia preserves a sliver of meta-ophiolitic sequence, referred to as the Matchless Amphibolite and with MORB geochemistry, considered by most authors as representative of the ophiolitic suture related to the closure of an oceanic basin located between the Congo and Kalahari cratons. The Matchless Amphibolite crop out as a narrow, 500-3000 m wide system of imbricate tectonic slivers that can be followed along the belt strike for > 300 km.

We have measured two traverses across the Matchless Amphibolite and we report here the evidence that these ophiolitic slivers emplaced during ridge-trench interaction and ridge subduction. We discuss the potential circumstances and/or characteristics of the Khomas oceanic basin that allowed preservation of such an old ridge-trench encounter into an ophiolitic suture.

Multiple events of melt-rock interaction recorded by undeformed spinel pyroxenites from the External Ligurian ophiolites

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Keywords: mantle, ophiolite, pyroxenite, Apennine, Os isotopes.

The External Ligurian mantle sequences are interpreted as deep subcontinental lithosphere exhumed to the ocean floor in response to Mesozoic lithospheric thinning and opening of the Jurassic Ligurian-Piedmontese basin. The sequences consist of spinel-plagioclase lherzolites with diffuse pyroxenite layers which have been related to recycling of crustal material (Montanini et al., 2012) or to eclogite-bearing peridotite sources (Borghini et al., 2016). The mantle lherzolite body considered in the present study (Monte Gavi) includes an undeformed, irregularly shaped body of spinel pyroxenites. This body has a thickness of 6-10 m, a length of about 50 m and encloses several meter-sized lherzolite lenses. Close to the main pyroxenite body, the host lherzolite frequently includes up to 10 cm thick spinel pyroxenite layers.

The pyroxenites are coarse-grained and consist of clinopyroxene- and Al-spinel-rich domains. Clinopyroxene is resorbed, variably replaced by orthopyroxene + plagioclase aggregates, and locally rimmed by titanian pargasite. Spinel-rich domains are largely transformed into Ca-rich plagioclase + Fe-rich olivine + Cr-spinel ± ilmenite. Clinopyroxene locally has relatively low Mg# (≈ 83) and Cr_2O_3 (≤ 0.3 wt%), and up to 10 wt% Al_2O_3 and 1.8 wt% Na_2O. The thin pyroxenite layers are characterized by Mg-rich clinopyroxene (Mg# = 0.89-0.90) and in places include forsterite-rich deformed olivine, which is interpreted to be a relic of the host lherzolite. The Fe-rich pyroxenites have basaltic, “melt-like” patterns of highly siderophile elements (HSE), whereas the Mg-rich pyroxenites are significantly enriched in Os and Ir. Bulk rock $^{187}Os/^{188}Os$ ratios recalculated for the age of the Ligurian-Piedmontese basin opening (165 Ma) vary from slightly to moderately radiogenic (0.185-0.518). We propose that the pyroxenites formed by crystallization of Al-rich melts derived by an aged pyroxenite/eclogite-rich source. In this view, the thick pyroxenite body represents a melt-dominated system, whereas the thin pyroxenite layers are hybrid rocks derived from melt/peridotite reactions. Resorption and extensive replacement of the primary clinopyroxene-spinel assemblage was most likely related to reactive migration of ultra-depleted melts under plagioclase facies conditions, during exhumation of the mantle sequence. The host lherzolites also show textural, mineralogical and geochemical evidence of melt infiltration and crystallization of plagioclase + orthopyroxene at the expense of spinel and clinopyroxene.

Borghini, G., Rampone, E., Zanetti, A., Class, C., Cipriani, A., Hofmann, A.W. (2016): Pyroxenite layers in the Northern Apennines upper mantle (Italy)-Generation by pyroxenite melting and melt infiltration. J. Petrol., 57, 625-653.

Montanini, A., Tribuzio, R., Thirlwall, M. (2012): Garnet clinopyroxenite layers from the mantle sequences of theNorthern Apennine ophiolites (Italy): Evidence for recycling of crustal material. Earth Planet. Sci. Letters, 351-352, 171-181.

The Intra-Pontide suture zone in the Tosya-Kastamonu area, northern Turkey: geological map at 1:50,000 scale

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Keywords: metamorphic units, Intra-Pontide suture zone, Tosya-Kastamonu area, northern Turkey.

The Intra-Pontide suture zone is the northernmost ophiolite-bearing suture zone of Turkey, stretching with an east–west trend more than 400 km from northwest to central Turkey. It testifies to the presence of an oceanic basin, the Intra-Pontide Oceanic basin, located between the Istanbul-Zonguldak terrane and the Sakarya composite terrane from the Middle Triassic to the Late Paleocene. The convergence processes that led the closure of the Intra-Pontide Oceanic basin started in the Middle Jurassic and continued until the complete closure of the oceanic domain in the Late Paleocene with the building of the nappe stack.

We present the first detailed geological map of the tectonic units documented in the easternmost branch of the Intra-Pontide suture zone in the Tosya-Kastamonu area (northern Turkey). The Main Map is at 1:50,000 scale and covers an area of about 350 km^2. It derived from 1:25,000 scale classic field mapping and represents a detailed overview of the complexities documented in the Intra-Pontide suture zone, a tectonic nappe stack originating from the closure of the Intra-Pontide Oceanic basin and the subsequent collision between the Istanbul-Zonguldak terrane and the Sakarya composite terrane. The map shows the orientations of superposed foliations, fold axes and mineral lineations on the basis of geometric cross-cutting relationships documented within the five tectonic units of the Intra-Pontide suture zone and provides information on its present-day architecture resulting from activity of the North Anatolian Fault.
More info in Frassi et al. (2016).

Frassi, C., Göncüoğlu, M.C., Marroni, M., Pandolfi, L., Ruffini, L., Ellero, A., Ottria. G., Sayit, K. (2016): The Intra-Pontide Suture Zone in the Tosya-Kastamonu area, Northern Turkey. J. Maps*,* DOI: 10.1080/17445647.2016.1192330.

Transition from oceanic subduction to continent collision tectonics in the Neo-Tethys: constraints from the Tuting ophiolite, Arunachal Himalaya, India

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Keywords: Neo-Tethys, ITSZ, Tuting ophiolite, subduction, collision.

One of the critical aspects of India-Asia convergence is the recognition that the nature of tectonics evolved from initial oceanic subduction in Late Jurassic to Early Cretaceous through Early Eocene continental subduction to finally Oligocene-Miocene continental collisions. Whereas the last two processes are recorded in the leading edge of the Indian continental lithosphere, signatures of oceanic subduction and closure of the Neo-Tethys are decoded from the ophiolite suite of rocks, exposed all along the Indus-Tsangpo Suture zone (ITSZ) from Nanga Parbat in the west through Namche Barwa in the east to Indo-Burmese ranges in the south-east. Petrological support for direct oceanic convergence and subduction channel dynamics in the ITSZ is, however, rather meagre, because of lack of continuous exposures of high-pressure/low-temperature metamorphic rocks and paleo-accretionary complexes, exceptions include the sporadic occurrences of lawsonite and epidote blueschists, eclogites and high pressure amphibolites in Shangla, Sapi-Shergol, Zildat in the western sector of the ITSZ, Xigaze and Saga in the central sector and Nagaland in the Indo-Burmese ranges.

Seen in this backdrop, thin, dismembered, mafic to ultramafic rock associations of presumably ITSZ ophiolite affinity occur in several areas of the Eastern Himalayan syntaxis. In the absence of detailed metamorphic investigations, it is, however, not clear whether these rocks were metamorphosed during continental collisions or record signatures of a pre-collision, oceanic subduction tectonics. In this work, we address this issue using metabasic rocks of the Tuting ophiolite, Arunachal Pradesh, India, which is exposed in the northern margin of the Siang dome at the southern extension of the Namche Barwa dome. Using integrated textural, mineral chemical, metamorphic reaction history and bulk geochemical studies, we establish (a) a general suprasubduction zone setting origin for the protoliths of the metabasites and (b) prograde greenschist to epidote amphibolite facies metamorphism along a medium-pressure/medium-temperature metamorphic field gradient, consistent with classical continent-continent collisional orogeny. The results demonstrate that the Tuting metabasic rocks are genetically linked with the ophiolites of the ITSZ and provide critical new insight into the changing dynamics during India-Asia convergence as the Neo-Tethyan subduction system at the northern margin of the Indian plate evolved into a continental collision setting.

Timing and interplay between melt infiltration and deformation in the External Liguride mantle (Italy)

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Keywords: melt-peridotite interaction, pyroxenite, EBSD analyses.

Mantle lherzolites in the eastern External Liguride ophiolites (northern Apennines) contain cm-thick pyroxenite layers that originated by deep (P > 1.5 GPa) infiltration of MORB-type melts (Borghini et al., 2016). Host peridotites locally display compositional banding (harzburgite and dunite) parallel to pyroxenite layers, and the whole layering is parallel to a well developed foliation. In a previous study (Borghini et al., 2013), we showed that geochemical gradients are nicely preserved across the pyroxenite-peridotite contact, and the host peridotites have been chemically and isotopically modified by reaction with pyroxenite-derived melts. Here we investigate the timing and interplay between melt-infiltration, melt-rock reaction and deformation, by combining *in situ* mineral geochemistry with EBSD observations. Along the pyroxenite-peridotite traverses, clinopyroxenes record systematic trace element variations, consistent with reactive porous flow at decreasing melt mass. EBSD analyses on the same peridotite-pyroxenite profiles revealed well developed CPO of olivine, orthopyroxene and clinopyroxene, consistent with deformation by dislocation glide at moderate temperature. In the whole mantle sequence, partial reequilibration at plagioclase-facies conditions (dated at 178 ± 8 Ma; Borghini et al., 2016) is documented by the crystallization of plagioclase-bearing granoblastic aggregates. Plagioclase is of metamorphic origin, being confined to the more fertile lithologies (pyroxenite and lherzolite) and absent in dunite and harzburgite. It shows a very weak CPO, consistent with postkinematic formation. The combined evidence of preserved geochemical gradient across the pyroxenite-peridotite boundaries, and developed CPO in spinel-facies minerals, is best explained by a synkinematic formation of pyroxenites. This is also suggested by the CPO oblique to the foliation, observed in clinopyroxene porphyroclasts of pyroxenites, consistent with crystallization in a simple-shear regime. The weak CPO in plagioclase further points that most deformation occurred at spinel facies. In addition, (pyroxene, spinel)-rich domains in the host peridotites (not observed in peridotites free from pyroxenite layers) indicate that small amounts of melts were present in the peridotites during their deformation, corroborating the synkinematic origin of pyroxenites. Sm-Nd isotopic investigations (Borghini et al., 2016), confirmed by recent Lu-Hf data, yielded Palaeozoic ages of pyroxenite emplacement. Overall, the pyroxenite-peridotite sequence here investigated provides evidence of an old Ordovician tectonic and magmatic evolution, still recorded in the exhumed subcontinental mantle of the Jurassic Tethyan oceanic lithosphere.

Borghini, G., Rampone, E., Zanetti, A., Class, C., Cipriani, A., Hofmann, A.W., Goldstein, S. (2013): Meter-scale Nd isotopic heterogeneity in pyroxenite-bearing Ligurian peridotites encompasses global-scale upper mantle variability. Geology, 41, 1055-1058.

Borghini, G., Rampone, E., Zanetti, A., Class, C., Cipriani, A., Hofmann, A.W., Goldstein, S. (2016): Pyroxenite layers in the Northern Apennines' Upper Mantle (Italy)-Generation by pyroxenite melting and melt infiltration. J. Petrol., 57, 625-653.

Dating of ultramafic rocks from the western Alps ophiolites discloses Late Cretaceous subduction ages in the Zermatt-Saas Zone

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Keywords: serpentinites, subduction metamorphism, microstructural analysis, U-Pb dating, Tethys opening.

Regional- to micro-scale structural analysis has been applied to Zermatt-Saas Zone (ZSZ) serpentinites to explore their tectonic history by means of *PT*Dt path reconstruction. ZSZ is a slice of oceanic lithosphere tectonically sampled from the Tethyan realm, characterized by a dominant *HP*-*UHP* metamorphic imprint, locally overprinted by greenschist facies metamorphism. Ages of oceanic protolith vary between 164 and 153 Ma. The Alpine metamorphic peak recorded during subduction is constrained between 50 and 39 Ma. Serpentinites and rodingites in the upper Valtournanche are dominated by a regional S2 foliation mapped with spatial continuity (Rebay et al., 2012; Zanoni et al., 2016). *HP* mineral assemblages underlining S2 indicate that physical conditions of Alpine metamorphism reached 2.5 ± 0.3 GPa and 600 ± 20°C (Rebay et al., 2012). Locally, in serpentinites clinopyroxene-I and zircon-I porphyroclasts are wrapped by S2 foliation and fringes and/or new grains of clinopyroxene-II and zircon-II define S2. New clinopyroxene-II fringes have compositions similar to those of new clinopyroxene grains marking S2. Trace element composition of clinopyroxene crystals is consistent with a crystallisation from a melt in equilibrium with plagioclase as it occurs in gabbroic percolation of oceanic mantle. Microstructures similar to those observed in clinopyroxenes characterise zircons. Under cathodoluminescence, zircon cores show sector zonings typical of magmatic growth. U-Pb data suggest that zircon cores crystallised during Middle Jurassic. The thin fringes overgrowing magmatic cores are parallel to the S2 foliation and U-Pb concordant analyses on these domains reveal an Upper Cretaceous blastesis age. These dates are interpreted as the ages of *HP* to *UHP* Alpine re-equilibration. These results allow widening the time span under which rocks of ZSZ recorded *P*-peak, and suggest that different portions of ZSZ reached the deepest part of the subduction system diachronically. Therefore, some sections of the ZSZ have likely experienced *HP* to *UHP* metamorphism earlier than previously thought. The obtained ages are comparable to those already described for the *HP* re-equilibration in the subducted continental crust of the Sesia-Lanzo Zone (SLZ) and this finding goes along with the cold thermal regime under which the SLZ was exhumed, which is compatible with on-going oceanic subduction.

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Zanoni, D., Rebay, G., Spalla, M.I. (2016): Ocean floor and subduction record in the Zermatt-Saas rodingites, Valtournanche, Western Alps. J. Metamorph. Geol., 34, 941-961.

Incompatible elements and Nd isotope signature of MORB generated beneath the Jurassic Liguria-Piedmont basin: inferences on mantle sources and melting processes

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Keywords: Jurassic ophiolites, basalt-sedimentary successions, Nd isotopes, whole rock and clinopyroxene trace element compositions.

The Bracco-Levanto (eastern Liguria) and Balagne (central-northern Corsica) ophiolites represent an oceanward and a continent-near paleogeographic domain of the Jurassic (ultra-)slow spreading ocean called Liguria-Piedmont basin. These ophiolites include thick basalt lava sequences associated with Middle-Upper Jurassic sediments, mainly ophiolitic breccias and radiolarian cherts (*e.g.*, Marroni & Pandolfi, 2007). In addition, the basalts in the Balagne ophiolite contain in places levels made up of quartzo-feldspathic clastic sediments derived from Permian continental material (see also Renna et al., 2017).

A geochemical study of massive basalt lava lenses occurring at different stratigraphic heights of the Bracco-Levanto and Balagne ophiolites has been carried out. Whole-rock analyses revealed that the Balagne basalts are slightly enriched in TiO_2, *LREE*, Nb and Ta with respect to the Ligurian counterparts. These variations are paralleled by clinopyroxene chemistry. In particular, the clinopyroxene from the Balagne basalts has higher TiO_2, Ce_N/Sm_N and Zr_N/Y_N compared to that from the Bracco-Levanto basalts. The basalts from the two ophiolites have homogeneous initial Nd isotopic compositions, within typical depleted mantle values, thereby excluding an origin from a lithospheric mantle source. These data also reject the involvement of contaminant crustal material, as associated clastic sediments and radiolarian cherts have a highly radiogenic Nd isotopic fingerprint.

Two major petrogenetic hypotheses may be formulated to explain the decoupling between incompatible elements and Nd isotopic signature of the Bracco-Levanto and Balagne basalt sequences. In the first, the different incompatible element signatures are related to different partial melting degrees of a compositionally homogeneous, depleted mantle source. The second hypothesis implies that the Balagne basalts formed by mantle sources with a relatively high proportion of a garnet-bearing enriched component. Following this hypothesis, mixing of primary melts efficiently homogenized the Nd isotopic compositions of the mantle sources, whereas heterogeneities in incompatible element ratios were at least partly preserved.

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Renna, M.R., Tribuzio, R., Sanfilippo, A., Tiepolo, M. (2017): Zircon U-Pb geochronology of lower crust and quartzo-feldspathic clastic sediments from the Balagne ophiolite (Corsica). Swiss J. Geosci., in press, DOI 10.1007/s00015-016-0239-y.

Oceanic and subduction ophicarbonates in the Champorcher Zermatt-Saas ophiolite (Aosta Valley, northwestern Alps)

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Keywords: Zermatt-Saas ophiolite, serpentinite, subduction, ophicarbonate, aqueous carbonic fluids.

The eclogite-facies Zermatt-Saas ophiolite comprises serpentinized peridotites with gabbro intrusions and minor metabasalts, covered by meta-quartzite, marble, and calcschist. In the study area this sequence includes a 50 m thick composite chaotic unit (CCU) interposed between serpentinite and calcschist; its block-in-matrix fabric has been interpreted as a record of mass transport processes occurred in the Jurassic Ligurian-Piedmont Ocean (Tartarotti et al., 2017). The CCU consists of four subunits of clast- to matrix-supported breccias. Clasts are pebbles to large blocks of serpentinite and ophicalcite, the matrix is mostly carbonatic. The ophicarbonate occurrence indicates interaction of ultramafic rocks with COH fluids, which partly took place near the seafloor of the Jurassic ocean, like in modern slow-spreading oceans. The CCU structural and petrographic features attest for a long-lived fluid-assisted evolution, from the oceanic stage to the Alpine subduction and exhumation. Clasts show complex metasomatic boundaries against the surrounding matrix: serpentine in clasts is overgrown by carbonate minerals (carbonation), while carbonatic matrix is replaced by tremolite + diopside (decarbonation). Carbonates also fill veins (pure carbonate and dolomite ± diopside ± chlorite) cutting the serpentinite blocks. The above evidences strongly suggest carbon mobility in fluids during subduction of the CCU, in particular a combined effect of C release by the matrix to COH fluids (highly reactive with ultramafic rocks) which led to serpentinite carbonation, as envisaged for other alpine settings (Scambelluri et al., 2016; Piccoli et al., 2016). From a geochemical point of view, the $\delta^{13}C$ isotopic signatures of the CCU range between -1 and +3‰, which is compatible with an oceanic origin, whereas the $\delta^{18}O$ isotopic composition varies within the different subunits. Ophicarbonates representative of the oceanic stage show oxygen isotopic values of +14/+16‰, whereas samples affected by subduction processes show a decrease of $\delta^{18}O$ down to +12/+13‰, suggesting an interaction with external metamorphic fluids at relative high temperature. The Champorcher complex thus displays both oceanic and subduction ophicarbonates.

Piccoli, F., Vitale Brovarone, A., Beyssac, O., Martinez, I., Ague J.J., Chaduteau, C. (2016): Carbonation by carbon cycling in subduction zones. Earth Planet. Sci. Letters, 445, 146-159.

Scambelluri, M., Bebout, G.E., Belmonte, D., Gilio, M., Campomenosi, N., Collins, N., Crispini, L. (2016): Carbonation of subduction-zone serpentinite (high-pressure ophicarbonate; Ligurian Western Alps) and implications for the deep carbon cycling. Earth Planet. Sci. Letters, 441, 155-166.

Tartarotti, P., Festa, A., Benciolini, L., Balestro, G. (2017): Record of Jurassic mass transport processes through the orogenic cycle: Understanding chaotic rock units in the high-pressure Zermatt-Saas ophiolite (Western Alps). Lithosphere, 1, L605.1.

Melt-rock reactions in the mantle peridotites from Tuscany ophiolites

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Keywords: peridotite, ophiolite, MORB, melt-rock reaction.

Here we present mineralogical and geochemical data on mantle peridotites from the "Monti Rognosi" Jurassic ophiolite from southern Tuscany. The ophiolites are included in Cretaceous-Eocene flysch formations and are mainly composed of serpentinitized peridotites containing small gabbroic bodies. Locally the serpentinites preserve lenses of relatively fresh mantle assemblages.

The samples selected for the present study are clinopyroxene-poor porphyroclastic lherzolites (Cpx = 5-7 vol%). The clinopyroxene mainly occurs as large exsolved porphyroclasts, frequently corroded most likely in response to reaction with a melt that crystallised thin gabbroic (Pl+Opx) veins and patches. The orthopyroxene occurs as large deformed porphyroclasts characterized by undulose extinction and irregular outlines. Olivine typically forms corrosion loops on orthopyroxene. Small amount of dark brown Cr-rich spinel with irregular shapes are generally rimmed by plagioclase.

Olivine has forsterite contents between 88.7-89.6 mol%. The cores of (exsolved) orthopyroxene porphyroclasts have Al_2O_3 and CaO contents up to 2.6 and 1.6 wt% respectively. Neoblasts have lower Al_2O_3 and CaO contents. Ca-in-Opx thermometry (Brey & Kohler, 1990) provides *T* of 1070 ± 50°C and 960 ± 40°C for the porphyoclastic and neoblastic Opx, respectively. The clinopyroxene (Mg# 88-90) has relatively high Al_2O_3 (about 7 wt%), TiO_2 (0.5-0.8 wt%) and Na_2O (0.2-0.5 wt%) contents. Plagioclase is highly calcic (An = 81-90 mol%). Mg# and Cr# composition of olivine and spinel plot off the mantle array. The highest Cr# values of the spinel (43-46) are associated with high TiO_2 contents (0.5-0.8 wt%). Similar chemical variations are commonly observed in plagioclase peridotites that experienced by melt/rock reactions.

Major element whole-rock compositions depart from the trends of residual peridotites, being characterized by higher Al_2O_3 and FeO_{tot}, and lower CaO and SiO_2. Hence, these chemical compositions are not compatible with products of simple partial melting. Bulk rock *REE* compositions apparently record small degrees (2-4%) of fractional melting in the spinel stability field, thereby arguing against clinopyroxene compositions. In fact, clinopyroxenes show a wide *REE* heterogeneity, ranging from markedly to slightly *LREE*-depleted (Ce_N/Sm_N = 0.02-0.40), with nearly flat and variable *HREE* contents (Yb_N = 10-22). We propose that the clinopyroxene compositional variations were related to infiltration and impregnation of the Monti Rognosi residual peridotites by a MORB-type (Opx-saturated) melt in the plagioclase-stability field.

Brey, G.P. & Köhler, T. (1990): Geothermobarometry in four-phase lherzolites II. New thermobarometers, and practical assessment of existing thermobarometers. J. Petrol., 31, 1353-1378

Time-progressive mantle – melt evolution and magma production in the eastern Mediterranean Tethys: a case study of the Albanide-Hellenide ophiolites

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Keywords: ophiolites, harzburgite, lherzolite, subduction initiation, Albanides, Hellenides.

We present a comprehensive overview of the melt evolution of the upper mantle peridotites and different lava types in the Jurassic Albanide-Hellenide ophiolites, based on new and extant geochemical data and trace element modelling. These ophiolites represent the remnants of the Tethyan oceanic lithosphere in the eastern Mediterranean area. Peridotites consist of lherzolites and harzburgites both showing spinel-facies mantle mineral phases, and are variably depleted displaying large compositional ranges. They show increased *LREE*/*MREE* enrichment patterns in parallel with increased whole rock depletion. The spatial-temporal relationships of volcanic rocks in the extrusive sequences indicate four discrete types with progressively younging ages: 1) High-Ti, N-MORB-like lavas (TiO_2 = 0.76–2.23 wt%); 2) Medium-Ti basalts (MTB) (TiO_2 = 0.67–1.09 wt%), strongly depleted in Th, Ta, and Nb; 3) Low-Ti, island arc tholeiitic (IAT) basalts (TiO_2 = 0.51–1.10 wt%), showing Th/Nb enrichment and *REE* depletion; and 4) Very low-Ti, boninitic rocks (TiO_2 = 0.12–0.35 wt%), displaying strong depletion in HFSE, Th/Nb enrichment, and U-shaped *REE* patterns. Our *REE* modelling, using non-modal batch partial melting for MORB and MTB type lavas and fractional melting for IAT and boninitic lavas, reveals that: a) the moderately depleted lherzolites represent N-MORB mantle residua produced by 10-20% partial melting of a depleted MORB-type mantle source. Melt extraction at this stage formed the high-Ti N-MORB lavas; b) In the very early stage of subduction, the residual lherzolite underwent 5-8% partial melting without any subduction influence (no *LREE* enrichment), producing the MTB magmas; c) following subduction initiation, these refractory lherzolites were enriched in *LREE* by subduction-derived fluids, and their partial melting (~10-20%) generated the IAT magmas; d) with continued subduction, the highly depleted harzburgites and cpx-poor lherzolites that were left after IAT melt extraction experienced significant *LREE* enrichment and underwent high degree (15-25%) partial melting under high temperature–high fluid flux conditions. Produced magmas formed the boninitic rocks. The residual mantle after boninitic melt extraction is represented by refractory harzburgites exposed in the eastern parts of the Albanide-Hellenide ophiolite belt. This progressive evolution of upper mantle peridotites and melt generation resulted in the coexistence in both time and space of production of different magma types such as MORBs and MTBs (in the west), and MORBs, IATs and boninites (in the east). In consequence, the apparent geochemical dualism (*i.e.*, MORB *vs.* supra-subduction zone affinities) observed in the Albanide-Hellenide ophiolites does not require separate tectonic settings of formation. We therefore suggest that the whole Albanide-Hellenide ophiolitic belt was formed in the same tectonic setting that is in a trench rollback system.

Geochemistry and tectono-magmatic significance of volcanic and subvolcanic rocks from Nain and Ashin ophiolites (central Iran)

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Keywords: ophiolite, pillow lava, sheeted dike, Nain, Ashin, central Iran, Cretaceous.

The Nain-Ashin ophiolites belong to so-called “Inner ophiolitic belt” of Iran, which consists of highly dismembered Mesozoic ophiolitic complexes bordering the central Iranian microplate (CIM). They therefore represent a key area for reconstructing the tectono-magmatic and geodynamic evolution of central Iran, which is still poorly known. The Nain-Ashin ophiolites are located in the westernmost edge of the CIM and both consist of ophiolitic mélanges. These mélanges mainly include mantle peridotites, though minor pillow lavas and sheeted dykes in Nain, and pillow lavas in Ashin can be found. In this contribution, we present new geochemical data on pillow lavas and sheeted dykes from these ophiolites with the aim of assessing the tectono-magmatic processes that characterized the western border of the CIM during Cretaceous times.

The studied volcanic rocks consist mainly of basalts and minor ferrobasalts and basaltic andesites, all showing a clear subalkaline nature (*e.g.*, Nb/Y = 0.03-0.21). Two samples from the Nain ophiolite are characterized by N-MORB normalized incompatible element patterns showing marked Th positive anomalies and Ta, Nb, Ti negative anomalies. Chondrite-normalized *REE* patterns show *LREE*/*HREE* (light *REE*/heavy *REE*) enrichment, with La_N/Yb_N = 3.2-4.3. These rocks are chemically similar to the calc-alkaline basalts (CAB), as also highlighted by many discrimination diagrams and are interpreted to have generated in a cordilleran-type volcanic arc setting.

All other samples from both the Nain and Ashin ophiolites display a wide range of chemical composition. However, the relatively less fractionated basalts are characterized by low TiO_2 (0.60-1.00 wt%), P_2O_5 (0.03-0.08 wt%), Zr (23-75 ppm) and Y (9-27) contents. Chromium (38-619 ppm) and Ni (22-220 ppm) contents show a wide range of variation. N-MORB normalized incompatible element patterns show rather flat trends and a general depletion (from 0.4 to 0.8 times N-MORB composition) coupled with a slight Th enrichment (1-3 times N-MORB). Chondrite-normalized *REE* patterns are generally flat and are characterized by either a slight depletion or a slight enrichment in *LREE* compared to *HREE* (La_N/Yb_N = 0.7-1.2). These overall chemical features resemble those of island arc tholeiites from many ophiolitic complexes. The depletion in incompatible elements compared to N-MORB suggests that these rocks were derived from partial melting of a depleted mantle source. Th enrichment with respect to Nb (Th_N/Nb_N = 2.6-12.4) suggests that mantle sources underwent enrichment in subduction-derived chemical components prior melting. Our data suggest that the Nain and Ashin ophiolites were formed in a subduction-related tectonic setting during the Late Cretaceous. The chemistry of the studied rocks is compatible with transition zone either from forearc to arc or from arc to backarc.

Igneous stratigraphy and lateral heterogeneity of a long *in situ* transect of the lower oceanic crust formed at the Atlantis Bank core complex (SW Indian Ridge): new results from IODP Expedition 360

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Keywords: gabbro, IODP, Atlantis Bank, oceanic crust.

International Ocean Discovery Program (IODP) Expedition 360 represents the first leg of a multi-phase drilling programme ("SloMo" project) aimed at investigating the nature of the lower crust and Moho at slow spreading ridges. As an initial phase, IODP Exp. 360 intended to recover a representative transect of the lower oceanic crust formed at Atlantis Bank, an oceanic core complex on the SW Indian Ridge. During this expedition, 89 cores of gabbroic rocks were recovered at Hole U1473A, drilled to 789.7 m below seafloor, subsequently deepened to 809.4 mbsf during transit Expedition 362T. The gabbroic section recovered at Hole U1473A consists of many gabbro variants dominated by olivine gabbro (76.5%), gabbro containing 1–2% oxide (9.5%), oxide-bearing gabbros (7.4% in abundance) and gabbro *sensu stricto* (5.1%). Felsic veins (1.5%) and diabase (<0.5%) were also recovered. Most of the gabbros show extensive high-temperature crystal-plastic deformation predating the intrusion of basaltic dikes. The different gabbroic lithologies appear randomly distributed throughout the section, although oxide gabbros seem to be more concentrated in the upper part of the section. Taken as a whole, the gabbroic section is characterized by meter-scale heterogeneity classically characterizing gabbros formed at slow spreading environments. Reaction textures in olivine gabbros and the occurrence of intrusive to sutured contacts between different rock-types indicate that the evolution of this section was controlled by the complicated interactions among fractional crystallization, melt-rock reactions and late-stage melt migration processes. This contribution describes the main features of these rocks and discusses the complexity of the igneous processes producing this ~ 800 m-long transect of lower oceanic crust. In addition, by comparison with the transect of Hole 735B we examine the lateral continuity of the lower ocean crust at Atlantic Bank, compared to the 1400 m Hole U1309D in the Atlantis Massif (Mid Atlantic Ridge).

Evidence from the New Caledonia peridotites for contrasting behavior of highly siderophile and chalcophile elements in supra-subduction zone and normal upper mantle

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Keywords: New Caledonia peridotites, highly siderophile elements, chalcophile elements.

The New Caledonia Peridotitic Nappe represents one of the largest exposures of mantle rocks worldwide and provides unique insight on upper mantle processes. The Peridotitic Nappe is dominated by a harzburgite-dunite association forming the Massif du Sud, but also includes minor lherzolites in the northern part of the island. The geochemical features of the harzburgites require a complex history, including episodes of melting and local overprint by fluids or hydrous melts in a supra-subduction zone setting, while lherzolites are relatively homogeneous, abyssal-type peridotites (Secchiari, 2016). In order to examine how these mantle processes affected the behavior of highly siderophile (HSE: Os, Ir, Ru, Rh, Pt, Pd, Au, Re) and chalcophile elements (S, Se, Te), a set of fully characterized (*i.e.*, major and trace elements; Sr, Nd and Pb isotopes) peridotites has been studied. The lherzolites display homogeneous $^{187}Os/^{188}Os_i$ (0.1273-0.1329), slightly subchondritic to chondritic Re/Os (0.04-0.11) and PGE, Au, Se and Te abundances, similar to other lherzolites from normal upper mantle. Sulfur contents are variable (202-1268 mg/g) and were likely increased by serpentinization. Harzburgites can be grouped in two sub-types. Type-A harzburgites ($epsilon_{Ndi}$=9.3-13.3) have subchondritic $^{187}Os/^{188}Os_i$ (0.1203-0.1254) coupled with low Os (0.554-1.513 ppb) and Re contents (0.017-0.021 ppb) and somewhat fractionated HSE patterns. The HSE display lower concentrations than in lherzolites, with Os-Ru enrichments over Ir (Os_N/Ir_N = 1.6-1.9; Ru_N/Ir_N = 1.5-1.7) and positive anomalies of Pt and Au. S-Se-Te have low contents (< 0.1 x primitive mantle) and approximately flat patterns, likely reflecting the presence of small amounts of sulphides. These features are consistent with high melting degrees that led to sulphide exhaustion and Os-Ru and Pt alloy stabilization. Type-B harzburgites ($-0.8 \leq \varepsilon_{Ndi} \leq +4.0$) are fresh rocks showing chondritic to suprachondritic measured $^{187}Os/^{188}Os$ (0.1273-0.1524) coupled with very low Os concentrations (0.003-0.277 ppb) and high $^{187}Re/^{188}Os$ ratios of up to 30. The HSE have melt-like patterns with low concentrations of Os and Ir, strong negative Pt anomalies and positive Au spikes. Sulfur, Se and Te concentrations are remarkably low (*e.g.*, a few mg/g S). HSE patterns are interpreted to reflect localized interaction and modification of type A harzburgites with oxidized (?) subduction-related fluids or melts, which destabilized residual mantle sulphides and PGE alloys, causing strong depletion of compatible PGE and S, Se, Te. The complex element patterns of these peridotites are unknown from mantle rocks that were exhumed in extensional environments. The data suggest that HSE fractionations (*e.g.*, Pt anomalies and Au enrichment) and chalcophile element abundances in arc magmas may at least partially reflect sub-arc mantle processes.

Secchiari, A. (2016): Geochemical and Sr, Nd, Pb isotope investigation of the New Caledonia ophiolite. Unpublished thesis, Università di Parma, 191 p.

The contrasting geochemical message from the New Caledonia gabbronorites: insights on depletion and contamination processes of the sub-arc mantle in a nascent arc setting

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Keywords: New Caledonia ophiolite, Sr Nd Pb isotopes, intra-oceanic arcs.

The New Caledonia ophiolite hosts one of the rare examples of crust-mantle sections formed in a nascent arc setting, thus providing the unique opportunity to improve our understanding of the formation of lower arc roots. This sequence includes ultra-depleted harzburgites that suffered very high melting degrees (□20-25%), overlain by mafic-ultramafic lithologies. The ultramafic rocks (mainly dunites and wehrlites) resulted from melt-peridotite reactions involving primitive arc tholeiites and boninitic melts. The mafic rocks are olivine gabbronorites occurring in the upper part of the sequence as metre-sized sills. In this study a comprehensive geochemical and isotopic (Sr, Nd, Pb) characterization of the New Caledonia olivine gabbronorites has been carried out. The gabbronorites are mainly formed (□50-80 vol%) by subhedral Ca-rich plagioclase (An up to 96 mol%). Mg-rich olivine (5-15 vol%, Fo = 87-89 mol%) occurs as irregularly shaped, resorbed crystals. Clinopyroxene (15-20 vol%) is generally rimmed by interstitial to poikilitic orthopyroxene (5-15 vol%). Fe-Ti oxides and hydrous phases are absent. Clinopyroxene shows high Mg# (88-92), low Al_2O_3 (1.5-2.4 wt%) and negligible TiO_2 and Na_2O contents. Whole rock compositions display high Mg# (86-92) and concentrations of incompatible trace elements lower than arc rocks worldwide. *REE* patterns show *LREE* depletion, nearly flat *HREE* segments ($0.82 \leq Dy_N/Yb_N \leq 1.00$), low *HREE* ($Yb_N = 0.2\text{-}0.9$) and positive Eu anomalies. Cpx trace element chemistry mirrors the extreme depletion shown by the whole rock. In contrast with this depleted nature, positive spikes for the most incompatible, fluid mobile elements (FME), *i.e.*, Pb and Sr, can be observed both for whole rock and Cpx. The calculated compositions of the putative melts in equilibrium with the gabbroic rocks are consistent with melting of a refractory mantle source in the spinel stability field. The inferred melts have high Mg# of 75-76. Trace element contents indicate derivation from ultra-depleted liquids, sharing some affinities with the most primitive boninites of the Bonin Islands, but with lower contents of *LREE* and other highly incompatible trace elements (Ba, Pb, Sr, Zr, Hf). FME enrichments, together with high Pb/Ce, Sr/Nd and Ba/Th ratios, shed light on the involvement of a subduction-related fluid in the magma genesis of these rocks. Nd isotopic data ($+8.2 \leq \varepsilon_{Ndi} \leq +9.2$) coupled with Pb isotopic values trending from DM to Pacific sediments compositions, also support an origin from a homogenous DM reservoir variably re-enriched by slab-derived fluids. We interpret the contrasting geochemical signature of the New Caledonia gabbronorites as reflecting a derivation from a refractory mantle source, which experienced contamination processes by fluids, some of which are related to slab dehydration during the onset of the Eocene subduction.

A hypothetical reconstruction of the hyperextended margin of the Tethys branch preserved in northern Calabria and Lucania, southern Italy

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Keywords: Calabria-Lucania ophiolites, hyperextended margin, Tethyan rifting.

It has been generally accepted that many of the ophiolites cropping out in the Alps, Corsica, and Apennines are not true fragments of oceanic lithosphere; most likely they are remnants of hyperextended continental margin developed at an ocean-continent transition. Based on the presence of continental crust, the degree of extension, and trace-element geochemistry, it has been possible to reconstruct the anatomy of hyperextended African and European margins, from continental proximal to true oceanic units.

We propose that similar elements of a hyperextended margin can be recognized in northern Calabrian and Lucanian geology. These elements in order of continent to oceanic settings are: 1) The Sila Unit in the Catena Costiera exposes detachment faults that separate Variscan lower continental crust, underplated gabbros, and ultramafic rocks. This unit represents preserved and weakly deformed continental crust that was thinned during pre-Tethyan Permo-Triassic rifting. 2) Timpa di Pietrasasso and Timpa della Murge preserve a section of pillow basalt separated from gabbro and serpentinite by a detachment fault. The serpentinite contains fault-bounded blocks of continental crust linking the section to continental setting; this are part of continental crust that was fully extended, exhuming gabbro and serpentinite on the ocean floor. 3) The Monte Reventino-Gimigliano Unit consists of a package of strongly folded metasediment, metabasalt, ophicarbonate, and serpentinite. It preserves an oceanic detachment fault separating metabasalt from serpentinite, without involvement of continental units.

As a whole these represent a fossil rests of a transect between continent and oceanic units. In our conceptual model, the basement exposures of the Sila Unit are analogous to the extended continental units of the Err Nappe; Timpa Pietrasasso and Timpa della Murge are similar to the exposed serpentinite of the Platta Nappe; and the Monte Reventino-Gimigliano Unit would be comparable to distal oceanic segments similar to the Chenaillet Ophiolite. Together, these may preserve the southernmost edge of the Italian sector of the rifted Tethyan margin

Amphibole and felsic veins from the gabbroic oceanic core complex of Atlantis Bank (Southwest Indian Ridge, IODP Hole U1473A): when the fluids meet the melts

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Keywords: ocean-floor metamorphism, amphibole chemistry, oceanic crust, seawater-derived fluids.

We present a petrological investigation of amphibole and felsic veins drilled during IODP 360 expedition at Atlantis Bank, a gabbroic oceanic core complex from Southwest Indian Ridge. The main purpose of this study is to unravel the role of seawater and magmatic components in the origin of these veins. Brown amphibole veins were collected at 90-170 mbsf and typically crosscut the crystal-plastic foliation of host gabbros at high angle. These veins include minor modal amounts of plagioclase and are associated with alteration halos made up of brown amphibole and whitish milky plagioclase in host gabbros. In this study, we also selected two sets of late magmatic felsic veins, which mostly consist of plagioclase and minor brown amphibole. The first set of felsic veins was found at 210-260 mbsf and is characterized by sharp planar boundaries against host gabbros. Similar to the brown amphibole veins, these felsic veins locally crosscut the crystal-plastic foliation of host gabbros at high angle. The second set of felsic veins was collected at 350-390 mbsf and is characterized by diffuse boundaries and frequent incorporation of gabbro material.

In the brown amphibole veins, amphibole has low Mg# and K_2O, high TiO_2, and significant Cl. The coexisting plagioclase has about 32 mol% of anorthite component and is K_2O-poor. Brown amphibole in the felsic veins has higher TiO_2 and K_2O, and lower Cl than in the brown amphibole veins. Plagioclase from the felsic veins is chemically heterogeneous; taken as whole, the core analyses show a decrease of anorthite component from 34 to 14 mol%, associated with increasing K_2O from 0.2 to 0.6 wt%. Amphibole-plagioclase geothermometry documents that crystallization of brown amphibole and felsic veins occurred in the 850-700°C interval. The development of brown amphibole veins at near surface levels is attributed to seawater-derived fluids migrating downward through cracks developing in the exhuming gabbro. To explain the high temperature estimates for the development of these shallow veins, we propose that the seawater-derived fluids not only interacted with host gabbros, but also with late magmatic melts (*i.e.*, compositionally similar to those feeding the felsic dykes) rising through the gabbroic sequence.

Magmatic-tectonic interplay during the early exhumation of the lower oceanic crust: the example of the Chenaillet ophiolite (western Alps)

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Keywords: ophiolite, high temperature deformation, oceanic crust, amphibole chemistry.

The Jurassic Chenaillet ophiolite essentially consists of a gabbro-mantle association exhumed to the seafloor through detachment faulting and covered by basalt lavas and minor sediments (Manatschal et al., 2011). The gabbroic bodies are mostly composed of undeformed troctolites including minor clinopyroxene-rich gabbros. The host mantle sequences consist of depleted spinel-plagioclase peridotites in places including spinel-plagioclase websterite layers.

The gabbroic bodies experienced localized high-temperature ductile deformation, as shown by development of protomylonite to ultramylonite structures in the clinopyroxene-rich gabbros. These sheared domains typically include a network of felsic dykes, which are commonly discordant with respect to the gabbro foliation. The mylonitized gabbros commonly preserve igneous clinopyroxene porphyroclasts, whereas primary plagioclase is mostly recrystallized into polygonal aggregates. With respect to undeformed gabbros, the sheared gabbros have higher amphibole modal amounts. Amphibole (titanian edenite) occurs as corona around the porphyroclastic clinopyroxene or as sin-kinematic phase, locally associated with neoblastic clinopyroxene. The felsic dykes essentially consist of albite-rich plagioclase and minor titanian edenite. Amphibole-plagioclase geothermometry documents that both the ductile deformation and the crystallization of the felsic dykes occurred at 700-750°C.

Undeformed and sheared gabbros from the Chenaillet ophiolite have similar major element compositions. Conversely, these two rock-types have contrasting incompatible trace element signature. The undeformed gabbros display a typical MOR-type geochemical signature, whereas the sheared gabbros show relatively high concentrations of incompatible trace elements. The felsic dykes are characterized by relatively low $Mg/(Mg+Fe^{2+}_{tot})$ and high concentrations of incompatible trace elements.

In the deformed gabbros, the concentrations of incompatible elements are positively correlated with amphibole modal amounts, thereby indicating that the ductile deformation was associated with metasomatism. Amphibole from both the deformed gabbros and the felsic dykes has relatively high K_2O and F contents, which document an origin by amphibole-saturated silicate melts. Because the amphibole has low Cl, these melts are inferred to retain a negligible seawater component. We conclude that the high temperature gabbro deformation was assisted by the amphibole-saturated melts feeding the felsic dykes and that melt-gabbro reactions led to the metasomatism of the deformed gabbros. The high temperature fault was presumably rooted in unsolidified melt-bearing gabbros, thereby allowing highly evolved residual melts to migrate.

Manatschal, G., Sauter, D., Karpoff, A.M., Masini, E., Mohn, G., Lagabrielle, Y. (2011): The Chenaillet ophiolite in the French/Italian Alps: an ancient analogue for an oceanic core complex). Lithos, 124, 169-184.

Kimberlitic chromites: a trace element and inclusion study

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Keywords: chromite, kimberlite, trace elements, inclusions.

Spinel commonly forms throughout kimberlite crystallization, thus the morphology and composition of groundmass spinel may be useful in deciphering the kimberlite crystallization history. In fact several authors showed that the composition of the core of groundmass spinel can be useful in distinguishing different phases of kimberlite.

In kimberlites several spinels crystallize spanning in composition from chromite to magnesio-ulvöspinel to magnetite but also magnesioferrite and pleonaste can occur. The kimberlite that we see is the end result of fairly rapid crystallization processes that start near 1200°C with the early crystallization of olivine and spinel *s.l.*, and continue to temperatures well below 600°C, at which point hydrous and carbonate minerals such as serpentine, pectolite, calcite and dolomite become stable phases. The distributions of minor- and trace elements in chromite recently provided new insights into the genesis and/or successive evolution (metamorphism) of the chromitites in ophiolitic rocks and mantle xenoliths. In this study we will report the first trace element analyses of spinels from Siberian (Mir, Aikhal, International'naya, Komsomolskaya), and US (Prairie Creek) kimberlites along with Australian (Ellendale) lamproite.

Backscattered analyses showed that most of the studied spinels present a core and rim zoning, with a common increase in Fe^{3+} and Ti content in the rim. The Cr# is usually higher than 0.5 apart from spinels of Mir and Aikhal pipes. Presence of silicate and carbonate minerals can be seen in the rim as well as in the core of spinels. Chemical and Raman analyses of these inclusions will be studied to verify possible differences among them and to possibly infer some hypothesis on the estimated depth/temperature path.

Session S15:
A promenade along the subduction plate interface from the sea to the mantle and back: a multidisciplinary point of view

Conveners:

Francesca Meneghini (Univ. di Pisa)
Francesca Remitti (Univ. di Modena e Reggio Emilia)
Laura Federico (Univ. di Genova)

Chaotic rock units as marker of the tectonic evolution of the Ligurian accretionary wedge: examples from the Curone and Staffora valleys (northern Apennines)

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Keywords: broken formations, sedimentary mélanges, subduction, accretionary complex, Northern Apennines.

Observations on modern accretionary complexes show that the shape and growth of the frontal wedge of modern accretionary complexes repeatedly change to maintain the dynamic equilibrium in the wedge through alternating tectonic and sedimentary (*i.e.*, mass transport) activities. Tectonic mélanges and highly sheared and disrupted rock units represent the products of tectonics occurring along the basal décollements in accretionary wedges and within the subduction plate interface. Mass-transport deposits and sedimentary mélanges (olistostromes) result from slope instability in the trench-inner slope and in the upper parts of frontal wedges. Through a detailed geological mapping, structural analysis and stratigraphic observations of different types of chaotic rock units previously designated as an "undifferentiated chaotic complex", this study documents the tectonic setting and geological evolution of the exhumed Ligurian accretionary wedge in the sector between the Curone and Staffora valleys (northern Apennines). Our findings allow differentiating of different types of broken formation and sedimentary mélanges (olistostromes) that were formed by contemporaneous to sequential operation of tectonic and mass transport processes that took place from subduction-accretion to collisional tectonic stages during the Late Cretaceous through Late Miocene, to maintain the dynamic equilibrium of this accretionary wedge. Four main tectonic stages were differentiated:

– *Late Cretaceous-Early Eocene*: the characteristics of the internal block-in-matrix fabric of Late Cretaceous ophiolite-bearing chaotic rock units and of the "Basal Complexes" of the Cassio Unit document tectonic and mass-transport processes, respectively, occurred in the frontal part of the Ligurian wedge during subduction stage.

– *Middle Eocene*: the random distribution of native and exotic blocks (of External Ligurian Units nature) in a clayey matrix, allow distinguishing a Middle Eocene sedimentary mélange (Baiso argillaceous breccias), which documents a regional-scale stage of gravitational instability, triggered by the tectonic uplift of the External Ligurian Units during the Mesoalpine stage.

– *Chattian-Early Miocene*: the occurrence of a different type of sedimentary mélange (Val Tiepido – Canossa argillaceous breccias), emplaced during slope deposition of the Antognola Formation, testify a new significant period of gravitational instability, which at regional-scale is related to the northern migration of the Apenninic thrust front.

– *Late Messinian*: evaporitic Messinian blocks randomly embedded in a fine-grained matrix represent a Late Messinian mass-transport deposit, which documents a new stage of gravitational instability triggered by a regional-scale tilting of the external sectors of the Apenninic thrust front.

Into deep and beyond: elements recycling through serpentinites and metaperidotites evolved at the plate-interface

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Keywords: serpentinites, fluid-mobile elements, OIB, chemical exchange.

A crucial role in the chemical cycling of elements is played by processes taking place at the interface between the downgoing plate and the upper mantle of subduction systems. As documented in several metamorphic terrains, the prograde fluid-mediated chemical exchanges between serpentinized mantle rocks with slab fluids derived from sediments and/or altered oceanic crust accreted at the plate interface can be tracked using fluid-mobile element (B, As, Sb, Sr, Pb) and isotopic tracers (B, Sr, Pb). During these interactions, serpentinized rocks can modify their original geochemical (oceanic) imprint after exchange with metamorphic slab fluids (Cannaò et al., 2015, 2016). In this way the antigorite-out reaction provide fluids with recycled crustal materials in terms of trace element and isotopic signatures (*e.g.*, negative δ^{11}B, radiogenic ^{87}Sr/^{86}Sr and Pb isotopes) contributing to magmatism associated with subduction zones (Scambelluri et al., 2015).

The example of Cima di Gagnone (Swiss central Alps), where de-serpentinized garnet- and chlorite-bearing metaperidotite are embedded in a sedimentary matrix in a top slab mélange, provide evidence that such metaperidotites still record subduction zone interaction between ultramafic rocks and sediment-derived fluids. Compared to several OIB volcanoes, the Sr and Pb isotopic signatures of the Gagnone metaperidotites fit a mantle source enriched with recycled sediment/crustal materials, such as the case of the Samoa lavas (Workman et al., 2004). This suggests that Gagnone-like metaperidotites may represent an end-member for the enriched mantle II component in OIB mantle. Therefore, deep sinking into the mantle of restitic material evolved at the subduction plate interface is an efficient mechanism to generate geochemical anomalies in the Earth mantle.

Cannaò, E., Agostini, S., Scambelluri, M., Tonarini, S., Godard, M. (2015): B, Sr and Pb isotope geochemistry of high-pressure Alpine metaperidotites monitors fluid-mediated element recycling during serpentinite dehydration in subduction mélange (Cima di Gagnone, Swiss Central Alps). Geochim. Cosmochim. Acta, 163, 80-100.

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Scambelluri, M., Pettke, T., Cannaò, E. (2015): Fluid-related inclusions in Alpine high-pressure peridotite reveal trace element recycling during subduction-zone dehydration of serpentinized mantle (Cima di Gagnone, Swiss Alps). Earth Planet. Sci. Letters, 429, 45-59.

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Ancient microstructures as a tool to decipher fault mechanisms of shallow megathrusts: an example from the Sestola Vidiciatico tectonic Unit

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Keywords: megathrust analogue, microstructures, calcite veins, weak faults, plate interface.

The shallowest part of active megathrusts has proved to be characterized by the unexpected coexistence of coseismic slips and aseismic creep, slow slip events, low and very low frequency earthquakes. Origins and interplays of these phenomena are actually little known, and related deformation structures are still poorly recognized and described. To shed light on these issues, the characterization of the microstructures recorded by exhumed shallow parts of ancient, "fossil" megathrusts represents a fundamental tool.

The Sestola-Vidiciatico tectonic Unit in the northern Apennines has been interpreted as an analogue of a shallow megathrust shear zone, which accommodated underthrusting of the Adria plate under the Ligurian prism during early-middle Miocene transporting sediments to depth corresponding to 150°C maximum temperature (Vannucchi et al., 2008).

Through detailed microstructural analysis on samples through optical, cathodoluminescence and scanning electron microscopy, we detailed a 5 m thick fault zone marking the base of the Sestola-Vidiciatico tectonic Unit. Here, strongly deformed siltstone and marls of various competence are characterized by mesoscopic cleavage, boudinage, extensional faults and low-angle thrusts coated by calcite veins. At the top of the shear zone, a 20 cm thick continuous shear vein cuts all other structures.

At the microscale, we identified a primary sedimentary layering, consisting of alternating fine and coarse-grained marly or shaly laminae that are crosscut by soft-sediment deformation bands derived from the reorientation of mineral grains without fracturing. Parallel to the sedimentary laminae, a pervasive foliation in clay-rich domains is segmented by S-C' shear bands. More competent, calcareous portions are strongly boudinaged and cut by calcite shear veins displaying crack-and-seal texture and locally implosion breccias. Multiple mutually crosscutting generations of extensional veins are recognizable, with dispersed orientations. Calcite veins appear partially dissolved by pressure-solution processes and progressively more folded and shortened perpendicular to the shear zone from top to bottom.

Microstructures suggest that deformation started acting on not completely lithified sediments, with a progressive embrittlement, enhanced on more competent portions while less competent ones still behaved in a ductile way. Cyclic high fluid pressures, testified by the widespread veins features, could be responsible for thrusting under low differential stress, with decoupling from the footwall and progressive migration and thinning of the shear zone, thus suggesting fluid-assisted weak thrusting as the principal shear mechanism.

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Burial and exhumation history of the Daday Unit (central Pontides, Turkey)

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Keywords: *P*-*T*-d-t path, *HP* metamorphism, exhumation, Intra-Pontide suture zone, northern Turkey.

In northern Turkey, the Intra-Pontide suture (IPS) zone divides the Istanbul-Zonguldak and the continental terranes (Göncüoğlu et al., 2000). It consists of an assemblage of several oceanic and continental units characterized by different age, metamorphic imprint and deformation history. In the central Pontides, the IPS zone is a pre-Late Paleocene imbricate stack where an ophiolite unit (Ayli Dağ ophiolite Unit) and an ophiolite-bearing mélange (Arkot Dağ Mèlange), derived from a NeoTethyan oceanic basin (the Intra-Pontide oceanic basin: Göncüoğlu et al., 2008) are associated with four metamorphic units (*i.e.*, Saka, Emirkoy, Daday and Domuz Dağ Unit) (Frassi et al., 2016).

In the Daday Massif, the Daday Unit is an assemblage of tectonic slices having a monogenic composition (micaschists, paragneisses, marbles, actinolite-bearing schists and quarzites) derived from a supra-subduction oceanic crust (Sayit et al., 2016) and related deep-sea sediments of Middle Jurassic age. Structural analyses, *P*-*T* estimates and Ar-Ar dating allow to elaborate a *P*-*T*-t-d path (Frassi et al., 2017) in which the D1 phase was acquired during the Late Jurassic by tectonic underplating at 35-42 km of depth. The following D2, D3 and D4 phases produced the exhumation up to shallower structural levels. The high geothermal gradient detected during the D2 phase indicates that the Daday Units was exhumed during a continent arc collisional setting. The structure of the IPS zone is unconformably sealed by the upper Paleocene-Eocene deposits and lately reworked by the North Anatolian Fault Zone (D5).

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Syntectonic sedimentation atop the Eclogite Belt of the western Alps (Tertiary Piedmont Basin-Ligurian Alps): a geological map

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Keywords: Tertiary Piedmont Basin, Eclogite Belt, western Alps.

Syntectonic sedimentary successions provide first-order constraints to investigate the mechanisms of (*U*)*HP* rock exhumation, and unambiguous documentation of orogen erosion and topographic growth through time. However, sedimentary successions exposed atop eclogitic rocks are not common, either because they are still below the sea level (*e.g.*, in active sedimentary basins atop the Neogene (*U*)*HP* belt of eastern Papua New Guinea), or because they have been largely eroded away and are no longer preserved, *e.g.*, in the pre-Cenozoic (*U*)*HP* belts of Dabie-Sulu (China) and in the Western Gneiss Region (Norway).

In the western Alps, the Tertiary Piedmont Basin includes the only syntectonic sedimentary successions resting directly atop the Eocene Eclogite Belt (Malusà et al., 2015, and references therein). We have mapped in detail (at 1/10,000 scale) the relationships between these sedimentary rocks and the underlying metamorphic units over an area of ~500 km^2. The map of this key area provides new stratigraphic and structural constraints to the exhumation of the Eocene Eclogite Belt of the western Alps, and, more generally, to exhumation processes in modern and ancient orogenic settings.

The study area, like other transects in the western Alps, includes eclogitic units derived from subducted European continental crust (Valosio Unit), enveloped by eclogitized ophiolites (Voltri Unit), which are tectonically coupled along a synmetamorphic shear zone, showing evidence of reactivation and fluid-rock interaction in the brittle field. These metamorphic units are unconformably covered by the Tertiary Piedmont succession, which shows major lateral variations both in lithofacies and thickness. The bottom of the Tertiary Piedmont succession is represented by the Molare Formation, chiefly consisting of Oligocene sandstones and conglomerates, locally including reef limestones attesting to extremely fast exhumation of the underlying Eocene eclogites, and their exposure close to sea level by that time. The Molare Fm is overlain by silty marls and fine sandstones (Rocchetta-Monesiglio Fm, Lower Oligocene-Aquitanian), marls, glauconitic sandstones and biocalcarenites/biocalcirudites (Visone Fm, Burdigalian), and turbiditic sandstones (Cortemilia Fm, Burdigalian-Langhian), recording a complex Oligo-Miocene syntectonic sedimentation controlled by a network of strike-slip, reverse and normal faults, that have been mapped in the field. These faults, often reactivating preexisting synexhumation faults, are marked by thick, continuous layers of cataclasites and fault breccias, and show evidence of a polyphase brittle evolution that is consistent with information provided by associated sedimentary successions.

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New insights into the geodynamics of Neo-Tethys in the Makran area: evidence from age and petrology of ophiolites from the Coloured Mélange Complex (SE Iran)

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Keywords: ophiolite, mélange, Neo-Tethys, Makran, Iran, Cretaceous.

In the Makran region, SE Iran, one of the largest worldwide accretionary wedges is exposed. This accretionary wedge is regarded as the result of the northward subduction of the oceanic lithosphere of the Oman Sea beneath the Lut and Afghan continental blocks. To the north, the accretionary wedge is bounded by the north Makran domain that can be regarded as the backstop of the accretionary wedge. The north Makran domain is represented by an imbricate stack of continental and oceanic units including the Coloured Mélange Complex, also referred as the Imbricate Zone.

The Coloured Mélange Complex is part of the north Makran domain (SE Iran) and consists of an assemblage of metric-to decametric-thick slices mainly represented by volcanic rocks, locally stratigraphically associated with radiolarian cherts. We had got new geochemical data on volcanic rocks and biochronological data on the associated cherts. Our data indicate the occurrence of a wide range of volcanic rocks-types, which are: 1) normal-type mid-ocean ridge basalts (N-MORB); 2) oceanic plateau basalts (OPB); 3) alkaline basalts; 4) calcalkaline basalts, basaltic andesites, andesites, and dacites; 5) volcanic arc tholeiitic basalts and dacites, and high pressure-low temperature metabasalts formed in deep levels of an accretionary wedge. The volcanic arc tholeiites range from Early (Late Hauterivian-Early Aptian) to Late (latest Cenomanian-lower Late Campanian) Cretaceous, whereas the calcalkaline rocks and OPBs are Late Cretaceous in age (Early Coniacian- Santonian and Early Turonian-Early Campanian, respectively). Alkaline basalts, OPBs, and N-MORBs represent remnants of the Mesozoic Neo-Tethys oceanic branch located between the Arabian plate and the Lut block. In this paper we document that this oceanic sector was characterized by the development of an oceanic plateau in the Late Cretaceous. In contrast, calc-alkaline and volcanic arc tholeiitic rocks represent remnants of a continental volcanic arc and forearc, respectively, developed onto the southernmost realm of the Lut block. The petrogenesis and age of volcanic rocks allow us to propose a new tectono-magmatic model for the evolution of the convergent margin developed in the northern sector of the Neo-Tethys from Early to Late Cretaceous. This model is basically constrained by the collision of the oceanic plateau with the continental arc, which led to the jump of the subduction toward the south, as well as to the formation of the imbricate pile of different units today observed in the north Makran area.

Microstructures in clay-rich exhumed faults

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Keywords: subduztion zone, clay-rich fault, scaly fabric.

Recent geodetic and seismologic data suggests that strain release at subduction plate boundaries can span a wide range of slip rates, from creeping to 'normal' earthquakes passing through intermediate slip rate as for slow slip, episodic tremor and low-frequency earthquakes. Especially updip and downdip of the so-called ‘seismogenetic zone’ these slip behaviors can coexist or alternate in time. The mechanisms that control the nature of slip as well as the relationships between rock physical properties, fault zone composition and fault slip behavior remain undiscovered. As a result, for instance, the propagation of the rupture to the trench and the extremely large coseismic slip (> 50 m) at shallow depths of the 2011 M_w 9.0 Tohoku-Oki earthquake were largely unexpected. In this specific case, the mechanical properties of the shallow megasthurst seem to be related to the frictional properties of smectite-rich gouge present along the shallow part of the fault zone (Chester et al., 2013). Since then, a strong effort of the research community has been put in better understanding the mechanical properties of the clay-rich material (*e.g.*, Ujiie et al., 2013, Ikari et al., 2015).

We propose that diverse and complementary information can derive from the study of exhumed faults cutting through pelagic clay-rich formation exposed in the northern Apennines of Italy as part of an ancient accretionary prism (*i.e.*, Argille Varicolori *Auctt.*).We sampled several faults displaying different degree of scalyiness and a variety of internal microstructures as ductile and/or brittle boudinage, foliation, sharp shear surfaces and cataclasis. All these structures suggest that shear localization in clay material can result from different mechanisms depending on the conditions at the time of shearing. Controlling factors probably includes the water content at the time of deformation, the slip rate, the mineralogical composition of the clay and the total displacement of the fault.

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Geodynamic evolution of a subduction plate interface: constraints from the study of lawsonite-bearing eclogite in the mélange of the Voltri Massif (Ligurian Alps, Italy)

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Keywords: lawsonite-bearing eclogite, thermodynamic modelling, subduction plate interface, low viscosity serpentinite channel, Ligurian western Alps, Voltri massif.

Lawsonite (lws) blueschists and eclogites are expected to be the prevailing lithotypes developing during deep subduction of the oceanic crust and should therefore be quite abundant in exhumed subduction complexes. Nevertheless, lws-bearing eclogites have been described only from few localities in the world. Moreover the occurrence of lws-bearing high-pressure metamorphic rocks, associated with eclogite facies rocks, could give important constraints on the coupling mechanisms between different tectonometamorphic slivers in subduction zones and on the interaction with fluids along the subducting slab.

Here we present the structural and petrological study of a lws-bearing eclogitic metagabbro, cropping out in the north-western sector of the metaophiolitic Voltri Massif (Ligurian western Alps, Italy).

The Voltri Massif occurs at the eastern end of the western Alps and in the study area is characterised by ocean-, continental- and mantle-derived slices of tectonometamorphic units, involved in the Alpine orogenesis.

The metagabbro body is a 20-m sized lens and shows a peculiar alternation of Na-amphibole-rich blue and Na-pyroxene-rich green layers, with a mylonitic texture. Both layers include isoclinal intrafoliar folds, which are the oldest recognizable deformation. The metagabbro was affected by a superimposed folding event, testified by isoclinal folds, deforming all the previous structures and causing the alternating green and blue banding. This body is in contact with glaucophane-bearing metasediment and both are interlayered with serpentine schists. Ophicalcites and serpentinites with a variable degree of carbonation (till their complete transformation into listvenites) also crop out in the area.

The thermodynamic modelling suggests that the metagabbro body reached metamorphic peak conditions at relatively low temperature (T = 465-477°C, P = 20.9-24.4 kbar), in a setting where H_2O was continuously provided to a cold system. H_2O under-saturated conditions, with the occurrence of both lawsonite and epidote, characterised the exhumation path.

The occurrence of carbonated serpentinites suggests that an intense and long-lasting circulation of CO_2-rich fluids affected the area. Further evidence of this circulation comes from an adjoining outcrop (La Pesca locality) some hundreds meters far; we therefore compared the two areas to constrain the timing of CO_2 fluid circulation and its role in the lawsonite preservation.

The metamorphic peak conditions recorded by the metagabbro body and the occurrence of variously carbonated serpentinites suggest that this area can be interpreted as a portion of the top of the subducted slab, coupled with a "cool" mantle wedge, where both H_2O- and CO_2-rich fluids were present; in particular we think that this area was nearby the slab-mantle interface. This sector was thus involved in a low viscosity serpentinite channel, where it was affected by a shear regime that brought these high-pressure rocks back to the surface.

Continental crust subduction-related structures: contrasting evolutions *vs.* contrasting memories

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Keywords: Sesia-Lanzo zone, numerical modelling, LPO, microstructures.

In this contribution, we will describe examples from the subducted continental crust of the western Alps, Austroalpine domain. We will integrate results from structural geology, petrology/geochemistry, and modelling, at different scales from lithosphere to atomic scale, emphasising the roles of contrasting tectono-metamorphic evolutions *vs*. the efficiency of rocks to memorize their promenade along the subduction plate interface or close to it. We will compare the evolution of continental crust slices found at different positions within the subduction architecture and recording specific structural features and metamorphic parageneses. We emphasise that the combined use of structural and metamorphic criteria is the only nowadays reliable method to fully investigate such an heterogeneous system.

Session S16:

Deformation and fluid flow in the crust from migmatites to epithermal systems

Conveners:

Giovanni Musumeci (Univ. di Pisa)
Francesco Mazzarini (INGV, Pisa)
Giulio Viola (Univ. di Bologna)
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Geochemical constraints on petrogenesis of Ca-rich leucosomes from Porto Ottiolu migmatites (NE Sardinia)

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Keywords: migmatites; Ca-rich leucosomes; fluxed melting; NE Sardinia.

Ca-rich leucosomes in sedimentary-derived migmatites have been described in different high-grade complexes all around the world, from Colombia to Himalaya (Zeng et al., 2012).

The sedimentary-derived migmatite of Porto Ottiolu, NE Sardinia shows trondhjemitic to tonalitic leucosomes reaching up to ~4% of CaO. The migmatite consists of dark, fine- to medium-grained, foliated mesosome hosting 5-10 vol% of folded leucosomes elongated according to the regional schistosity. The contact between leucosome and mesosome is rarely marked by biotite-rich melanosomes. Both leucosome and mesosome have a similar mineral assemblage, mainly consisting of quartz, unzoned plagioclase (An_{29-32}), biotite, muscovite, fibrolite and very rare K-feldspar; kyanite relics are rarely found in plagioclase. Muscovite occurs as relics enclosed in feldspars, in elongated trails with biotite and sillimanite and as large retrograde crystals; its silica content ranges between 6.03-6.18 a.p.f.u., with the highest values found in relics. Biotite (X_{Mg} 0.50-0.62) is commonly associated with fibrolite and/or muscovite.

Leucosomes are enriched in SiO_2 (75.41-82.90%), CaO (1.73-3.74%) and Na_2O (2.90-4.59%), respect to mesosomes (average values 63.88%, 1.71%, 1.88%, respectively). Al_2O_3 is more constant in leucosomes (10.29-14.83%) than in mesosomes (9.04-20.95%). K_2O, Fe_2O_3, MgO, Mn_2O_3 and TiO_2 in leucosomes (0.39-1.80%, 0.29-1.66%, 0.11-0.60%, 0.004-0.06%, 0.04-0.16%, respectively) are strongly depleted compared to mesosomes (average values 3.59%, 7.38%, 2.84%, 0.08%, 0.91%, respectively).

Among trace elements a particular attention must be paid to Rb, Sr and Ba because their concentration is controlled by the involvement of micas and plagioclase in melting processes. Rb and Ba are depleted in leucosomes whereas Sr is strongly enriched.

REE patterns are slightly fractionated for both leucosomes and mesosomes and are characterized by a positive Eu anomaly in the former and a negative one in the latter. In addition, leucosomes are moderately depleted in *LREE* and *MREE*, but not in *HREE*.

Different processes have been invoked as responsible of the formation of Ca-rich leucosomes, including: partial melting in the presence of water at relatively high pressures; fractionation of a granitic melt; subsolidus processes. The geochemical signature of Porto Ottiolu leucosomes (high CaO and low K_2O, low Rb/Sr ratio, moderately marked Eu anomaly, slightly depletion of *REE* with respect to mesosome) together with petrographic (low K-feldspar amount, presence of kyanite relics) and microstructural evidences (absence of subsolidus structures, trace of former melt presence), suggest that Porto Ottiolu trondhjemitic/tonalitic leucosomes originated by fluxed melting of metapelites at relatively high pressure.

Zeng, L., Gao, L.E., Dong, C., Tang, S. (2012): High-pressure melting of metapelite and the formation of Ca-rich granitic melts in the Namche Barwa Massif, southern Tibet. Gondwana Res., 21, 138-151.

Occurrence of foliated leucocratic bodies within Migmatite Complex of NE Sardinia: preliminary data

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Keywords: foliated leucocratic bodies, migmatite complex, Variscan basement, NE Sardinia.

In the High-Grade Metamorphic Complex of Sardinia, near Cala Banana (north of Olbia), several meter- to hectometer-wide, dike-shaped, foliated leucocratic bodies crop out. These felsic bodies are mainly characterized by abundant garnet (up to centimeter) and muscovite visible at the naked eye, but beyond that they are quite different from structural, petrographic and geochemical point of view. In the field some of these bodies exhibit a gneissic aspect with a pervasive foliation marked by mica alignment whereas some others are massive to poorly foliated. Grain size (from medium to very coarse) and degree of foliation sometimes gradually change within the same body with fine grained parts usually better foliated than coarser ones. The contact can be either concordant or discordant with the foliation of their host rocks, brittle (*i.e.*, marked by centimetric cataclastic belt) or ductile. When hosted in paragneisses the contact is commonly marked by centimetric, elliptic fibrolite nodules, elongated according to the pervasive foliation.

The modal composition is quite variable from Kfs-rich granite, to granite, to tonalite. Plagioclase (An_{2-9}) is usually subhedral and unzoned. Muscovite occurs as oriented subhedral crystals or as large discordant flakes sometimes hosting oriented sillimanite needles. Biotite content is generally very low and its composition ranges between X_{Mg} 0.12-0.37. Garnet can be either euhedral and without inclusions or totally anhedral with several inclusions. Both types have sometimes been found even in the same sample; despite this, its composition is quite constant (Alm_{80-86}, Sps_{8-10}, Py_{4-9}, Grs_1). One of these bodies contains large tourmaline crystals.

Almost all analyzed samples show high SiO_2 (> 75%) and Al_2O_3 (> 12%) contents. CaO is commonly lower than 1% but few samples are strongly enriched (up to ~ 3%). K_2O content mostly ranges between 3.17-6.19%, but is significantly lower (up to 0.57%) in Ca-rich samples. Na_2O content is quite variable (2.50-5.77%). FeO is commonly lower than 1% except in three samples where it is slightly higher; the other metal oxides are even less concentrated (mostly lower than 0.5%). All samples are peraluminous and have a calcalkaline affinity.

REE patterns indicate different geochemical signatures. Few samples have a flat pattern with a marked negative Eu anomaly, others have an almost flat pattern without Eu anomaly, others again are slightly fractionated with negative or positive Eu anomaly.

On the basis of the above presented data these bodies could be interpreted as Variscan, anatectic, foliated granitoids as described by Carmignani et al.(2016) and the differences between them could reflect different sources and/or different melting conditions. Further data combined with geochronology are needed to decipher their petrogenesis.

Carmignani, L., Oggiano, G., Funedda, A., Conti, P., Pasci, S. (2016): The geological map of Sardinia (Italy) at 1:250,000 scale. J. Maps, 12, 826-835.

Lithological control on fluid circulation, volume expansion and ore mineralization: the case of Topinetti, Island of Elba (Italy)

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Keywords: ore deposits, lithological control, volume expansion, Elba island.

We present a novel dataset recording the interaction between hydrothermal ore fluids and host rock in a vein-type ore mineralization formed at shallow crustal depth. The study area is located at Topinetti, along the eastern shore of the island of Elba and close to the historical, 5.3 Ma Fe-skarn deposit of Rio Marina (Lippolt et al., 1995). The Topinetti vein-type mineralization is a clear example of pervasive *vs.* channelized fluid flow (Oliver, 1996). Pervasive flow exploited lithological horizons and produced porosity reduction, which ultimately lead to fluid overpressure and channelized fluid flow.

The Topinetti mineralization is hosted by the Triassic Verrucano Fm. in the inverted limb of a large, late Miocene antiform (Massa et al., 2016). Geological, structural and mineralogical constraints provide five evolutionary steps for the genesis of this system:

1) during the initial stages of mineralization, a pervasive fluid flow caused the precipitation of disseminated pyrite within the host quartzites of the Verrucano Fm., producing a decrease of host rock permeability;

2) at a later stage, an increase of ore fluid pressure lead to the failure of the host rocks and to the formation of a breccia (breccia I) in which clasts of quartzite were hosted by a massive sulphide matrix (assemblage: *e.g*., pyrite, chalcopyrite);

3) then, a distinct Fe-bearing ore fluid was involved in the mineralization process. This new fluid caused localized failure of breccia I and formed a new breccia (breccia II) consisting of clasts of quartzite and breccia I embedded within a very fine-grained, dark hematite matrix. The volume expansion caused by this process is testified by the matrix-supported texture of breccia II (Jébrak, 1997) and by the formation of breccia dikes and veins cutting across the host rock. At progressively increasing distance from the main breccia II body, the mineralized veins change systematically from hematite- to quartz-hematite veins;

4) large hematite ore bodies (> 5 m in size) formed parallel to the bedding of the Verrucano quartzite;

5) minor, moderate east dipping normal faults successively dissected both host rocks and ores, as testified by striated slickenside on ore bodies and breccia II.

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Lippolt, H.J., Wernicke, R.S., Bahr, R. (1995): Paragenetic specularite and adularia (Elba, Italy): Concordant (U+Th)-He and K-Ar ages. Earth Planet. Sci. Letters, 132, 43-51.

Massa, G., Musumeci, G., Mazzarini, F., Pieruccioni, D. (2016): Coexistence of contractional and extensional tectonics during the northern Apennines orogeny: the late Miocene out-of-sequence thrust in the Elba Island nappe stack. Geol. J., 52, 353-368.

Oliver, N.H.S. (1996): Review and classification of structural controls on fluid flow during regional metamorphism. J. Metamorph. Geol., 14, 477-492.

Fluids within a rock matrix: evidences from passive seismics

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Keywords: passive seismic, seismic anisotropy, geo-fluids.

Fluids at crustal and upper-mantle scale play a fundamental role in a number of geophysical processes, from earthquake enucleation to metamorphisms to partial melting. Due to their intrinsic nature, geo-fluids can be sampled at the Earth's surface, but can not be directly imaged at depth. Magnetotelluric data are widely used to infer the depth position of geo-fluids, measuring the resistivity of the rock matrix. But interpretation of the resistivity images can be not-unique due to, *e.g.*, the presence of not-interconnected fracture networks. In this contribution, I will present some recent studies where passive seismics has been used to locate fluids at depth. Passive seismics is a novel approach for the exploration of the Earth's crust and upper-mantle, based on the exploitation of natural seismicity. Passive seismics can give insights in both local decreases in S-wave velocity and regions of localized seismic anisotropy. Both these observation can be related to the presence of fluids at depth. At shallow crustal level, the magnitude of the seismic anisotropy can be used to discriminate fluid phases within the rock fracture network. Across subduction zones, at sub-crustal depths, the signature of intense seismic anisotropy can be used to map fluids escaping from the subducted crust. Conversely the disruption of the signals from anisotropy materials can be related to the final stages of eclogitization or to de-serpentinization of the subducted upper-mantle.

Automated mapping and fractal clustering of putative mud volcanoes within Arabia Terra craters (Mars): insights on fluid source depth

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Keywords: mud volcanism, evaporites, fracture systems, DTM, Mars.

Arabia Terra is a region of Mars characterized by pervasive past-water presence, both with surface and subsurface. In particular in several craters in Arabia Terra such as Firsoff and an unnamed southern crater, large scale spring deposits and putative mud volcanoes have been described by several authors (Rossi et al., 2008, Pondrelli et al., 2011; Pondrelli et al., 2015). Several mounds (from 30 m of diameter in the case of monogenic cones, up to 3-400 m in the case of coalescing mounds) present an apical vent-like depression resembling subaerial Azerbaijan mud volcanoes and gryphons (Bonini, 2012). To this date, a rigorous landform analysis through numerical classification on topography has never been attempted.

We hereby present a landform classification method that led us to perform an automatic mapping of putative mud-volcanoes based on morphometric parameters in Firsoff and the southern crater, thus avoiding false positives/negatives due to visual misinterpretation. We based our mapping on CTX stereo-derived DTMs (~ 20 m) and we used high resolution HiRISE DTMs (1 m) used as testing sites. The mapped cones are then used to calculate their fractal clustering, helping to identify the thickness of the fractured medium and the possible depth of a putative fluid reservoir feeding the cones. Indeed, it has been shown that on Mars percolating fractures systems be studied in terms of fractal clustering based on spatial distribution of vents, thus deriving the depth of fluid reservoirs (Pozzobon et al., 2015).

It results that both Firsoff and southern craters have a distinct fractal upper cutoff threshold that corresponds to a depth between 2 and 2.5 km , defining the position of past fluid reservoirs feeding the putative mud volcanoes. New outcomes from ExoMars TGO and CaSSIS will help to better characterize the areas in terms of composition, broad DTM coverage and search for associated outgassing activity.

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Pondrelli, M., Rossi, A.P., Le Deit, L., Fueten, F., van Gasselt, S., Glamoclija, M., Cavalazzi, B., Hauber, E., Franchi, F., Pozzobon, R. (2015): Equatorial layered deposits in Arabia Terra, Mars: Facies and process variability. Geol. Soc. Am. Bull., B31225.1.

Pozzobon, R., Mazzarini, F., Massironi, M., Marinangeli, L. (2015): Self-similar clustering distribution of structural features on Ascraeus Mons (Mars): implications for magma chamber depth. In: "Volcanism and tectonism across the inner solar system", T. Platz, M. Massironi, P.K. Byrne, H. Hiesinger, eds. Geol. Soc., London, Spec. Publ., 401, 203-218.

Rossi, A.P., Neukum, G., Pondrelli, M., van Gasselt, S., Zegers, T., Hauber, E., Chicarro, A., Foing, B. (2008): Large-scale spring deposits on Mars? J. Geophys. Res., E113, E08016.

Cyclic fault-controlled mass transfer during gold mineralisation in carbonated ultramafites (Bisciarelle stream, Voltri Massif, Ligurian Alps)

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Keywords: thrust fault, carbonate-coated grain, mass transfer, hydrothermal alteration, gold mineralisation.

In this work, we examine a thrust fault developed within carbonated ultramafites of the Voltri Massif (Ligurian Alps), exposed along the Bisciarelle stream. Different rock types characterise the damage zone of this fault, namely carbonate and chalcedony-quartz veins at the footwall and intensely fractured and hydrothermally altered lherzolite at the hangingwall. The fault core hosts unusual carbonate-coated grains (CCGs), in a *ca*. 50 cm-thick level, cut by chalcedony shear veins at the top.

We have combined petrographic data with SEM-EDS and LA-ICP-TOFMS (Laser Ablation-ICP Time of Flight-Mass Spectrometry) analyses, and with mass transfer calculations in order to: 1) determine the chemical properties of fault core rocks, and 2) monitor chemical exchanges that took place between hydrothermal fluids flowing within the fault at the time of its slip and the host lherzolite. The used samples were collected at the fault damage zone and along a sampling profile orthogonal with respect to the fault strike.

Fault core CCGs are mm to cm-sized, have a surprisingly regular round shape, and are rarely in contact with each other. The largest CCGs show complex internal textures, in which relatively thick and fibrous dolomite bands alternate with thinner, massive, and partly laminated dark carbonate bands, suggesting a cyclic growth process; the smallest CCGs show simpler internal textures.

High-resolution (10 µm), large-format (1 cm^2) LA-ICP-TOFMS maps of the major-, minor-, and trace-element distributions highlight systematic compositional difference between the thin massive and the fibrous dolomite bands; the first ones have relatively high concentrations of Mn, Al, K, Pb, Cr, Co, and Cu, whereas the second are only enriched in a small number of metals (*i.e.*, Fe, Sr, and W). Chalcedony shear veins contain Al_2O_3, Na_2O, and K_2O in addition to SiO_2, and show a peculiar enrichment in Sb, Ag, In, Pb, and Au.

Mass transfer calculations show that the fluid transferred consistently volatiles (CO_2 and H_2O) and Sb to the rock, whereas the rock transferred Si, Fe, Co, and Cr to the fluid.

Our dataset shows that the thrust hosted a gold-bearing hydrothermal fluid, which was responsible for the rhythmic growth of the CCGs. Such growth was syn-kinematic and at equilibrium with the fault fluid, but was not coupled with any substantial grain-size reduction of the fault core.

Mass transfer data show that hydrothermal formation of CCGs and chalcedony was entirely fault-controlled, and that the host rock provides a poor record of this circulation. The evidence for transfer of Si, Fe, Co, and Cr from the protolith to the fluid provides a strong indication that the enrichment of these elements within CCGs and chalcedony was made possible by fluid-rock interaction.

In conclusion, the occurrence of CCGs with a peculiar composition, their texture, and the lack of grain-size reduction suggest that the hydrothermal precipitation controlled the composition of the Bisciarelle fault rocks.

Multi-phase flow and rock deformation: poro-elasticity from the fluid perspective

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Keywords: poro-elasticity, multi-phase, fluid flow, deformation, porous media, compaction, reservoir induced seismicity, Pertusillo lake.

The linear theory of poro-elasticity describes the mechanical coupling between a porous rock and the fluid that occupies pores and fractures. According to the theory, fluid and solid rock are both affected by changes in pore pressure and stress: the solid skeleton reacts to these changes through deformation, while the effects on the fluid phase are expressed in terms of changes in fluid content within the control volume. The theory identifies the specific coefficients that govern the relations among these four variables: stress, strain, pressure and fluid content. The value of these coefficients depends on both the properties of the rock and of the fluids: the scientific literature acknowledges that rocks saturated by gas display a different mechanical behaviour than rocks saturated by liquid. However, few constraints exist to characterise porous media that host a multi-phase fluid, where both phases (gas and liquid) coexist.

This presentation suggests a possible way to approach the problem. Poro-elastic coefficients are computed as a function of gas volumetric fraction to specifically account for the different contribution of gas and liquid to the deformation of the porous matrix. Presented results refer to the compaction of a confined aquifer caused by water level changes in an artificial impoundment. Simulations show that the presence of a free gas phase within the aquifer affects not only the pore pressure change caused by the water level fluctuation in the impoundment, but also the temporal evolution and spatial extent of the resulting pressure perturbation. These results have interesting implications for the study of the reservoir induced seismicity at Pertusillo lake, in Italy.

Evidence of regional-scale hydrothermalism and polymetallic mineral deposition across northern Italy: the Early Permian to Early Triassic siderite-rich deposits in the southern Alps

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Keywords: siderite, southern Alps, hydrothermal, sulfide, basement, Permian, Triassic.

The southern Alps in northern Italy host a wealth of siderite-rich orebodies forming a mineralized belt from western Lombardy to the Venetian Alps. Mineralization occurs as veins rooted in the greisenized cupolas of late Variscan granites as well as crosscutting the Variscan basement and the overlying Lower Permian volcano-sedimentary cover (Collio Fm); and as both veins and conformable stratabound orebodies in the Upper Permian (Verrucano Lombardo and Bellerophon Fms) and Lower Triassic sedimentary sequences (Servino and Werfen Fms) of the Lombardian and Venetian Alps. Accessory siderite is common also in the fault-controlled uranium mineralization hosted by the Collio volcanoclastic units in the Orobic Alps (Novazza-Val Vedello deposits). In the deposits siderite is a major component, often associated with dolomite and calcite, in highly variable assemblages encompassing quartz, baryte, fluorite, bitumen, oxides (wolframates, cassiterite), Cu-Zn-Pb-Fe-Mo-Hg sulfides, Cu-Bi-Ag-Co-Fe-As-Sb sulfosalts and native Bi and Au. Local geological settings, assemblages and ore textures are characteristic of polyphase hydrothermal deposition from hypo- to epithermal conditions. When applicable, geothermometry based on coexisting siderite, Fe-rich dolomite and calcite provided crystallization temperatures ≥ 250°C. However, all types of deposits show similar major-element and *REE* patterns, suggesting a common mineralizing event. New and previously published $\delta^{13}C$ and $\delta^{18}O$ isotope data on southern Alpine siderite display signatures according to local lower to higher temperature conditions. But geochemical modelling, supported by *REE* and stable isotope analyses and mineral chemistry, also suggests that the hydrothermal fluids depositing Fe-carbonates in the basement and in the overlying Lower Permian cover were primarily derived from freshwater, which leached Fe and C from volcanic rocks and organic carbon-bearing continental sediments. U-Th-Pb microchemical dating of uraninite associated with siderite in the Novazza-Val Vedello deposits constrains the onset of hydrothermalism to 275 ± 13 Ma (Early–Mid Permian), coeval to the plutonism and the volcanic-sedimentary cycle occurring in the same area (Orobic Basin). In the youngest Fe-mineralizing stage, represented by orebodies in Lower Triassic shallow-marine limestones, the siderite-forming fluids contained a seawater component, interacted with the underlying Permian units and eventually replaced the marine carbonates at temperatures ≥ 250°C. The absence of siderite in younger rocks suggests an Early Triassic upper limit for the iron pulse in the southern Alps, which thus predates the Middle Triassic magmatism. Based on the overlap between hydrothermalism, extensional tectonics and, in part, magmatism, the genesis of siderite in the southern Alps may be related to plutonic activity and/or magmatic underplating occurring since the Permian in a geodynamic scenario preluding the opening of the Neo-Tethys ocean.

Session S17:
Geodynamic systems from western Mediterranean to Himalaya: a natural laboratory for a multidisciplinary approach

Conveners:

Fabrizio Berra (Univ. di Milano)
Stefano Tavani (Univ. "Federico II", Napoli)
Alberto Zanetti (CNR, Pavia)

Miocene-Pleistocene magmatism mirroring the compression to strike-slip tectonic shift at the Eurasia-Arabia-Anatolia triple junction

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Keywords: Neogene volcanism, eastern Mediterranean, triple junction, petrology, geochemistry, geodynamics.

Widespread Neogene volcanism occurs west of the Karliova Triple Junction in eastern Anatolia (Elazig, Tunceli, and Bingöl provinces). Here the Eurasia-Arabia convergence resulted in the hard collision marked by the Bitlis suture (~ 12 Ma), shortly followed by the onset of the North Anatolian dextral transform Fault (NAF). At ~ 5 Ma the formation of the East Anatolian sinistral transform Fault (EAF) marked the separation of the Anatolian block as a kinematically independent plate.

Volcanic activity developed during four different phases of activity, the Mazgirt, Tunceli, Karakoçan and Elazig volcanics. Mazgirt volcanics span in age from 16.2 to 14.8 Ma, exhibit a calcalkaline geochemical affinity, with products varying in composition from basalts to rhyolites, with $^{87}Sr/^{86}Sr$ ranging from 0.7054-0.7077 and $^{143}Nd/^{144}Nd \approx$ 0.51246-0.51265. Tunceli volcanics (11.4-11.0 Ma) are basaltic lavas with a transitional-alkaline affinity, and quite variable geochemical characters, including large variations in $^{87}Sr/^{86}Sr$ (0.7039-0.7068) and LILE/HFSE ratios (*e.g.*, Ba/Nb from 13 to 36). The Pliocene Karakoçan (4.1 Ma) and Pleistocene Elazig (1.6 Ma) volcanics are SiO_2 undersaturated Na-alkali basaltic lavas with a clear HiMu-OIB imprint, with high LILE and HFSE contents, and lower LILE/HFSE ratios (Ba/Nb = 6.9-21 and 7.5-15, respectively) compared to the two previous groups, low $^{87}Sr/^{86}Sr$ (0.7036-0.7048 and 0.7033-0.7038) and high $^{143}Nd/^{144}Nd$ (0.51270-0.51290), showing compositions resembling oceanic intraplate magmas.

The geochemical characters of the volcanism clearly mirror the geodynamic framework of the region: the Mazgirt volcanics, derived from a mantle source metasomatized by subduction component, were emplaced in Early-Middle Miocene magmas, during the Eurasia-Arabia convergent setting. The Late Miocene Tunceli basalts, on the contrary, postdate the emplacement of the Bitlis suture and the onset of post collisional tectonics in eastern Anatolia, with the formation of North Anatolian Fault; Karakoçan and Elazig volcanics, sourced in a sub-slab asthenosphere, were emplaced after the full development of strike-slip tectonics in the region, after the formation of East Anatolian Fault and the development of small pull apart basins, which favoured asthenosphere passive upwelling.

The source-to-sink sediment system in the Po plain-northern Adriatic foreland basin: 3*D* tectono-sedimentary evolution and sediment flux during Plio-Pleistocene time

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Keywords: Po plain, foreland basin, 3*D* modelling, sediment flux.

The eastern Po Plain-Northern Adriatic Foreland (PPAF) contains the most important gas fields of Italy; hydrocarbon occurrences derive from a variety of clastic systems which are the result of the complex tectono-sedimentary evolution of the basin. Since Late Miocene, changes in basin shape were the primary consequences of the severe Northern Apennine (NA) migration, coupled with climate-driven eustatic variations mostly occurred since Calabrian time, when climate cooling and cyclicity increased the most. During Plio-Pleistocene time, the foredeep setting was relatively confined (*i.e.*, without significant sediment escape) because largely surrounded by collisional belts (Alps, NA and Dinarides) providing a fairly high siliciclastic input and producing a quite continued sedimentary record. This work presents a detailed basin-scale 3*D* model of the PPAF infilling derived from the interpretation of a dense seismic network with more than 300 2*D*-profiles and more than 100 well logs (dataset provided by ENI). The resulting 3*D* subsurface architecture was obtained by means of correlation and time-to-depth conversion (using a 3*D*-velocity model) of 6 chronologically constrained regional unconformities, generated by tectono-eustatic phases during the building of the NA. According with the sequence stratigraphy approach by Ghielmi et al. (2013), the surfaces are referred as: base Pliocene, intra-Zanclean, intra-Piacenzian, intra-Gelasian, base Calabrian and Late Calabrian.

The 3*D* model, including 3*D* decompaction of sedimentary units to avoid compaction-related bias, enables to investigate step-by-step the basin geometry and to quantify the volume distribution though space and time (*i.e.*, basin-scale thickness maps and sediment flux delivered from the surrounding mountain belts). Those maps make clear that the PPAF evolution developed through alternating stages of simple and fragmented foredeep. During the Zanclean-Gelasian time, from the inner region (Emilia-Romagna) to the outermost sector (Veneto and Adriatic Sea) repeated phases of outward migration of two large and deep depocenters caused intense tectonic subsidence continuously compensated by the high sediment supply. Afterwards, since the Middle Pleistocene, the inner side of the Emilia-Romagna arcs evolved into an elongated and deep thrust-top basin due to a strong foredeep fragmentation, and then, in the Late Pleistocene a strong decrease of the tectonic activity becomes evident. Considering that the coeval sediment flux kept high rate and allowed to completely fill the PPAF basin, it is possible to argue that the Quaternary glaciation-related climate was at least as efficient as Pliocene tectonics in triggering sediment production.

Ghielmi, M., Minervini, M., Nini, C., Rogledi, S., Rossi, M. (2013): Late Miocene-Middle Pleistocene sequences in the Po Plain-Northern Adriatic Sea (Italy): The stratigraphic record of modification phases affecting a complex foreland basin. Marine Petrol. Geol., 42, 50-81.

Plume head dragged with continental lithosphere: insights from the Mesozoic magmatism of the central High Atlas, Morocco

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Keywords: Mesozoic central High Atlas basalt, Canary Islands mantle plume, continental lithosphere.

The Moroccan Atlas domains were affected, during the Mesozoic, by an intense magmatic activity occurring during Late Triassic-Early Jurassic (200-195 Ma), and Middle-Late Jurassic to Early Cretaceous (from ~ 170 to ~ 120 Ma). The first period was related to the evolution of the Central Atlantic Magmatic Province (CAMP), which originated from mantle upwelling impinging at the base of the continental lithosphere of the supercontinent Pangea, and determined continental breakup and successively sea-floor spreading with the formation of the central Atlantic basin.

During the second period, basaltic lava flows and subvolcanic intrusive complexes were emplaced mostly in the Central High Atlas (CHA). Overall, the Mesozoic CHA basalts display transitional to moderately alkaline geochemical signatures with enrichment in incompatible elements typical of continental intraplate magmas. Their geochemical and radiogenic isotope signature is paramount to bridge the gap from the CAMP magmatism to the Neogene-Quaternary magmatism occurring in the Atlas domains of Morocco and eventually culminating in the present-day plume activity of the Canary Islands. The European and African CAMP basalts derived from a depleted mantle source which experienced metasomatic enrichment(s) due to pre-Triassic subduction processes. In contrast, the Canary Islands (CI) and the Neogene-Quaternary Anti Atlas and Middle Atlas (NQAMA) basalts point to an enriched mantle source typical of intraplate basalts. The Mesozoic CHA basalts form a *trait d'union* between these two contrasting mantle sources.

Geochemical data provide support to a geodynamic scenario suggesting that the present-day Canary Islands mantle plume was impinging and flattening at the base of the lithosphere underneath CHA since 170 Ma and produced the Mesozoic CHA basalts with geochemical signature intermediate between continental lithosphere-type and plume-type mantle. Successively, owing to central Atlantic sea floor spreading and NNE Africa (Morocco) plate movement, the plume head was passively dragged along the Moroccan continental lithosphere forming an asymmetric flattened plume head akin the well-known case of the Hawaii mantle plume. This determined a progressive lithosphere delamination and created a direct route to the surface of plume-type magmas generating the NQAMA volcanoes occurring in the Anti Atlas and Middle Atlas mountain ranges. The plume is currently located underneath the Canary Islands although the asymmetric flattened plume head is still producing magmas in the Atlas mountain ranges. This geodynamic evolution can explain the occurrence of the anomalously thinned lithosphere (*ca.* 60 km thick), located beneath the Atlas domains and forming a narrow ENE–WSW corridor overlain by the abovementioned Mesozoic and Cenozoic intraplate volcanoes, which represent the trail of the dragged plume head delaminating the lithosphere.

The architecture of the Lower Permian Orobic Basin (central southern Alps, N Italy) and its bearings on the post-Variscan extensional tectonics

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Keywords: post-Variscan extension, Early Permian, Orobic Basin, synsedimentary tectonics, low angle normal faulting.

Despite significant Alpine shortening, key-structures inherited from the Permian structural grain are still preserved in the northern part of the Lower Permian Orobic Basin (southern Alps, BG). We recognized two fault systems related to the Early Permian extension. The former consists of low-angle normal faults (LANFs) along which the Variscan basement is juxtaposed to the Lower Permian ignimbrites and volcaniclastic successions (Mt. Cabianca Volcanite and Devil Peak *Fm.*). The LANFs dip to the ESE and continuously outcrop in a large area. The original Permian fault rocks are variably preserved; they consist of several cataclasite layers, often associated with tourmalinites. Alpine cleavage and crenulation developed along each fault segment, but they do not completely obliterate the original fault zone structures. The latter shows NE-SW trending high-angle normal faults, that provide, combined with the LANFs, an asymmetric basin architecture. High angle horst-and-graben structures developed in the hangingwall of the LANFs and root along the main low-angle fault plane. A syn-sedimentary activity of these secondary faults is recorded by peculiar structures in the basal sediments of the Devil Peak *Fm.* Symmetrical horst-and-graben related to conjugate fault systems and planar dominoes are often associated to liquefaction and dewatering structures like ball-and-pillow, flames, and sand dikes. All together, these features suggest that deformation occurred in hydroplastic conditions. As these structures are confined to small stratigraphic intervals, they identify short time spans of intense fault activity, possibly related to seismic activity as suggested by the occurrence of seismites in the nearby area. Syn-depositional tectonic activity is further documented by sharp vertical and lateral facies changes that characterize the Lower Permian succession in the study area and eastward.

Field surveys combined with structural and stratigraphic analyses allowed us to reconstruct the architecture of the fault systems that controlled the opening and evolution of the Orobic Basin. The Permian extension produced half-grabens in which sedimentation and facies distribution were strongly influenced by syn-tectonic activity along major ESE-dipping LANFs and associated antithetic high-angle structures. Thanks to their dip, the resulting crustal stretching was considerably higher than it could have been in a tectonic context ruled solely by high-angle normal faults.

According to our findings, the Lower Permian Orobic Basin developed in a pure extensional regime where LANFs played a key role in accommodating most of the extension. This implies that the classic view of the post-Variscan tectonics chiefly controlled by transtension, in the wide context of a dextral mega shear zone developed between Gondwana and Eurasia, does not fit with our original information suggesting alternative interpretations characterized by the dominance of pure extension.

Unravelling the radiogenic isotope signature of the mantle source from evolved magmas: the case study of Ischia Volcano

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Keywords: Ischia volcano, mantle-source signature, Sr-Nd-Pb-Hf radiogenic isotopes.

The active volcano of Ischia, the well-known island off-shore the city of Naples, has been having a discontinuous volcanic activity characterized by caldera-forming paroxysmal eruptions, lava flows, and lava domes for > 150 ka. The overall geochemical composition of erupted magmas varies from shoshonite, latite, and trachyte/trachyphonolite. Casalini et al.(2017) demonstrated that the radiogenic Sr isotope variation of Ischia magmas with Sr < 100 ppm occurred in a closed system environment, and depicted a scenario contemplating a complex magma chamber reservoir made up of multiple melt lenses isolated by largely crystalline mush portions.

Here, we focus on the origin of the radiogenic isotope (Sr, Nd, Hf, Pb) signature of Ischia latites and trachytes with 100en route to the surface. Parental mantle-derived basalts with MgO > 10 wt.% outcrop in the nearby, a few kilometers apart, Procida island suggesting that the evolved latites and trachytes at Ischia might be originated by crustal assimilation processes affecting Procida basalts. However, Energy Constrained Assimilation and Fractional Crystallization modelling (Spera & Bohrson, 2001) set robust constraints against this hypothesis and provide geochemical arguments for a pristine mantle-derived radiogenic isotope signature for trachytes and latites, implying that they also evolved in a closed-system environment akin trachytes with Sr < 100 ppm. This result corroborates the model of Casalini et al.(2017) suggesting a complex magma chamber reservoir formed by discrete melt lenses and mush portions.

The Sr, Nd, Pb, Hf isotope composition of latites and trachytes permits to set constraints on the metasomatic process affecting this sector of the Apennine chain even though no mantle-derived magma outcrop in the island.

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No significant Oligocene cooling/exhumation in the Bitlis-Pütürge collision zone (southeastern Turkey)

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Keywords: thermochronology, Bitlis-Pütürge collision zone, SE Anatolia, Arabian Platform, geodynamic.

The integration of (i) (U-Th)/He analyses on zircons, (ii) fission-track analyses on apatites, and (iii) preexisting U-Pb and Ar-Ar age determinations on zircons, amphiboles, and micas across the Bitlis-Pütürge collision zone of SE Turkey-*i.e.*, the area of maximum indentation along the > 2,400 km-long Assyrian-Zagros suture between Arabia and Eurasia-provides for the first time an overall picture of the thermochronometric evolution of this collisional orogen. The dataset points to ubiquitous latest Cretaceous metamorphism of a passive margin sedimentary sequence and its igneous basement not only along the suture zone but across the entire width of the Anatolia-Tauride block north of the suture. The basement complex of the Bitlis and Pütürge massifs along the suture was rapidly exhumed between *ca*. 65 and 55 Ma and eventually overlain by Eocene shallow marine sediments. The entire Oligocene is characterized by a rather flat thermochronometric evolution, contrary to the widely held belief that this epoch marked the inception of the Arabia-Eurasia collision and was characterized by widespread deformation. During the Middle Miocene, the Bitlis-Pütürge orogenic wedge underwent a significant and discrete phase of rapid growth (Okay et al., 2010) both by (i) frontal accretion, as shown by cooling/exhumation of the foreland deposits on both sides of the orogenic prism, and (ii) underplating, as shown by cooling/exhumation of the central metamorphic core of the orogenic wedge. Low-temperature thermochronological data for the Eurasian foreland north of the Bitlis-Pütürge suture zone suggest that the tectonic stresses related to the Arabian collision during mid-Miocene time were transmitted efficiently over large distances, focusing preferentially at rheological discontinuities located as far as the Lesser Caucasus (Cavazza et al., 2015) and the eastern Pontides (Albino et al., 2014). Since the late Middle Miocene a new tectonic regime is active as the westward translation of Anatolia is accommodating most of the Arabia-Eurasia convergence, thus decoupling the foreland from the orogenc wedge and precluding efficient northward stress transfer.

Albino, I., Cavazza, W., Zattin, M., Okay, A.I., Adamia, S., Sadradze, N. (2014): Far-field tectonic effects of the Arabia-Eurasia collision and the inception of the North Anatolian Fault system. Geol. Mag., 151, 372-379.

Cavazza, W., Albino, I., Zattin, M., Galoyan, G., Imamverdiyev, N., Melkonyan, R. (2015): Thermochronometric evidence for Miocene tectonic reactivation of the Sevan-Akera suture zone (Lesser Caucasus): a far-field tectonic effect of the Arabia-Eurasia collision? Geol. Soc. Sp., 428, DOI: 10.1144/SP428.4.

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Contemporaneous subduction-related and intraplate Quaternary magmatism in Cappadocia (central Anatolia)

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Keywords: central Anatolia, Quaternary magmatism, petrology, geodynamics.

Widespread volcanism occurred in central Anatolia during the Quaternary in response to continental collision among Eurasia, Africa and Arabia plates. As a result of this event, the southern part of Eurasian plate was dismembered and, subsequently, the Anatolian block began to be expelled westward along the North and East Anatolian faults. In this scenario, the petrochemical evolution of the volcanism is strictly related with the tectonic evolution of the area. The Cappadocia region, confined by the Tuz Golu and Ecemis strike-slip fault systems (also known as Central Anatolia Fault System), is characterized during the Quaternary by volcanic products with bimodal petrological and geochemical features. Indeed calc-alkaline and Na-alkaline volcanic rocks, with subduction-related and within plate characters, respectively, do occur intimately associate in space and slightly differentiated in time. Calc-alkaline volcanic rocks range in composition from basalts to rhyolites. They are found around the Acigol caldera, the Gollu Dag dome and around the Hasan Dag and Ercyies Dag stratovolcanoes. Within-plate related Na-alkaline volcanic rocks range in composition from basanites to alkali basalts. They are found as monogenetic centres in Karapinar, along the WSW flank of Hasan Dag and near the Kizilirmak river, north-west of Nevsehir. No clear evidence for a time-related shift from calc-alkaline to Na-alkaline volcanism is observed, differently from what occurring in the western and eastern Anatolia regions where calc-alkaline volcanic rocks are distinctly older than Na-alkaline ones. In Cappadocia, calc-alkaline and alkaline rocks mostly have similar age range (1.98-0.018 Ma) and sometimes a complete time overlapping between subduction related and within-plate volcanic rocks is observed, as in the case of the Acigol-Nevsehir Complex. In addition, there is a limited variation in the radiogenic isotopic compositions of subduction-related and within-plate volcanic rocks with $^{87}Sr/^{86}Sr$ within the ranges from 0.70395 to 0.70458 and from 0.70334 to 0.70553, respectively and $^{143}Nd/^{144}Nd$, 0.51268-0.51287 and 0.51268-0.51293, respectively. The genesis and ascent of the different type of magmas is clearly related with the complex tectonic setting of the area in which strike-slip faults are associated to the formation of local extensional pull-apart basins. In this frame, the geochemical features of the calc-alkaline magmatism of this region are consistent with derivation of magmas from a mantle modified by a subduction component, whereas Na-alkaline activity may derive from a deeper asthenospheric mantle source not affected by this metasomatic event.

The Cima Pedani tectonic window (Alpine Corsica): insights in tectono-metamorphic evolution during the exhumation of continental crust

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Keywords: deformation, metamorphism, exhumation, continental crust, Alpine Corsica.

The Alpine Corsica consists of a stack of high-pressure continental and oceanic units. As in the western Alps, the stack of continental metamorphic units occurs at the base of the high-pressure oceanic and transitional units, *i.e.*, the Schistes Lustrés complex. These units are regarded as fragments of the thinned European margin that experienced continental subduction and subsequent syn-convergent exhumation in the Early Tertiary (Malasoma et al., 2006; Molli et al., 2006). In the central Corsica, the tectonic window of the Cima Pedani area offers a remarkable snapshot of the tectonic setting of these continental units. This tectonic window is characterized by a stack of three metamorphic continental units, namely as Canavaggia, Pedani and Scoltola Units.

These continental units include a Paleozoic basement, made up of Carboniferous metagranites and their country rock, both covered by a Permian meta-volcanosedimentary complex grading to a Triassic-Jurassic, mainly carbonate, metamorphic sequence unconformably covered by metabreccias and siliciclastic metarenites of Eocene age.

These units are affected by a polyphased tectono-metamorphic history acquired in a time lapse running from Priabonian (Late Eocene) and Aquitanian (Early Miocene). The reconstructed *P*-*T* paths and the related deformations for the continental units describe a retrograde history acquired during their progressive exhumation, *i.e.*, along their transfer from the deepest position reached in the orogenic wedge up to the surface, whereas no trace of the older prograde history has been conserved. In all the reconstructed *P*-*T* paths, the *P*-peak corresponds to the maximum depth reached by these unit, and ranges from 34.3, 45 and 44.7 km, whereas the subsequent history includes a progressive *P*-decrease associated to a coeval *T*-increase. The deformation history related to exhumation includes three deformation phases. In particular, the D2 phase is characterized by non-coaxial and flat-lying ductile structures parallel to the boundaries of the units observed in the Cima Pedani tectonic window. It is noteworthy that the sense of shear during the D2 phase is generally top-to-the W, *i.e.*, toward the Alpine foreland.

The collected data provide the evidence that the continental units were deformed and metamorphosed by ductile exhumation during their ascent path in the subduction channel in which the upper boundary is represented by the former accretionary wedge built-up during the oceanic sudbuction, and actually represented by the Schistes Lustrés Complex.

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Molli, G., Tribuzio, R., Marquer, D. (2006): Deformation and metamorphism at the eastern border of Tenda Massif (NE Corsica): a record of subduction and exhumation of continental crust. J. Struct. Geol., 28, 1748-1766.

The stacking of Piemonte-Ligurian units in the Urtier valley (Cogne, western Alps): a new structural setting for the Penninic domain south of the Aosta Valley

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Keywords: western Alps, Piemonte-Ligurian units, nappe stack of Penninic domain, structural geology.

In the western Alps two different stacks of continental and oceanic units are classically recognized. In an upper stack, Adria basement rocks are emplaced over Piemonte-Ligurian Combin unit, with both continental and oceanic units characterized by a blueschist facies metamorphism. In the lower stack, fragments of Adria basement rocks are emplaced over the Zermatt-Saas unit. In the lower stack both continental and oceanic units are characterized by eclogite facies metamorphism. While this structural setting is generally shared on the Swiss side of the western Alps and in the northern region of the Aosta Valley, the geometric reconstructions proposed for the Piemonte-Ligurian nappe stack in the southern Aosta Valley are often contradictory and the different interpretations remain highly controversial. This contribution deals with the geological and structural reconstruction of the Urtier Valley, located south of the Aosta Valley, where it is possible to study the complete nappe stack of the Axial Belt domain, from the lowermost Briançonnais-type Penninic basement of Gran Paradiso and its cover, to the uppermost Sesia continental basement slices. In detail, two types of Piemonte-Ligurian units were recognized, differing in lithostratigraphic and metamorphic features. The first one is represented by the blueschist Broillot unit, characterized by a well-preserved lithostratigraphic succession including ophiolites and their metasedimentary cover and correlable with Combin unit. This unit is overthrusted by the eclogitic Bardonney unit, consisting of a chaotic assemblage with ophiolitic clasts and/or slices from centimeter to kilometer in size, embedded in carbonate/quarzitic and/or metabasic matrix. The Bardonney unit is correlable with the Zermatt-Saas unit. The nappe pile proposed for the Urtier valley differs from the geological stacking that is described north of Aosta Valley. In fact, contrary to what is observed in the north, in the Urtier valley the eclogitic units are on top of the blueschist units. The apparently contradictory regional scale nappe pile, north and south of the Aosta Valley, can be solved hypothesizing the existence of a regional scale fold structure formed during the early stages of exhumation, involving eclogitic units in the core of blueschist units. The nappe pile observed north and south of Aosta Valley correspond to the normal and the inverted limbs of such a regional fold.

Currently, the normal and the inverted limb of the regional fold outcrop at the same structural level, north and south of the Aosta Valley respectively, due to the Late Oligocene-Neogene Aosta-Ranzola normal fault system activity.

The North Anatolian Shear Zone (Turkey): geometric, kinematic and age characterization of a crustal scale strike-slip fault

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Keywords: North Anatolian Shear Zone, plate boundary, strike-slip deformation, northern Turkey.

The North Anatolian Shear Zone (NASZ) (Şengör et al., 2005; Ellero et al., 2015) is a major continental strike-slip deformation zone bounding the Anatolian plateau, along the continental collisional zone where the African Plate collides with the Eurasian Plate. Although the NASZ is one of the world's major active fault system, geometry and kinematics of the tectonic structures associated to the NASZ are relatively little studied and its time-space evolution is still matter of debate. This contribution illustrates the results of a geological-structural field study carried out in the central part of the NASZ in the Kurşunlu-Tosya/Araç-Kastamonu area, where the NASZ overprinted the Intra-Pontide suture zone originated by the middle Paleocene continental collision between Istanbul-Zonguldak and Sakarya terranes, two terrains with Eurasian affinity. In the study area, the NASZ can be considered as a broad up to 30-40 km-wide deformation zone, with a general right-lateral strike-slip deformation distributed along interlinked systems of faults bounding elongated blocks. Overall, the deformation history assumed for the NASZ is characterized by two main tectonic stages showing the switch from left-lateral to right-lateral strike-slip movement associated to the rotation from NNE- to NW- trending maximum stress axis. This evolution model can be applied also for the Taşcilar basin, a pull-apart basin that we have identified inside the NASZ, making a contribution for dating the onset of the NASZ activity. The age of the NASZ activity is commonly inferred from the dating of deposits of the associated pull-apart basins, with a general rejuvenation from east to west, ranging from the late Miocene in the eastern branches of the shear zone, to Pleistocene to the west, in the Marmara Sea region. New biostratigraphic and structural data from the Taşcilar basin suggest an evolution within a strike-slip tectonic regime since the Ypresian, during a first transtensional stage by the activation of releasing step-over areas along left-lateral strike-slip master faults. In a second stage, the rotation of the maximum stress axis re-activates the master faults as dextral strike-slip faults in agreement with the general strike-slip movement of the NASZ. The proposed geodynamic model provides new insights for the timing of the onset of the NASZ activity that is located within the Ypresian, just after the collision between Anatolian and Eurasian plates.

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Transpressional deformations within the High Atlas belt, Morocco: new insights on the Cenozoic geodynamics of northwestern Africa

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Keywords: High Atlas, transpression, geodynamic evolution, Morocco.

The growth of the High Atlas mountain belt still remains a debated issue in the geology of northwestern Africa. The High Atlas belt has been considered either as an Alpine-type orogen that formed during convergence between Africa and Eurasia, or as an intracontinental belt characterized by moderate crustal shortening and mainly resulting from isostatic and dynamic topography effects. However, most geodynamic models do not consider in full the geometry and kinematics of deformation structures observed in the field. Here, we describe the field geology evidence along a transect across the western High Atlas. In the study area, the main deformation structures consist of NE-SW trending high-angle dextral strike-slip faults and sub-parallel thrust faults, linked together to form asymmetric, positive flower structures. These structures are associated with folds involving the Mesozoic-Cenozoic successions at the northern and southern boundaries of the orogen, and point to a transpressional evolution of the double vergence western High Atlas belt. Paleostress reconstructions based on fault-slip data are supportive of strike-slip tectonics controlled by WNW-ESE $\sigma 1$ axes. Similar evidence is documented along the whole High Atlas belt (Ellero et al., 2012), which can be interpreted as a giant flower structure resulting from the reactivation of pre-existing pre-Alpine faults. Cenozoic reactivation took place during two main deformation events: the first one is referred to the Late Eocene-Oligocene, the second one started in the Pliocene-Pleistocene, and is still active today. Our results support a plate tectonic model for northwestern Africa that includes an independent Moroccan Plate (Schettino & Macchiavelli, 2016), and emphasize the role of transpressional tectonics during convergence between Africa and Eurasia.

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Evidences for a Late Cretaceous continental arc in the central Pontides: new insights on alternative geodynamic reconstructions for the Neotethys in northern Turkey

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Keywords: continental arc magmatism, volcaniclastic succession, geochemistry, structural geology, Late Cretaceous, central Pontides, Turkey.

In the geodynamic evolution of Turkey, the North Anatolian Shear Zone (NASZ) plays a key role, representing a long-lived crustal scale strike-slip shear zone that coincides with the Intrapontide Suture Zone (ISZ), originated by the closure of the Intrapontide ocean that with the Izmir-Ankara-Erzincan ocean belongs to the Neotethyan realm in the Anatolia region. The NASZ dismembers the nappe stacking formed by the continental collision between Istanbul-Zonguldak and Sakarya terranes with Eurasian affinity, generating a complex tectonic setting where tectonic units with different geodynamic meaning are juxtaposed. The identification inside the fault-bounded blocks of tectonic units belonging to the nappe stacking represents the first step for a correct interpretation of the orogenic belt as they can act as markers of the deformation history. In this contribution, we present the results of a multidisciplinary study that allowed the definition of a new tectonic unit that can be used for deciphering the geodynamic evolution of the Neotethys in northern Turkey.

This unit outcrops in elongated blocks comprised in the mountain range between Tosya and the northern boundary of the Çankırı Basin. The unit is formed by three formations, from the bottom:

i) the Basal Volcanic Complex, including basalts to basaltic andesites, interrupted by a confined and brief episode of calcarenite deposition. The geochemistry points to an active continental margin setting as evidenced by the enrichment in Th and *LREE* over HFSE, and by the relative enrichment in Nb compared to N-MORB;

ii) the Volcaniclastic Sandstone Formation, including breccias and turbiditic sandstones, feeded by a mixed carbonatic-volcaniclastic intrabasinal source area, represented by the reworking of the volcanic rocks and coeval carbonate platforms;

iii) the Marly-calcareous Turbidite Formation, derived from a continental margin source area that starts to influence the mixed carbonatic-volcaniclastic intrabasinal component.

The age of the sedimentary cover is constrained by the nannofossil assemblages to the Late Santonian-Middle Campanian (CC17-CC21 Zones).

Therefore, the trace element systematics of the volcanics and the petrographic characteristics of the sedimentary succession point to an origin of the studied unit from an active continental margin. This active continental margin could be located in three possible alternative geodynamic settings within the Neotethyan realm, depending on whether it is related to the closure of Izmir-Ankara-Erzincan or Intrapontide oceans. In the first hypothesis, this unit could belong to the southern or northern Sakarya margins. Alternatively, in the second case, the unit could be restored on the southern margin of Istanbul-Zonguldak terrane.

The petrography of sands ejected during the blast-induced liquefaction test (Mirabello, Ferrara, Italy) as a tool to identify the provenance of the source level

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Keywords: sand liquefaction, blast-test, provenance, fluvial sands.

The study reports the composition of sands ejected during the blast-induced liquefaction test carried out at Mirabello (Ferrara, Italy) in May 2016. The area was largely affected by liquefaction phenomena during the M_w 6.1 Emilia earthquake. The aim of this research is to provide a better understanding of earthquake-induced liquefaction mechanisms, using textural and petrographic parameters to identify the possible source layers of the sand blows. Sand samples analyzed in thin section (34 samples, 300 points for each sample, fraction 0.125-0.250 mm) include blast-induced sand blows, sands from 2 cores at different depths in the subsurface (from 2 to 20 m) and sands from 2 trenches in the blast site representative of 2012 liquefied sands.The sands from the cores show a clear trend from lithoarenitic to quartz-feldspar-rich compositions. The sands at shallow depth (up to 7 m) are the most lithoarenitic, with sedimentary fine-grained rock fragments (shales and siltstones) as the dominant lithic type. Lithic fragments derive mostly from the erosion of sedimentary terrigenous and carbonate successions of Apenninic affinity. These shallow sands are well distinguishable from the deeper sands (at depth > 7 m) that show composition slightly enriched in quartz and feldspars and impoverished in lithic fragments. A similar composition suggests affinity with the Po river sands. The composition of ejected sands largely overlap that of the shallow Apenninic sands at depth of 6 to 7 m. Similarly the sands from the 2012 dikes show a composition of Apenninic affinity compatible with that of the shallow sands.Results from the blast test fit well with data obtained from the study of the sands injected in the San Carlo area (Fontana et al., 2015) during the M_w 6.1 earthquake. Also in this case, the composition and fabric characteristics, such as grain-size distribution, indicate that liquefaction processes affected mainly sand layers at relatively shallow depth (at depth of 6.8-7.5 m) referable to the paleo Reno River (1536-18th Century). The study indicates that the petrography of sands represents a significant tool to identify the possible source layers of the sand blows and for the recognition of critical levels prone to hazardous sand liquefaction phenomena.

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Sapphirine-bearing gabbroic dykes from the Finero mantle massif: evidence of melt-rock interaction at mantle conditions

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Keywords: sapphirine, Rb-Sr, O, Finero, mantle, Triassic, metasomatism.

The Finero Phlogopite-Peridotite (FPP) is a mantle massif recrystallized through several events of melt migrations. These events have enriched the FPP in hydrous phases (amphibole and phlogopite) and crustal components. They have been commonly interpreted as related to a subduction/post orogenic geodynamic setting. One of the latest of these metasomatic events crystallized composite sapphirine-bearing gabbroic dykes. Dykes are formed by a Leucocratic Zone at the nucleus and a melanocratic zone formed by two reaction zones (the Opx Zone in contact with the host and the Late Amph Zone in contact with the Leucocratic Zone) and a cumulus zone (the Early Amph Zone). This structure is interpreted as the result of the interaction of channelized migrating melts with the host rock, and the first cumulates in a two-steps intrusion process. In the first step, the melt reacted with the FPP rocks forming the Opx Zone and evolved by fractional crystallization of amphibole cumulates. In the second step, the evolved melt reacted with the first cumulates producing metasomatic sapphirine and segregating plagioclase-rich bands containing abundant apatites at the nucleus of the dikes.

New O and *in situ* Sr isotopes on minerals suggest a more complex evolution. *In situ* Sr isotope analyses were performed at the CIGS laboratory of the Università di Modena e Reggio Emilia using a Thermo Fisher Scientific Neptune™ coupled to a 213 nm Nd:YAG laser ablation system (New Wave Research™). During the analytical sessions a new in house plagioclase reference material for Rb-Sr systematic, named BC84, has been successfully tested and used.

The $\delta^{18}O$ increases from 5.81‰ in orthopyroxenes at the dykes' border to ~ 6.90‰ in cumulitic amphiboles and 8.60‰ in plagioclases. The $^{87}Sr/^{86}Sr$ values for plagioclase and coexisting apatite show isotopic disequilibrium between the two phases (plagioclases at 0.70474±0.00033, n = 23, and apatites at 0.70369±0.00025, n = 6). These isotopic variations could be explained with a progressive contamination of the parent melt of the gabbroic dykes during its fractionation through an AFC-like process between mantle-derived melt(s) and a crustal-enriched host (the FPP).

The occurrence of abundant apatite and carbonate inclusions together with the alkaline geochemical affinity suggest possible relationships between the gabbroic dykes and other alkaline/apatite-rich metasomatic events in the Finero area. This evidence suggests a possible Triassic age for the gabbroic dykes' intrusions.

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Impact of mineral fertility and bedrock erosion on single-mineral detrital studies: insights from detrital apatite of the Po river catchment

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Keywords: detrital thermochronology, apatite, trace elements, Nd isotopes.

Detrital studies based on single-mineral analyses (*e.g.*, geo/thermochronologic analyses on apatite and zircon) and on the lag-time approach are increasingly employed for paleotectonic and paleoclimatic reconstructions. Their geologic interpretation can be challenging, because the impact of each eroding source on the detrital record is controlled by a range of factors including the rate of erosion and the fertility of chosen minerals in eroded bedrock. Here, we combine (i) a dataset of trace element and Nd isotope fingerprints of detrital apatite, (ii) a comprehensive dataset of apatite-fertility measurements (Malusà et al., 2016), (iii) fission-track data, and (iv) cosmogenic-derived erosion rates from the Po river catchment (Wittmann et al., 2016), to test the impact of mineral fertility and bedrock erosion on the single-mineral detrital signal preserved in the final sediment sink. Our results show that the information provided by accessory minerals, when complemented with accurate mineral fertility measurements, are fully consistent with information provided by the analysis of more abundant framework minerals. Trace element and Nd isotope analyses provide a reliable tool to disentangle the complex single-mineral record of orogenic erosion. Such a record is largely determined by high-fertility source rocks exposed within the drainage. In order to ensure a correct identification of the sediment sources, and of the exogenic and endogenic processes monitored in the stratigraphic archive, lag-time detrital thermochronology studies should thus include independent provenance discriminations, and would benefit from independent mineral fertility characterization of the potential source areas.

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The Central Atlantic Magmatic Province (CAMP) in Morocco

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Keywords: Large Igneous Province, Pangea break-up, basalt.

The Central Atlantic Magmatic Province (CAMP) consists of basic rocks emplaced as shallow intrusions and erupted in large lava flow fields over a surface in excess of 10 million square km on the supercontinent Pangea. CAMP peak activity ranged from about 201.6 to 201.1 Ma, but late activity went on for several Ma, into the Sinemurian. Emplacement of the CAMP straddled the Triassic-Jurassic boundary and was synchronous with the end-Triassic extinction.

In Morocco, intrusive rocks are represented by up to 300 km long isolated dykes and by sills cropping out in the Anti Atlas, mainly. Lava fields were erupted as short-lived pulses and can be traced over distances of several hundred km within sedimentary basins of the High and Middle Atlas and the Meseta. They consist of either compound or simple pahoehoe flow fields erupted sub-aerially or under shallow water. A progressive syn-eruptive subsidence is indicated by field observations and volcanological features.

Lava flow sequences show systematic time-related geochemical changes, evidenced by major and trace elements as well as by Sr-Nd-Pb-Os isotopic compositions. These features allowed definition of several magmatic units – Lower, Intermediate, Upper and Recurrent, from bottom to top. Geochemically, the lavas and the intrusive rocks can be well correlated. In general, all the rocks are basaltic with an enriched composition compared to Mid Ocean Ridge Basalts and different from Atlantic Ocean Island Basalts. The enriched composition of CAMP basalts can be attributed only in part to crustal contamination, a process that affected in particular the Intermediate lava flow unit, while the Lower and Upper basalts are virtually uncontaminated. Hence, the enriched signature of CAMP basalts reflects that of subducted upper and lower continental crust material that enriched the shallow upper mantle from which CAMP basalts were generated, probably. Os isotopic compositions well below those of the Primitive Upper Mantle for several Moroccan CAMP basalts point to an involvement of subcontinental lithospheric mantle sources. While a contribution from a deep mantle-plume is not required by with geochemical and thermometric data, it remains unclear which heat source caused mantle melting on a scale of 10 million square km leading to the formation of the CAMP.

A revised subduction inception model to explain the Late Cretaceous, doubly vergent orogen in the pre-collisional western Tethys: evidences from the northern Apennine

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Keywords: doubly vergent orogen, ocean-continent transition, subduction initiation, northern Apennine.

Orogenic processes can be strongly controlled by inherited structures. The paleogeography and tectonic configuration of the converging margins, might influence the location of subduction initiation, the distribution of deformation between upper and lower plate, the shape of the accretionary prism and of the subsequent orogeny, *i.e.*, the development of single or doubly-vergent orogens, and, as a corollary, the modality of exhumation of metamorphosed units.

The alpine belts around the Mediterranean are characterized by complex architectures, that are the result of a long geological evolution, going from subduction to collision, but that are also a heritage of the rifting-related continental margins configuration. The northern Apennine is a segment of these belts originated during Late Cretaceous-Early Oligocene closure of the Ligure-Piemontese ocean, and collision between the Europe and Adria plates. The different configuration of the Adria and Europe continental margins, inherited from an asymmetric rifting, is recorded in the Ligurian Units, that preserve incorporation into the subduction factory of fragments of oceanic domain (Internal Ligurian Units), and portions of the Ocean-Continent Transition Zone (OCTZ) toward Adria (External Ligurian Units).

We have reviewed the structural and sedimentological characteristics of the External and Internal Ligurian Units successions, and the ages of the tectono-metamorphic events recorded in these units. These data suggest that at 80 Ma, a doubly-vergent, accretionary prism was growing between the deposition basins of the two groups of units, and feeding both basins with clasts belonging to the ocean realm, the continental crust and the subcontinental mantle. We propose therefore that closure of the Ligure-Piemontese ocean occurred through subduction that nucleated inside the OCTZ, and developed a doubly-vergent prism by accreting continental extensional allochthons and ocean-derived rocks from the OCTZ, and then rocks and sediments from the oceanic realm.

This revised location of subduction onset, and the subsequent pre-collisional architecture, inherited from the rifting and spreading phases, allow reconciling most of the controversies on the pre-collisional geodynamic evolution of the Apenninic orogeny.

Lateral variations of the mechanical stratigraphy and basal décollement rheology and the growth of thrust wedges: insights from analogue modelling

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Keywords: analogue modelling, thrust wedges, mechanical stratigraphy.

This study aims at investigating on the influence of lateral variations of the rheology of the basal décollement layer on the evolution of thrust wedges. In particular, the presence and thickness of evaporites significantly influences the evolution of fault-fold arrays in terms of mechanical balance, geometry, and relative chronology of thrusts development. Evaporites at the base of pre-orogenic sedimentary successions commonly produce particular geometry of deformation fronts, as in the Jura in the Alps or the Salachk Arch in the Oman Mountains. In many thrust-fold belts, evaporites are also present in the foredeep deposits, as in the Apennines, the Pyrenees, the Zagros etc. and cause the development of strong structural complications. Lateral changes in the mechanical stratigraphy of the pre-kinematic successions, including the basal décollement rheology, can occur because of paleo-environmental variability. In this contribution we present results of an experimental programme designed for testing the influence of the lateral and vertical variability of the pre-kinematic mechanical stratigraphy on the growth of thrust wedges. The model mechanical stratigraphy was constructed by using dry quartz sand to simulate frictional upper crustal rocks and silicone putty for simulating viscous materials such as evaporites. Experiment were run at 4 mm/hour convergence rate to ensure the proper scaling of viscosity and strength between natural evaporitic rocks and silicone putty. Our experiments illustrate the significant changes in the geometry and kinematics of thrust wedges that are induced by varying the position and lateral extent of evaporite layers at the base and/or within pre-kinematic multilayers.

Structure of the Elba Island: constraints for the tectonic evolution of the northern Tyrrhenian sea

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Keywords: Elba Island, structure, tectonics, pluton, aureole.

The Northern Tyrrhenian Sea (NTS) belongs to the hinterland portion of the northern Apennine belt. This area was in turn affected by the formation of Apennine wedge during the Oligocene followed by nappe stacking, normal faulting, out-of-sequence thrusting, basin development and magmatism during the Miocene-Pliocene. Such complex evolution led to contrasting interpretations on the geodynamic setting of the NTS: 1) a back arc basin in which magmatism is a result of adiabatic mantle and lower crust rise (Rosenbaum & Lister, 2004), 2) an area under crustal shortening, where extensional features are confined to upper crustal levels and are expression of internal wedge reequilibration (Bonini et al., 2014)

The Elba Island, located in the middle of the NTS, is invaluable to understand the tectonic evolution of this sector. Elba is characterized by a first-order nappe stack that was intruded by Late Miocene plutons and subsequently cut by brittle faults, in particular by the Zuccale Fault (ZF), which has been classically regarded as a low angle extensional fault.

Recent research conducted in eastern Elba highlighted that shortening characterized the Middle-Late Miocene period (post 14 Ma) with out-of-sequence thrusting involving the whole nappe stack (Massa et al., 2016). Furthermore the contact aureole of the Porto Azzurro pluton (5.9-6.7 Ma; Musumeci et al., 2015) is affected by ductile to brittle thrust shear zones and widespread deformation, coeval with thermal peak. The brittle overprint over ductile structures is a consequence of the vanishing thermal pulse and proves that thrusting over lasted the end of thermal anomaly. This architecture is lately displaced to the east by the flat lying ZF (Musumeci et al., 2015).

The reconstructed geometry holds strong implications for the Miocene-Pliocene evolution of the area. The relationships between magmatism and deformation suggest that the ductile to brittle evolution of eastern Elba occurred during crustal shortening. In this framework the ZF can be explained, consistently with the overall deformation, as the flat portion of a large scale thrust system.

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Massa, G., Musumeci, G., Mazzarini, F., Pieruccioni, D. (2016): Coexistence of contractional and extensional tectonics during the northern Apennines orogeny: the late Miocene out-of-sequence thrust in the Elba Island nappe stack. Geol. J., 52, 353-368.

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Rosenbaum, G. & Lister, G.S. (2004): Neogene and Quaternary rollback evolution of the Tyrrhenian Sea, the Apennines, and the Sicilian Maghrebides. Tectonics, 23, 1-17.

Detrital contribution to the northern Apennine foredeep from elusive Paleogene magmatic arcs: evidence from U-Pb zircon dating (Elba Island, Tuscany)

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Keywords: zircon age, Hf model age, sediment provenance, Apennine foredeep.

Volcanic arc(s) of the Alpine-Apennine belts remain elusive, and any igneous product, either in place or reworked, is therefore critical to place constraints on paleogeographic and geodynamic settings. Elba Island is a keystone in the transition between the Alps and Apennine belts. There, the Phyllite and Metasiltstone of the Porticciolo Fm., part of the Acquadolce tectonic unit, record *HP* metamorphism and have a controversial age and paleogeographic origin, either in the Ligurian oceanic or the Tuscan continental domain. New U-Pb zircon dating of detrital zircons have been performed to provide better age constraints of the Phyllite and Metasiltstones. Surprisingly, detrital zircons as young as *ca*. 30 Ma have been found. The lack of any ages between 30 and 20 Ma, a common age range in potential sediment sources of Sardinia, Provence and the Alps, suggests that the depositional age has to be close to the Rupelian-Chattian boundary, an age most likey pointing to deposition along the Adria continental margin.

Analysis of the whole age spectrum of detrital zircon allows to place constraints also on the provenance of sediments. For Cenozoic zircons, potential sources with zircon-bearing rocks that were exposed at *ca*. 30 Ma are found on both European plate and Adria plate. In this frame, ages around 40 Ma are recorded only in the Adamello intrusion in southern Alps, and also the Permian-Carboniferous and Ordovician zircon ages have a distribution most similar to southern and western Alps detritus, that is in turn similar to the population of the Aveto Fm. The Paleoproterozoic-Archean minor population is most typical of Adria old cratons, and also the Hf model ages point to the involvement in the magma that produced the zircons of very old crust, typical of Adria more than Europe. Thus, the distribution of pre-Mesozoic zircons is inferred to derive from southern and western Alps, even if a partial recycling through the Aveto basin cannot be excluded.

Therefore, the paleogeographic scenario at the mid-late Oligocene includes a basin located on the south-eastern side of the Apennine accretionary wedge, on the continental margin of the Adria plate, that is going to be overridden by the wedge itself. In conclusion, also considering the stratigraphic succession underneath the Porticciolo Fm., the Phyllites and Metasiltstones are interpreted as the most internal record of the Macigno foredeep, fed along strike from the north, then involved in subduction at high pressure conditions and exhumation in a few Ma.

Last sea-level cycle in the northern Adriatic Sea: sediment provenance of the shelf deposits

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Keywords: last sea-level cycle deposits, northern Adriatic Sea, petrographic analysis, sand sediments.

The low-gradient northern Adriatic shelf recorded different generation of partially preserved transgressive barrier-lagoon systems. These features developed and have been drowned *in situ* during the last sea-level rise that occurred since the end of Last Glacial Maximum. The recognition and characterization of these deposits has been carried out analysing a large dataset of very high resolution seismic profiles, cores, bathymetric and isopach maps. These deposits represent isolated and elongated reliefs on the seafloor showing a dominant longshore trend, similar to the modern highstand coastal wedge deposits. In particular, they lay on an erosive surface of regional extent (transgressive surface) that truncates older low-stand deposits, while their top is generally marked by a ravinement surface, often coinciding with the maximum flooding surface.

The sand portions of eight distinct bodies, located offshore between -35 and -15 m mean sea level, were studied through petrographic analysis in order to delineate their composition and sand provenance. Basal sand portions of some cores have also been characterized to compare the different composition of broad alluvial plain that was largely drowned during the modern high sea-level interglacial. Three different petrofacies, marked by distinct terrigenous supplies were recognized and linked to different phases of sea-level rise. The deeper deposits belong to the Petrofacies I; this is characterized by a quarzolithic composition with abundance of metamorphic rock fragments and it is associated with a paleo Po river supply. The shallow-water deposit highlights a litharenitic signature largely dominated by carbonate fraction (Petrofacies III) linked to the Tagliamento river supply, while several mid-water deposits are characterized by a mixed composition (Petrofacies II); this latter is referred to different supplies from major eastern southalpine rivers as the lowstand sediments on which lay the investigated sand bodies.

The petrographic results allow a preliminary paleogeographic reconstruction of the northern Adriatic shelf during the last relative sea-level cycle.

The Late Jurassic to mid-Cretaceous kinematics of the Iberia-Eurasia plate boundary

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Keywords: rifting, Bay of Biscay, Pyrenees, extensional deformation, pate kinematics.

The geological information concerning the nature and kinematics of the Late Jurassic to mid-Cretaceous plate boundary between Iberia and Eurasia is revisited. This information includes: (1) timing and occurrence of rifting-related processes, such as basin subsidence onset and termination, evidence of evolving thermal gradients, crustal thinning, uplift, mantle faulting and exhumation, and oceanic crust formation; (2) kinematic constraints, such as directions of extension in the various basins at the plate boundary and the presence of regionally-relevant transfer faults. Reappraisal of available data indicates a dominant divergent motion of Iberia with respect to Eurasia over a 60 My time interval. This time-lapse encompasses the Late Jurassic onset of rifting and the mid-Cretaceous mantle exhumation and onset of oceanic spreading. Onset of rifting was coeval in an area that extended from the Bay of Biscay to the west, up to the France SE Basin to the east, and the Central Iberian rift to the south. Increased divergence during Early Cretaceous led to deformation localisation, mostly concentrated along a northern system, but also focused in a southern one, with the Ebro crustal block in between. The northern system included (1) the Bay of Biscay arm, where rifting eventually led to oceanic crust production, and further eastwards, (2) the Pyrenean arm, and (3) the Vocontian basin of SE France, where rift development arrested at the mantle exhumation stage and crustal thinning stage, respectively. The Central Iberian rift to the south, where crustal hyper-thinning actively participated to the divergent movement between Iberia and Eurasia, kinematically decoupled these two plates from the Ebro crustal block in between. Occurrence of intraplate extensional deformation at the eastern termination of the Pyrenean arm and in the Central Iberian rift to the south, testifies for an eastward delocalisation of the plate boundary, which became diffuse, impeding the assumption of rigid plates behaviour and preventing the application of Euler's motion to model the evolution of the Iberia-Eurasia boundary.

Early Jurassic extensional tectonics in the Arabian passive continental margin of the Neo-Tethys. Field evidence from the Lurestan region of the Zagros fold-and-thrust belt, Iran

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Keywords: fold and thrust belt, extensional faults, inherited structures, inversion tectonics.

Building of the Zagros in the Lurestan region involved the deformation of different crustal domains of the Arabian passive margin of the Neo-Tethys. These include the proximal domain and the distal Bisotun crustal block, which became divided from each other by the development of the Radiolarite trough in between. The age of this trough remains partly obscure, as rifting at the southern portion of the Neo-Tethys is assumed to be Permo-Triassic, but the older sediments filling it are Early Jurassic in age. The availability of exposures of the Upper Triassic to Jurassic sequence of the proximal domain and of the older portion of the sedimentary sequence of Radiolarite trough, offer the opportunity to constrain the tectono-stratigraphic evolution of this part of the Arabian passive margin by means of field data. Information about style and age of the extensional events which shaped the margin and led to the development of the Radiolarite trough is provided. In detail, an Early Jurassic age is proposed for the Radiolarite trough, as indicated by the occurrence of Early Jurassic angular unconformities syn-sedimentary extensional faults, which occur in both the proximal domain and in the older sediments of the Radiolarite trough.

Triassic magmatism in eastern Alps

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Keywords: Triassic magmatism, eastern Alps, geological constraints, geochemistry, genetic implications.

The Triassic units in the southern eastern Alps include a unique suite of magmatic products, from lamprophyres, basalts and gabbroic rocks, to rhyolites and granitoids. Only few studies exist that consider this magmatic province as a whole and geochemical data are still missing that can help constraining the main magmatic processes. The latter issue is mostly related to the high level of syn- and post-magmatic alteration of the igneous suites, which hampers the interpretation of crustal processes and mantle sources. Moreover, the complex paleogeography and the lack of a comprehensive review about the geology of this area make it difficult to link these magmatic events to the geodynamic evolution. In this work, we discuss new petrological data on carefully selected Triassic magmatic rocks from the Dolomites and Carnic Alps, Italy, and compare them to the existing data on Triassic magmatism in the eastern Alps.

Accurate fieldwork and careful sample selection allowed to examine low contaminated rock types through mineralogical, chemical and Sr, Nd and Pb isotopic investigations, which in turn allowed to interpret their involved mantle source(s) and their grade of crustal contamination. Major element geochemistry show a bimodality between the magmatic products of the Dolomites and Carnia regions, which might reflect a selective depletion of the crust occurred during Palaeozoic times. Overall, the data suggest a dynamic history strongly influenced by the tectonic domains of the ALCAPA (Austroalpine-West Carpathian and Pannonia) whose terrains suffered several orogenic and extensional geodynamics in the past. We will bring arguments to explain that the genesis of the investigated magmas seems not to be related to an arc-back arc system, as invoked by several authors, but rather to a pure transtentional-extensional geodynamic setting.

Considering the palaeogeographic position of the investigated area within the Pangea supercontinent, it is worth noting that it is located at the edge of the intra Pangea dextral shear zone, which was probably active in Triassic times. This zone corresponds to where, at the end of the Triassic, Gondwana and Laurasia broke up and a large igneous province was emplaced (the Central Atlantic Magmatic Province). We therefore suggest that the tectonic and magmatic events in the eastern Alps can be considered a forerunner of the future break-up of Pangea into Gondwana and Laurasia.

Zircon and rutile in Cenozoic flysch from Krk and Rab (Croatia): age and trace element determination for provenance study

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Keywords: zircon, rutile, provenance, flysch, trace elements, age dating.

Here we present new data on the heavy mineral assemblage of Cenozoic sandstones from Krk and Rab Islands in the northern Kvarner (Croatia).

The Kvarner Islands are located in the central part of the Adriatic plate, whom evolution is still strongly debated. Several authors suggested that the rigid part of this plate was one of the largest Mesozoic carbonate platforms of the Perimediterranean region, known as Adriatic Carbonatic Platform. The platform existed from the Paleozoic (the oldest basement is dated Upper Carboniferous to Middle Permian) until the main compressional events started during Late Cretaceous in the Internal Dinarides, and followed in their external part during the Paleogene. As proposed by a few authors, uplift and re-working of ophiolitic and associated sedimentary masses from the Internal Dinarides provided sources of clastic material during progressive deformations. These deformations originated several flysch basins filled by detrital material including heavy minerals. Heavy mineral studies already present in literature report data for the older Bosnian and Istrian basins while the heavy mineral assemblage of these islands is poorly known.

Heavy minerals have been concentrated in the 63-250 µm fraction through magnetic and tetrabromohethane separation. Here we will focus on zircon and rutile so that the mineralogical identification has been performed through optical microscope and Raman spectroscopy. Zircons appears as euhedral, sub-euhedral and broken crystals, rutile as elongated crystals close to 100 µm.

Cathodoluminescence and LA-ICP-MS analyses have been performed in order to find out information on possible sources through trace element and dating. These data will allow to make comparisons with the material found in the older flysch of the area to infer new information about paleogeography.

Pre-Mesozoic basement units in the NW part of the central-eastern Iran ,icrocontinent: the Jandaq Complex (central Iran)

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Keywords: central Iran, ophiolites, accretionary wedge.

Central Iran consists of several terranes, mainly derived from Gondwana and accreted to the Eurasian margin during the Cimmerian orogeny. In its NW part, three metamorphic complexes containing dismembered "ophiolites", the Anarak, Jandaq and Posht-e-Badam, occur. The age of metamorphism, geodynamic significance, and palaeogeographic provenance of such units are largely debated. The evolution of the Anarak complex is, until now, the best understood among the others. It has been interpreted as an allochthonous crustal fragment belonging to the accretionary belt developed during Carboniferous times on the southern margin of Eurasia. The mechanism and timing of large-scale deformation during Mesozoic and Cenozoic times that brought the Anarak unit in its present-day position are poorly understood. An undefined Precambrian to early Palaezoic age has been instead inferred for the Posht-e-Badam and Jandaq complexes.

The Jandaq complex is divided in two subunits: the Arusan ophiolitic mélange and the Jandaq metamorphic unit. To the north, the complex is in tectonic contact with the Airekan basement, mainly made of Lower Cambrian granites. The ophiolitic mélange consists of serpentinized harzburgites, metagabbros, prasinites and quartzites, the last likely representing metacherts. Minor marbles lenses also occur. The ophiolites were equilibrated at upper greenschist facies conditions. Only minor relics of phase assemblages of higher grade (hornblende + epidote + plagioclase) have been rarely recognized. The basement is made of metapelites with minor amphibolites. The metamorphic peak phase assemblages in micaschists is made of garnet, kyanite, staurolite, plagioclase, biotite and muscovite. Garnet is stable in mafic rocks, indicating that the Jandaq metamorphics reached P-T conditions well within the garnet amphibolite facies.

The age of metamorphism and deformation of the Arusan ophiolites is unknown, but a minimum age is provided by new zircon dating performed by us giving early Norian ages for granites that intruded the complex. A Middle Jurassic age of metamorphism has been suggested in the past for the Jandaq metamorphic unit. This age is controversial as undeformed pegmatitic dikes crosscutting the early Norian granite that intruded the complex provided a Toarcian $^{40}Ar/^{39}Ar$ age.

All these data suggest that the two subunits of the Jandaq complex experienced a different tectonometamorphic evolution before they have been stacked together and before being intruded by lower Norian granites. The complex was finally non-conformably covered by the Upper Jurassic-Lower Cretaceous Chah Palang Conglomerate. The described time constraints indicate that the Jandaq complex formed in the frame of the Cimmerian or even older orogenic event. In the last case, it could represent a fragment of the Carboniferous belt, as the Anarak complex, displaced to its present-day position along the Great-Kavir-Doruneh fault system during Mesozoic and Cenozoic times.

Towards a comprehensive reconstruction of the Lower Permian to Lower Jurassic geodynamic evolution of the Finero Complex (northern Ivrea-Verbano Zone)

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Keywords: lower crust, Ivrea-Verbano Zone, Finero Complex.

In the last five years a comprehensive work has been dedicated to the geochronological reconstruction of the geodynanic evolution of the northernmost part of the Ivrea-Verbano Zone, which is represented by the so-called Finero Complex, and well-documented along the Val Cannobina section. Here, the crystalline basement is represented by the amphibolites-facies metasediments and metavolcanics of the the Kinzigite formation, which experienced, according to U-Pb zircon and monazite age, metamorphic re-equilibration during Upper-Carboniferous to Lower Permian times, as commonly found throughout the IVZ. The development of significant tectono-magmatic Triassic events is instead recorded by the stratigraphycally higher intrusive unit of the Finero Mafic Complex, *i.e.*, the External Gabbro. This intruded the bottom of the crystalline basement during the Lower Permian, but was deformed and pervasively intruded by magmatic liquids in Triassic time, with the deformation ending at *ca*. 180 Ma. A broadly similar evolution can be depicted for the lowermost part of the Finero Complex, which consists of the Phlogopite-Peridotite mantle unit showing primary, magmatic contact with the crustal intrusives of the Layered Internal Zone and Amphibole Peridotite units. U-Pb zircon data, petrologic features and field relationships suggest that such a sequence represented a very deep lithological and structural lithospheric discontinuity since the Lower Permian up to its Lower Jurassic exhumation at shallower crustal level. As whole, the Val Cannobina section can be considered a tectonically-thinned, very condensed, representation of the Lower Crust of the Adriatic plate.

Is the contact between mantle and crustal units in the Finero Complex a fossil Permian Moho?

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Keywords: Finero Complex, Ivrea-Verbano zone, mantle peridotites, crustal intrusives.

The Finero Complex (northern Ivrea-Verbano Zone; southern Alps) is composed by the Phlogopite Peridotite mantle unit (FPP), which is surrounded by mafic-ultramafic rocks interpreted as intrusive crustal bodies. The crustal unit placed in contact with the FPP is the Layered Internal Zone (LIZ), which is overlaid by the Amphibole Peridotite and the External Gabbro units. With the aim of characterising the nature of such transition, a detailed field, structural and petrochemical investigation has been carried out. In the transition area, no apparent melt injection from the LIZ into the FPP is observed. A few meters far from the contact, the mantle rocks are similar to those forming the typical FPP sequence. They are phlogopite-amphibole-bearing harzburgite showing a foliation parallel to the contact. The amphibole chemistry is characterised by large Mg# and Cr, Th and U contents, large and linearly-fractionated *LREE*/PM values, and low Nb, Ta and *HREE*. Towards the LIZ, the olivine grain-size decreases and the peridotite becomes richer in orthopyroxene, phlogopite and amphibole. At the contact with the LIZ, the harzburgite is replaced by a layer, up to 1-m-thick, of weakly-deformed coarse-granular amphibole-biotite-bearing orthopyroxenite. As a whole, approaching the contact, the minerals show larger Fe and Al, and lower Cr. Concomitantly, the amphiboles are still enriched in Th, U, and *LREE*, and depleted in *HREE*, but with greater absolute values than in the harzburgite farther from the contact. The LIZ starts with dm-thick hornblendites, followed by amphibole gabbro layers containing garnet and clinopyroxene. Both hornblendites and gabbros preserve magmatic textures, with modest deformation and subsolidus recrystallisation. Hornblendites are made by titanian pargasites, definitely richer in Fe, Al and Ti than the FPP amphiboles. Besides, they show *L-MREE*-enriched convex-upward normalised patterns and local enrichment in Nb and Ta, suggesting segregation from alkaline melts. More complex processes are recorded by the amphibole gabbros, in which amphibole and clinopyroxene show lower *LREE*, associated to a huge positive Eu anomaly in the normalised pattern: the latter is commonly considered evidence of assimilated plagioclase component into a melt. The results of this study evidence that contact between FPP and LIZ is made by weakly-deformed reactive/magmatic rocks. The observation that the mantle ultramafics at the contact show mineralogy and trace element composition consistent with those of the rest of FPP suggests that they were segregated during the same pervasive metasomatic event that produced phlogopite-bearing mineral assemblages. The hornblendites and amphibole gabbros of LIZ record the migration of different melts, locally involving the assimilation of early gabbroic cumulates. This suggests that the FPP-LIZ transition has likely worked for a very long time as a primary discontinuity, representing a preferential level of channelling for the uprising melts.

Session S18:
Integrating multiple techniques to constrain the evolution of basement geology

Conveners:

Chiara Montomoli (Univ. di Pisa)
Eugenio Fazio (Univ. di Catania)
Salvatore Iaccarino (Univ. di Pisa)
Igor M. Villa (Univ. di Milano-Bicocca)

Forward and inverse phase equilibria modeling of residual migmatites and granulites: an evaluation of the melt-reintegration approach

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Keywords: residual migmatite, granulite, melt loss, melt-reintegration, melt productivity.

Suprasolidus continental crust is prone to loss and redistribution of anatectic melt to shallow crustal levels. These processes ultimately lead to differentiation of the continental crust. The majority of granulite facies rocks worldwide has experienced melt loss and the inverse phase equilibria modeling is becoming an increasingly popular approach to reconstruct the prograde history of melt-depleted rocks. It involves the stepwise down-temperature reintegration of a certain amount of melt into the residual bulk composition along an inferred *P–T* path, and various ways of calculating and reintegrating melt compositions have been developed and applied. Here different melt-reintegration approaches are tested using El Hoyazo granulitic enclaves (SE Spain) and Mt. Stafford residual migmatites (central Australia). Various sets of *P–T* pseudosections were constructed progressing step by step, to lower temperatures along the inferred *P–T* paths. Melt-reintegration was done following one-step and multi-step procedures proposed in the literature. For El Hoyazo granulites, inverse modeling was also performed reintegrating the measured melt inclusions and matrix glass compositions and considering the melt amounts inferred by mass-balance calculations. The overall topology of phase diagrams is pretty similar, suggesting that, in spite of the different methods adopted, reintegrating a certain amount of melt can be sufficient to reconstruct a plausible prograde history (*i.e.*, melting conditions and reactions, and melt productivity) of residual migmatites and granulites. However, significant underestimations of melt productivity may occur and have to be taken into account when inverse modeling is applied to highly residual ($SiO_2 < 55$ wt.%) rocks or to rocks for which H_2O retention from subsolidus conditions is high.

What can we learn from the exhumation of the metamorphic core of the Himalayas?

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Keywords: Himalayan belt, collision, exhumation, Greater Himalayan Sequence, tectonic discontinuity, metamorphic discontinuity, U-Th-Pb geochronology.

The understanding of the exhumation mechanisms of deep-seated metamorphic rocks in collisional orogens has been greatly improved by the discovery of contemporaneous contractional and normal-sense shear zones active in the same vertical section in orogenic belts such as the Hellenides, Canadian Cordillera, Appalachians, western Alps and the Variscan belt. In the Himalayas the normal sense top-to-the-NE South Tibetan Detachment (STD) and the contractional top-to-the-SW Main Central Thrust (MCT), bound the crystalline core of the belt (Greater Himalayan Sequence: GHS) to the top and to the bottom respectively. They are regarded as the most classic example of a coupled faults acting contemporaneously but with opposite kinematics in a collisional belt, active between ~ 24 and 17 Ma. They play a fundamental role in all the tectonic models envisaged for the exhumation of the GHS such as: extrusion, channel flow, channel flow followed by extrusion, critical taper and wedge insertion. In this framework the GHS is regarded as a coherent tectonic units exhumed by the shearing along the STD and MCT.

Field-based work followed by meso- and micro-structural and petrographic analysis joined with U-Th-Pb *in situ* geochronology in the central Himalayas allowed to recognize an internal tectonic organization of the GHS far from a simple ductile wedge or channel of melted rocks. A regional scale tectonic discontinuity (Higher Himalayan Discontinuity: Montomoli et al., 2015), stretching for more than 800 km along the belt, has been recognized within the GHS active between ~ 28 and 17 Ma. Its activity triggered the exhumation of its hanging-wall before the activation of the MCT whereas the footwall continued to underwent increasing P and T. An older tectonic discontinuity was active in the uppermost part of the GHS since the Middle Eocene and triggered the earliest exhumation of the GHS at ~ 41-30 Ma (Carosi et al., 2016). In western Nepal the activity of the STD has been constrained to be older than 24 Ma whereas the MCT is much younger, between 17 and 13 Ma.

The new data do not confirm the previous models of exhumation of the GHS mainly driven by the MCT and STD but need a new model able to explain the occurrence of the regional discontinuities within the GHS active since ~ 41 Ma. New geochronological data point to a lacking of contemporaneous activity of the STD and MCT along several sections of the belt. A self-organized expression of the dissipation of the accumulated potential energy of the thickened crust (Weinberg, 2016) is able to explain the complex behaviour of the STD through time in response to the progressive activation of contractional shear zones in the mid crust.

Carosi, R., Montomoli, C., Iaccarino, S., Massonne, H.-J., Rubatto, D., Langone, A., Gemignani, L., Visonà, D. (2016): Middle to late Eocene exhumation of the Greater Himalayan Sequence in the Central Himalayas: Progressive accretion from the Indian plate. Bull. Geol. Soc. Am., 128, 1571-1592.

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The Higher Himalayan Discontinuity in the Marshyangdi valley, central Nepal

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Keywords: geochronology, tectonics, Himalaya, exhumation, mid-crust, tecto-metamorphic discontinuities.

The Greater Himalayan Sequence (GHS) is one of the major tectonic units of the Himalayan belt, running for more than 2400 km along strike. It exposes the mid-crust of the Himalayas and it has been considered as a coherent tectonic unit bounded by the South Tibetan Detachment to the top and the Main Central Thrust to the bottom.

In the last few years integrated studies by different techniques allow recognition of several ductile shear zones in the core of the GHS along the belt, with top-to-the S/SW sense of shear (Higher Himalayan Discontinuity: HHD, Montomoli et al., 2013, 2015). *In situ* U-Th-Pb monazite geochronology indicates ages older than the Main Central Thrust, along the same structural profile. Data on the pressure (*P*) and temperature (*T*) evolution testify that these shear zones affected the tectono-metamorphic history of the belt and different *P-T* conditions have been recorded in the hanging-wall and footwall of the HHD. This tectonic feature, running for several hundreds kilometres, is documented in several sections of the belt dividing the GHS into two different portions.

We present the results of a structural and geochrononogical transect in the GHS of Marshyangdi valley (Annapurna massif). Close to the transition between sillimanite-bearing gneiss and kyanite-bearing gneiss, a few km north of Syangie village (Pecher, 1989), we identified a high-temperature ductile shear zone with kinematic indicators pointing to a top-to-the S sense of shear.

In situ U-Th-Pb and trace element analysis of monazite, joined with chemical compositional maps, performed by LASS at Santa Barbara, California on samples from the shear zone and its footwall provided ages ranging from ~ 8 to 32 Ma. The age of the HHD is constrained to between ~ 25 and 18 Ma in good agreement with the ages of the HHD detected along strike in the GHS (Montomoli et al., 2015), before the activation of the Main Central Thrust along the same section (Catlos et al., 2001).

The occurrence of the HHD, detected by structural analysis and geochronology in the Marshyangdi valley allows us to fill a gap in the recognition of the HHD between western and central Nepal.

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Numerical modelling of flash heating associated to *HT*-pseudotachylites outside the seismogenic zone

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Keywords: finite difference, pseudosection modelling, granite, partial melting, shear heating.

Pseudotachylites are fault rocks produced by frictional melting after a seismic rupture. Theoretical considerations and experimental evidences suggest that frictional melting of felsic, quartz-bearing, rocks is most likely within a temperature range between about 250–400°C. In simple rheological models such this thermal boundary represents the brittle-ductile transition zone, that is, the base of the seismogenic layer. However, the seismic behavior of crustal rocks at high temperature (T > 800 K), in the ductile field, is not impossible as demonstrated by the rare but systematic occurrence of lower crustal earthquakes. In this contribution, we evaluate the *P*-*T*-*t*-*d* history of Variscan pseudotachylites developed within an orthogneiss domain settled within a large migmatitic massif in northern Sardinia (Italy). Pseudotachylites developed during ongoing exhumation, and partial melting, of the crust and pseudosection modeling indicates that the seismic deformation occurred at minimum pressure of about 0.5 GPa, whereas the temperature of frictional melts is roughly constrained between 1700–2300 K. These paradoxical *UHT*-pseudotachylites developed out of the classical seismogenic zone and might be explained in terms of transient shear heating, fluid pressurization, or dynamic propagation of plastic instabilities. The applicability of these models has been tested by numerical modeling. The code solves the momentum, continuity and heat equations on a staggered grid using a marker-in-cell algorithm combined with conservative Finite-Difference method for primitive variables (P, Vx, Vz). The Eulerian grid (45 by 61 nodes) has too low resolution to replicate spontaneously the development of thin pseudotachylites; however, the results of experiments show a consistent build-up of stress within the orthogneiss domains which supports faulting.

P-T-t-d **paths of the Yalaxiangbo detachment zone, SE Tibet**

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Keywords: Yalaxiangbo, gneiss domes, petrochronology, *in situ* U-Th-Pb geochronology, SE Tibet, pseudosections.

The Yalaxiangbo gneiss dome (SE Tibet), in eastern Himalaya, is one of the most important gneiss domes of the metamorphic culminations referred as North Himalayan Gneiss Domes (NHGD). It is divided into three main tectonic units by an upper brittle and a lower ductile detachment shear zone. The upper unit, above the upper brittle detachment, is made by unmetamorphosed to low-grade metamorphic Triassic-Lower Cretaceous slate and metapsammite. The middle unit, sandwiched between the upper and lower detachment faults, consists of mylonitic granite, staurolite-garnet-two mica schist and biotite-plagioclase gneiss affected by the ductile top-to-the north extensional shearing of the Yalaxiangbo detachment shear zone, as supported by our meso- and micro- structural analyses. The lower unit consists of mylonitic gneiss, leucogranite pluton and the associated dikes and sills,.

Pressure (*P*)-Temperature (*T*) conditions and *P*-*T*-deformation paths for samples from different structural units were derived with the aid of pseudosections in the MnNKCFMASHT system. Staurolite-garnet-muscovite schist, from the footwall of the upper detachment, contains garnet with prograde compositional zoning and yields a *P*-*T* estimates of 7-9 kbar and 520-540°C. Staurolite-two mica schist in the lower detachment shear zone, with garnet partially-replaced by biotite and muscovite, experienced a prograde *P*-*T* path from 8 kbar-530°C up to 12.5 kbar-580°C. Kyanite-staurolite-garnet-two mica schist beneath the lower detachment reveals an equilibration *P*-*T* range of 7.2-8.0 kbar and 650-660°C.

Integrating macro-/micro-analyses, petrology and mineral chemistry, LA-ICP-MS *in situ* U-(Th)-Pb monazite geochronology, from a selected staurolite-garnet-mica schist of the middle unit affected by ductile shear, we constrain the activity of the Yalaxiangbo detachment shear zone from *ca*. 22 to 16 Ma. The kinematic, geochronology and petrologic features of Yalaxiangbo detachment fault were similar to the South Tibetan Detachment systems, STDS, (28-11 Ma; Montomoli et al., 2017) outcropping to the south, supporting its correlation with the STDS exposed at the bottom the Tethyan Sedimentary Sequence.

Montomoli, C., Carosi, R., Rubatto, D., Visonà, D., Iaccarino, S. (2017): Tectonic activity along the inner margin of the South Tibetan detachment constrained by syntectonic leucogranite emplacement in western Bhutan. It. J. Geosci., 134, 1-27.

Heterogeneous dominant fabric distribution in metamorphic basement: an example of dominant blueschist-facies imprint in the Eclogitic Micaschist Complex (Lago della Vecchia, Sesia Lanzo Zone, western Alps)

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Keywords: multiscale structural analysis, tectono-metamorphic evolution, dominant fabric, subduction metamorphism, blueschist-facies, Sesia-Lanzo Zone.

The Sesia-Lanzo Zone is classically subdivided into units on the base of rock types and dominant metamorphic imprints. One of these units is the Eclogitic Micaschists Complex that is connoted by a dominant Alpine fabric developed under eclogite facies conditions. Indeed, the more recent literature shows a dominant retrograde metamorphic imprint under blueschist facies conditions linearly distributed along EMC-strike. All these heterogeneities in the dominant tectono-metamorphic imprint open a question about the actual distribution of the eclogitic tectono-metamorphic imprints in the EMC and, in generally, on the complexity of the *P*-*T*-*d*-*t* evolution in the SLZ. In fact, a rock volume characterized by a specific dominant fabric may record different tectono-metamorphic evolutions and adjacent rock volumes showing different dominant fabrics may reveal the same *P*-*T*-*d*-*t* evolution but heterogeneous memories of the successive deformation stages.

In this contribution, we show an example of multiscale structural analysis performed to characterise the tectono-metamorphic evolution of the Lago della Vecchia (upper Cervo valley, Biella) metaintrusive belonging to the Eclogitic Micaschists Complex of the Sesia-Lanzo Zone. Mesoscale observations, relative chronology of metamorphic assemblages inferred by microstructural analysis and qualitative and quantitative thermo-barometric estimates are used to reconstruct of *P*-*T*-*d*-*t* paths. The multiscale analysis reveals seven groups of superimposed structures. Pre-Alpine M0 relicts consist of igneous features preserved as low-strain domains within tectonitic and mylonitic metaintrusive. Alpine stages consist of: S1 foliation (D1) developed under eclogitic facies conditions; S2 foliation (D2) is the most pervasive fabric in the area and developed under blueschist facies conditions; D3 and D4 consist of localised shear zones and open folds marked by greenschist facies assemblages; and D5 km-long cataclastic-mylonitic shear zones developed under greenschist facies conditions; M6 stage consists of the intrusion of andesitic dikes. Microstructural analysis leads to reconstruct the equilibrium mineral assemblages of superposed structural and metamorphic overprints in the different rocks types. The reconstructed structural deformation stages, mineral-growth sequence and mineral chemical analysis permit to apply geothermobarometric estimates to constrain the *P*-*T* conditions and paleo-thermal gradients.

The development of pervasive blueschist-facies D2 fabric in this area is in contrast with the dominant fabric develops under eclogitic conditions, generally recorded in the EMC. This difference suggests that entire SLZ could be characterised km-scale heterogeneities in the dominant tectono-metamorphic record. Thus, reconstructing and comparing the *P*-*T*-*t* path and fabric evolution of different areas could provide a more accurate interpretation of the tectono-metamorphic evolution of the SLZ crustal slices involved in Alpine subduction.

Trace-element geothermometry in metapelitic granulites from Jubrique (Betic Cordillera, southern Spain)

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Keywords: trace-element geothermometry, granulite, Betic Cordillera.

Constraining the *P-T* conditions in high-grade metamorphic terranes is crucial for a better understanding of high-grade metamorphism and evolution of metamorphic basements. Recently, new trace-element geothermometers (Ti-in-quartz, Zr-in-rutile and Ti-in-zircon) have been developed and successfully used to reconstruct the prograde and retrograde history of polymetamorphic rocks. In this study we apply these thermometers to mylonitic granulites from the bottom of the Jubrique sequence, which is located on top of the Ronda peridotite slab (Betic Cordillera, S Spain). This sequence constitutes a complete, though strongly thinned crustal section. This study offers the opportunity to compare results from this new technique vs. previously published data using conventional tools.

Several quartz, zircon and rutile crystals, both included in garnet porphyclasts and present in the rock matrix, were investigated. Zircon was imaged by cathodoluminescence in order to reveal its internal structure: most zircons show a complex core and an irregular, homogeneous or weakly zoned, anatectic rim. Rutile and zircon were analyzed by LA-ICP-MS, giving contents of 1000-2800 ppm Zr and 7-25 ppm Ti, respectively. Ti in quartz was measured by EMP, resulting in 100-260 ppm. Pressure values used for calculations are 13 kbar for minerals included in garnet, 5 kbar for matrix quartz and zircon, 9 kbar for matrix rutile, in agreement with previous estimates.

We recognized two types of quartz included in garnet: 1) large (≈800 µm) irregularly shaped inclusions, both at the rim and at the core of garnet, yielding an average Ti-in-quartz temperature of 880 ± 80°C; 2) small (< 50 µm) single-crystal inclusions, at the garnet core only, yielding an average temperature of 910 ± 90°C. Matrix quartz gave temperatures of 690 ± 70°C (in melanosome) and 660 ± 60°C (in leucosome). Crystallization temperatures calculated for rutile are 850 ± 40°C (in Grt) and 810 ± 40°C (in matrix). Average Ti-in-zircon temperatures for zircon included in garnet are 730 ± 20°C (rim) and 750 ± 20°C (core), whereas for matrix zircon the average temperatures are 780 ± 20°C (rim) and 760 ± 20°C (core).

The simultaneous application of Ti-in-quartz and Zr-in-rutile thermometers on minerals included in Grt gives peak metamorphic temperatures in agreement with the previously published results, of ≈ 850°C at 12 kbar. However, our study seems to suggest that these rocks likely reached temperatures approaching *UHT* metamorphism conditions, as indicated by quartz in garnet (≈ 900°C). Lower Ti-in-zircon temperatures for Zrn included in Grt might record either disequilibrium of zircon at peak conditions, or equilibration/growth of zircon during cooling from peak temperatures. Lower temperatures calculated for matrix quartz (< 700°C) probably record dynamic recrystallization during deformation. These temperatures are much lower than those previously obtained through conventional techniques.

P–T conditions in mylonitic gneiss from Posada Shear Zone, NE Sardinia

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Keywords: mylonitic gneiss, geothermobarometry, NE Sardinia, Variscan orogeny.

The Posada Valley shear zone is part of a regional-scale mylonitic belt that runs from Posada (NE Sardinia) to Asinara Island (NW Sardinia) separating the Variscan Medium Grade Metamorphic Complex to the south from the Migmatite Complex to the north. In the Posada Valley, a dextral top–to–the SE shear belt developing ductile and brittle–ductile D2 mylonites has been recognized. In southern Gallura the dextral shear movement follows a sinistral top–to–the NW shear belt, coeval to the initial D2 post–collisional phase. At Punta Orvili, a few kilometers north from Posada village, a sequence of mylonitic gneiss with subordinate calc–silicate nodules and metabasite lenses crop out. The main foliation at the mesoscale is the S2 schistosity striking N 60–80°and dipping 30°–50° SE. Locally, the S2 schistosity is affected by centimetre size, sinistral strike–slip greenschist shear zones, striking N 30° and dipping 60° SE. Three mineral lineations have been recognized on the S2 schistosity: a feldspar+quartz lineation trending N 30°–50° and plunging 20°–30° SW; a quartz lineation trending N 40°, plunging 30° SW; a biotite ± chlorite lineation trending N 20° and plunging 15°–30° SW. The mylonitic gneiss consists of quartz, plagioclase, K-feldspar, biotite, white mica, fibrolite, ± garnet. Centimetric garnet porphyroblasts, locally observed, are $Alm_{58–68}$, $Pyr_{8–12}$, $Grs_{2–3}$, $Sps_{16–31}$. The mylonitic gneiss is characterized by the widespread occurrence of millimetre– to centimetre–sized nodules enveloped by the S2 foliation. The nodules occur in four textural types: (i) quartz–rich, (ii) K-feldspar–rich, (iii) plagioclase–rich, and (iv) sillimanite–rich nodules. The K-feldspar–rich nodules are made up of polygonal aggregates of submillimetric K-feldspar crystals or by elongated, anhedral K-feldspars up to 5 mm in length associated with smaller quartz–feldspathic grains. Perthite exsolutions and very thin albite rims are often observed in K-feldspar. The plagioclase–rich nodules consist of plagioclase (An_{20}) aggregates with subordinate quartz and K-feldspar. The feldspar rich–nodules probably document an incipient melting affecting the rock prior of the mylonitic deformation. Application of the garnet–biotite geothermometer and GASP geobarometer to some selected mylonitic gneiss yielded *P–T* conditions of $P \sim 6$ kbar, $T = 540–620$°C. These *P–T* conditions most likely refers to the development of the D2 deformation, *i.e.*, to the development of the sinistral top–to–the NW shear deformation. In conclusion, the Posada shear zone is first characterized by a medium– to high–grade sinistral shear movement followed by dextral shear movement as shown by Carosi et al.(2012) in southern Gallura.

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Nappe stacking and metamorphic evolution in the western Tauern Window

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Keywords: Alps, CARG, geothermobarometry.

The western Tauern Window is a key area for the reconstruction of the tectonic evolution of the eastern Alps. Here basement units derived from the European margin are stacked together with their parautochthonous post-Variscan cover in a south-vergent crustal scale duplex that also involves remnants of the Penninic ocean (Glockner nappe).

The major lithostratigraphic units comprise: i) a polymetamorphic basement consisting of mainly amphibolites, migmatites, orthogneisses, and locally pre-Mesozoic ultramafic to mafic bodies; ii) the Tux and Zillertal orthogneiss that intruded unit (i) during Early Permian times; iii) the parautochthonous metasedimentary cover including meta-conglomerates, calcitic and dolomitic marbles, calcareous micaschists, quartzites, and subordinate greenschists; iv) the Glockner Nappe, km-thick sequences of calcschists with interbeddings of prasinites, amphibolites and ultramafic bodies. Along the tectonic contact between the northern and southern duplex antiforms a slice (about 1 km-thick, wedging out westward) of graphite-rich garnet micaschists with minor quartzites and calcschists ("Greiner schists" *Auct.*) occurs.

A peculiar feature of the parautochthonous metasedimentary cover is the occurrence of static recrystallization of amphibole, micas, garnet, and staurolite ("Tauerncrystallisation" *Auct.*) crosscutting the main foliation, D2; this late metamorphic stage is controversial in the Glockner nappe, as poorly visible on the field, but possibly characterized at a microscopic scale by a secondary stage of growth of biotite and garnet in micaschists. Garnet and chloritoid were found in structural units of the Glockner nappe close to metasedimentary cover. Garnet amphibolites were recovered in units stacked to the Zillertal gneiss only.

Two phases of roughly coaxial isoclinal folding, the first one of these responsible for the regional foliation, have been recognized in the post-Variscan cover of the "Zentralgneiss".

In the frame of the of the South Tyrol Province CARG project, devoted to 1:10,000 mapping of the Vipiteno sheet, the goal of this work is to provide the constraints to identify tectonometamorphic units with coherent structural and metamorphic evolution. Preliminary results display significant differences among the reconstructed *P-T* paths of the Glockner schists and metasedimentary rocks of the post-Variscan cover of the Tux and Zillertal gneisses. Systematics of mineral chemistry has highlighted that garnets grown in micaschists synchronous to regional foliation in the Glockner nappe show Ca-Mg rich rims to a relatively Ca-Mg-poor core, with a zonation pattern revealing two stages of growth. On the contrary, in the metasedimentary rocks the Ca content in the garnet tends to decrease from core to rim, as Mg increases. A set of 49 whole rock analyses, both on metapelites and on calcschists, provide us the constraints to infer the features of protolith, and to compute pseudosections for thermobarometric estimates.

Editing a geological map of the Manaslu area by remote sensing, petrographic and spectrofotometric analysis

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Keywords: remote sensing, Himalayan geology.

Remote sensing in Himalayan belt is increasingly used for glacial and geological mapping purpose (Quincey et al., 2007). Rock composition analysis is indeed possible by studying the signal reflected from the surface and captured by remote sensors. In this way the remote sensing approach allows to obtain a synthetic framework of the structures and lithologies present in areas of interest. Cloud and snow covers, extensive glaciers, vegetation and steep topography are however among the major problems to overcome when dealing with satellite images acquired on Himalayan belt. The examined area is located in the Gandaki region between the Budhi Gandaki and the Marshyangdi valleys which delimit the Manaslu massif (Pecher & Fort, 2011) in central Nepal (central Himalaya). This work aims to apply the remote sensing tecniques in order to investigate the possible structural and lithological correlations among the valleys cited above and other nearby structural transects within the Greater Himalayan Sequence, the metamorphic core of the Himalaya, where the occurrences of high-temperature shear zones have been previously reported (Montomoli et al., 2013, 2015). The final goal will be an updated geological map of Manaslu area as much detailed as possible, considering the difficulties due to altitude and limited accessibility. The multispectral analysis has been applied on a ASTER (Advanced Spaceborne Thermal Emission and Reflection Radiometer) image which include 9 bands in the VNIR (Visible and Near Infrared) and SWIR (Shortwave Infrared) wavelength range. Vegetation, snow and ice were masked to isolate and filter rocky pixels and to focus the image only on its potential geological aspects. Afterwards we have carried out the interpretation on false color composition obtained from Principal Components elaborations of the masked images. The resulting preliminary geological map was particularly useful as a guidance at the field work. A further improvement of the geological map will be provided lithological discrimination by bands ratios and supervised classification based on spectra obtained from ROI and collected samples. In particular in addition to the rock type spectral signatures, we intend to use also lichen signatures as proxies of different kind of lithologies (see also Bertoldi et al., 2011). We show, how according this procedure, an accurate geological map could be obtained, with the aim to investigate lateral continuity of geological units and of tectonic discontinuities along the between the Budhi Gandaki and the Marshyangdi valleys and to investigate relationship between plutons and low-angle-normal fauls.

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1:10,000 structural map of the Corte Slices in the area between Golo and Tavignano valleys (central Corsica)

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Keywords: geological map, structural geology, Corte Slices, Schistes Lustrés Complex, Alpine Corsica.

The area between the Golo and Tavignano valleys (central Corsica) provides a good opportunity to study the relationships between the Hercynian Corsica, the Corte Slices (*i.e.*, Lower Units) and the Schistes Lustrés Complex (Di Rosa et al., 2017).

The Hercynian Corsica consists of a paleozoic basement (Roches Brunes Fm. intruded by Permo-Carboniferous monzogranites) covered by Mesozoic and Tertiary sedimentary successions. Despite the occurrence of several shear zones of Tertiary age, the Hercynian Corsica is considered a domain not involved in the Alpine Orogeny.

The Corte Slices and the Schistes Lustrés Complex, that belong to the Alpine Corsica, are the remains of the oceanic crust and the European continental margin, both involved in the E-dipping oceanic and continental subduction (Late Cretaceous to Early Tertiary). The subduction was associated with an exhumation whose end is regarded as pre-Burdigalian in age (Malasoma & Marroni, 2007). In the study area the Schistes Lustrés Complex is represented by metaserpentinites, metagabbros, metabasalts and calc-schists, whereas the Corte Slices consist of three tectonic units similar in their lithostratigraphy (*i.e.*, Paleozoic basement covered by Mesozoic to Tertiary metasediments) but different in the metamorphic degree.

The structural setting of the Alpine Units is characterized by a polyphased deformation history: within the Corte Slices, three phases are recognized at all the scale of observation (D1-D3). The D1 produces F1 sheath folds and a S1 foliation, almost completely transposed by the D2 phase, characterized by F2 isoclinal folds with a subvertical axial plane foliation, a S2 and a L2 stretching lineation. The D3 is associated to F3 folds with a subhorizontal axial plane foliation. A post-D3 brittle deformation phase is associated to the Central Corsica Shear Zone, a strike-slip faults system that cuts all the previous structures.

The Schistes Lustrés Complex shows a higher grade of deformation, acquired within the accretionary wedge during the oceanic subduction. However, the Schistes Lustrès Complex is folded by the same structures of the D3 phase recognized in the Corte Slices, that deform the previous phases within the Schistes Lustrés Complex as well as the tectonic contacts between it and the continental units. The occurrence of the Schistes Lustrés Complex as slices sandwiched between the Corte Slices, suggests an interaction between these two groups during the coupling of the continental units, *i.e.*, in a pre-D3 phase.

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Three-steps exhumation for the Corte Slices (Alpine Corsica)

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Keywords: chlorite-phengite thermobarometry, *PT* paths, continental subduction, Corte Slices, Alpine Corsica.

In latest Upper Eocene-Early Miocene time, the European continental margin was involved in the Alpine processes of subduction and exhumation, as detected in the western Alps as well as in the Alpine Corsica. In the Corte area, central Corsica, several strongly deformed and metamorphosed tectonic units (*i.e.*, the Corte Slices) provide a full record of these processes. The Corte Slices are characterized by a polyphase deformation history consisting of three phases, from D1 to D3.

The investigated samples from the Corte Slices are fine grained metapelites composed of chlorite (25-30 vol%), phengite (30 vol%), quartz, feldspars, calcite and many accessory minerals. These rocks show a complex microtectonic fabric including two well developed foliations (S1 and S2) defined by the dynamic recrystallization of three generations of chlorite-phengite-quartz-albite (two in the S1, one in the S2), and a late phase of folding (S3) to which is not associated any metamorphic recrystallization. Chlorite and phengite are 100 µm long when oriented along the S1 foliation, but only up to 50 µm along the S2. The mineral compositions of the phyllosilicates strongly vary depending on their textural position: the oldest phases that constitutes the S1 foliation consist in a Si-rich phengite (celadonite) and Mg-rich chlorite (Mg-amesite), whereas the thinner phases grew along the S2 foliation are K-poor phengite (pyrophyllite) and Al-rich chlorite (Mg-sudoite). The systematic variation in chemical composition of these minerals reflects changings in the *P*-*T* conditions during their growth. Particularly, all the samples are characterized by three points in the *P*/*T* diagram where the chlorite are thermodynamically in equilibrium with phengite: a *P*-peak (*HP*-*LT*) and *T*-peak (*LP*-*HT*) events related to the first and the second generations of chlorite-phengite contained in the S1 foliation, and another equilibrium condition (*LP*-*LT*) related to the chlorite-phengite contained in the S2 foliation.

According to the pressure decrease within the S1 foliation, the onset of the rise up of the Corte Slices already happened at the end of the D1 phase. Furthermore, differences in the *P*-peak and *T*-peak values among these tectonic units suggest that they were coupled at the end of the D2 phase, and then exhumed together during the D3 phase.

The three-steps exhumation presumed for the Corte Slices is therefore framed out by the metamorphism: a blueschists facies is reached by the units at the end of their underthrusting (12.2 – 7.5 kbar, 250-365°C), quickly followed by rising with the *P*-decrease and *T*-increase (8.2-5.6 kbar, 280-435°C) already during the D1 phase. Subsequently, a decrease of *P* and *T* occurred (4.5-2.1 kbar, 310-180°C) during the D2 phase whereas during the D3 phase the Corte Slices are deformed together (D3 phase) in a *P*-*T* conditions too low for a new generation of chlorite-white mica, compatible with their parking at very shallow levels.

Strain-rate estimation of syn-tectonic plutonic rocks: a multiple approach combining paleopiezometry, flow law and *PT* pseudosection

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Keywords: shear zone, paleopiezometer, strain rate, pseudosection, syn-tectonic pluton.

The Symvolon pluton was syn-tectonically emplaced at 22 Ma (Dinter et al., 1995) in the southern part of the Rhodope Core Complex (southeastern Greece) along an extensional shear zone. It mainly consists of granodiorites, which were affected by ductile deformation during cooling, showing an increasing strain gradient approaching the hosting Hercynian gneisses (Punturo et al., 2014). The NE-SW elongated shape of the pluton reflects strong regional scale tectonic control (Brun & Sokoutis, 2007); mesoscopic structural features such as mylonitic foliation and stretching lineation are averagely oriented (dip direction/dip) 290°/15° and 75°/10° respectively. A quantitative microstructural analysis of quartz domains was performed on samples collected along a transect oriented roughly perpendicular to the long axis of the pluton (from the pluton centre to the periphery). *PT* shear conditions were estimated by thermodynamic equilibria of syn-shearing assemblages via pseudosection tool. These estimates, in combination with quartz paleopiezometer and flow law, allowed us to infer the strain rate for these syn-tectonic intrusive rocks.

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Punturo, R., Cirrincione, R., Fazio, E., Fiannacca, P., Kern, H., Mengel, K., Ortolano, G., Pezzino, A. (2014): Microstructural, compositional and petrophysical properties of mylonitic granodiorites from an extensional shear zone (Rhodope Core complex, Greece). Geol. Mag., 151, 1051-1071.

Reconstruction of sequential pattern deformation within the multistage evolution of the Montalto Shear Zone (Aspromonte Massif – Calabria)

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Keywords: mylonites, flow perturbation folds, deformation history.

A well exposed ductile shear zone (Montalto shear zone- MSZ) in the Aspromonte area (southern Calabria-Italy) shows structural features depicting a complex deformational evolution, overprinting, in a multistage non-coaxial regime, previously Variscan (Aspromonte Unit) and Alpine (Madonna di Polsi Unit) prograde metamorphic evolution (Pezzino et al., 1990; Fazio et al., 2010, 2016). During this retrograde evolutionary stages, which allows the superimposition of these two units, the upper one (*i.e.*, Aspromonte Unit), locally characterized by the presence of granitoid rocks, developed complex mesoscopic to microscopic structural features such as mylonitic foliations with occurrence of spectacular asymmetric winged objects, intrafoliar folds and curvilinear up to sheath folds. The unraveling of this sequential evolution is not always straightforward because visible structures can be potentially ascribed to different causes: i) are they the effect of a single deformational episode which evolves through time (*i.e.*, invariant stress field orientation)?; ii) or rather they can be associated to different deformational episodes implying a change of principal stress orientation? This aspect is crucial for a correct interpretation of the tectono-metamorphic evolution of the orogenic system. In this view, overprinting relationships and progressive development of folds from the study area provided some clues, which suggest an alternative deformational sequence, by proposing the activity of flow perturbation folds developed during a single Oligo-Miocene evolutionary stage rather than the occurrence of an additional post-mylonitic isoclinal folding as previously hypothesized (Pezzino et al., 1990, Ortolano et al., 2005).

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New insigths on the tectonic evolution of the Hercynian upper continental crust exposed in Calabria (southern Italy)

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Keywords: Stilo-Pazzano phyllite unit, Mammola paragneissic unit, mylonites.

According to literature data, the Paleozoic upper continental crust exposed in the Serre Massif (Calabria, southern Italy) is made up of two metamorphic units: the Stilo-Pazzano Phyllite Unit (hereafter SPU) and the Mammola Paragneissic Unit (hereafter MPU). While the age of the protolith of the paragneisses is unknown, the phyllites belong to a former sedimentary succession of Ordovician–Visean age. Hercynian tectonics was responsible for the juxtaposition of these two metamorphic units, that happened through a mylonitic contact; subsequently they were affected by the emplacement of Late Carboniferous granodiorite magma at a level of about 7 km. The tectono-metamorphic evolution has been reconstructed by previous studies, but indipendently for each unit. As a consequence, on the basis of the different metamorphic imprint, it is generally believed that the low-amphibolite facies MPU underlies the low-greenschist facies SPU. However, neither the juxtaposition of the two tectonic units nor the mylonitic contact and kinematics have been geometrically constrained at all.

Therefore, the mylonitic contact between the MPU and the SPU represents a fundamental structural marker for the post-Visean tectono-metamorphic evolution, necessarily shared by these two units. Thus, a detailed geological mapping was carried out in the Levadio stream area (southern Serre Massif), in a strategic location for both structural analysis and petrographic observations on the mylonite and its hanging- and foot-rock.

Net of post-Paleozoic crustal tilting towards SE, the following main results are derived from the geological mapping and the structural analysis: (i) extensional tectonics was responsible for the juxtaposition of the SPU, over the MPU. During this tectonic phase, lower-grade greenschists facies conditions affected both units, promoting retrograde metamorphism in the MPU; (ii) a subsequent contractional tectonic phase, that occurred under the same lower-grade greenschists facies conditions, determined the formation of a map-scale recumbent, nearly isoclinal synform, that inevitably folded the mylonitic contact; (iii) then, with the emplacement of the granodiorite, both the MPU and the SPU were affected by contact metamorphism.

Tracking deep crustal processes by U-Pb zircon geochronology and isotopic compositions of metaigneous and metasedimentary granulites, Serre Massif, Calabria, southern Italy

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Keywords: SHRIMP dating, oxygen isotopic composition, lower crust, Calabria-Peloritani orogeny.

Mafic and felsic granulites from the lower crust exposed in the Serre Massif (Calabria-Peloritani Orogen) have long been considered to originate from *MP*/*HT* Variscan metamorphism of pre-Variscan gabbros and siliciclastic rocks, respectively. Reliable U-Pb zircon ages of ~ 300 Ma have been obtained for the late Variscan metamorphism, while more doubtful ages of ~ 593-564 Ma have been proposed for the protoliths of the metagabbros (*e.g.*, Fornelli et al., 2011). Similarities with Permian-Triassic gabbroic intrusions in the lower crust of northern Calabria, as well as with the Permian Ivrea crustal section of the southern Alps, suggest that the Serre metagabbros might also represent late-to-post Variscan magmatic underplating. To investigate this possibility a metagabbro sample has been dated by SHRIMP zircon U-Pb. Dates obtained range from ~ 3.2 Ga to ~ 270 Ma. Most of the older cores yield ~ 720 – 450 Ma, the youngest of which possibly places an upper limit on the age of magmatism. The maximum age for the metamorphism is ~ 313 Ma. All of the metamorphic zircon has high $\delta^{18}O$ (9.3 – 10.6 ‰), indicating crystallization in the presence of sediment-derived fluids. Older zircon cores have lower $\delta^{18}O$ (6.1 – 9.2 ‰), only three of which are < 7.5 ‰. The oxygen isotopes have a strong sediment signature, consistent with the large amount of detrital zircon in the sample. The εNd value of the metagabbro sample at 290 Ma is -2.1, within the reported range of -0.9 to -3.4 for similar samples (-0.8 to -2.4, at 550 Ma). The data indicate a high degree of older crust in the mantle derived magma. Both the O and Nd isotopic signatures of the metagabbro therefore suggest that prolonged residence of a sediment-contaminated mafic magma in the deep crust has largely modified the zircon $\delta^{18}O$ and some U-Pb dates, making it hard to determine the original gabbro $\delta^{18}O$ and emplacement age. If the ~ 450 Ma zircon age is that of a detrital zircon, however, the gabbro magmatism must be younger. This hypothesis has been tested by studying two samples of felsic granulites hosting the metagabbro. Prolonged residence in the deep crust also caused zircon Pb mobilization in those granulites, but reliable ages were nevertheless obtained for the growth of new metamorphic zircon, indicating granulite facies metamorphism at ~ 300 Ma. Furthermore, in one of the felsic granulite samples, it was possible to obtain a well constrained age of ~ 400 Ma for the youngest zircon core population, providing a best estimate for the maximum depositional age of the arenite protoliths, and supporting the conclusion that the gabbro is not latest Precambrian, but rather ~ 400 Ma or younger.

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Structural setting of a transpressive shear zone: insights from geological mapping, quartz petrofabric and kinematic vorticity analysis along a transect of the Posada-Asinara Line (Sardinia) in the Baronie region

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Keywords: transpressional tectonics, vorticity of flow, quartz crystallographic preferred orientation, EBSD.

The Posada-Asinara Line (PAL) is a regional transpressive shear zone cropping out in the northern Sardinia and related to the Carboniferous phase of the Variscan Orogen. The PAL played an important role on the exhumation of the high-grade metamorphic complexes of the Sardinian Variscan basement (Carosi & Palmeri, 2002).

The main structural features in the study area are N-verging kilometric scale isoclinal folds (F2) and an associated mylonitic foliation (S2). S2 strikes mainly N70-90° and dips 70-80° to the S. On the S2, object mineral lineation L2, trending nearly E-W and plunging 05-20° to the E are present. Kinematic indicators, such as S-C-C' fabric, indicate a top-to-the-W/SW sense of shear. A late crenulation cleavage, S3, is localized within D3 deformation domains forming crenulated belts oriented subparallel to the S2. The sequence of mineral assemblages and microstructures suggest that the PAL evolution is part of a retrograde metamorphic history. This path is supported by the superposition of subgrain rotation recrystallization (SGR) on previous grain boundary migration recrystallization (GBM) in the quartz-rich tectonites, that increases from S to N, approaching the PAL core. Crystallographic Preferred Orientation (CPO) data, obtained through Electron Backscattered Diffraction analysis of quartz-rich tectonites, allowed to analyze quartz slip systems and constrain deformation temperature, vorticity of flow (Wn), finite strain ratio (R_{XZ}) and then the shortening perpendicular to the shear plane (S) (Xypolias, 2010). Kinematic vorticity analysis suggests Wn values near 1, testifying simple shear dominated flow. Quartz deformation temperatures of 400 ± 50°C are nearly homogeneous along the transect, in agreement with the post-metamorphic peak mineral assemblages and the late microstructures observed in quartz. Differential stress and strain rate estimates increase approaching the PAL core and this trend could justify the increase of the SGR intensity. Compared to the literature data on the same area (Carosi & Palmeri, 2002; Carosi et al., 2005), our kinematic vorticity data suggest an increase of the simple shear component (from 28 – 62% to 76 – 100%) during the PAL evolution. Coupling field evidence with Wn data, a horizontal extrusion process is suggested. According to this model, deformation continued to shallower structural level, where a strain hardening process led the formation of the D3 crenulation belts.

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Using field mapping, petrology and geochronology to infer the pre-Cenozoic evolution of the Aghil Range (western Tibetan Plateau): a missing piece in the Tibet-Pamir-Karakorum geopuzzle

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Keywords: pre-Cenozoic evolution, Aghil range, western Tibetan Plateau, field mapping, petrology, geochronology.

The Tibetan Plateau (TP) is the highest and largest topographic relief on Earth: understanding its formation and evolution is fundamental for clarifying the geodynamic processes responsible for crustal thickening and continental growth. The TP derives from the accretion of several Gondwana-derived microplates (Cimmerian terranes) to the southern margin of Asia since the Late Paleozoic. Although the first order geodynamic processes responsible for the pre-Cenozoic evolution of the plateau are quite well-known, many issues are still debated, among which is the timing of collision of each terrane with the southern margin of Asia. Even more uncertain is the pre-Cambrian history of the Cimmerian terranes, due to the poorness of basement exposures.

As a contribution to understand the pre-Cenozoic evolution of the TP, we focus on the Aghil Range, a remote and poorly investigated area of western Tibet (Groppo & Rolfo, 2008; Rolfo et al., 2014). Along the investigated transect, located between Kunlun and Karakorum (Xinjiang, China), both metamorphic and magmatic rocks are exposed. The metamorphic rocks belong to two tectonic units: the metasedimentary "Bazar Dara Slates" (BDS) unit, and the "Surukwat Complex" (SC), a composite sequence of metamorphic thrust sheets deriving from both magmatic and sedimentary protoliths. Two granodioritic bodies (Aghil Granodiorite, AG, and Sughet Granodiorite, SG) are tectonically interposed between these metamorphic units. The tectono-metamorphic and the magmatic evolution of the Aghil Range are investigated using a multidisciplinary approach, which combines detailed field mapping, petrological modelling (optimal thermobarometry and pseudosections) and geochronology (SHRIMP U-Pb on titanite, zircon, monazite and xenotime).

We demonstrate that the SC is a coherent slice of Neo-Proterozoic (772-778 Ma) crystalline basement with a Late Paleozoic sedimentary cover deposited on a passive continental margin during the Gondwana break-up. This represents the westernmost exposure of a pre-Cambrian crystalline basement known so far in the TP. Moreover, our petrological and geochronological results allow to reconstruct the Mesozoic poly-metamorphic evolution of both the BDS and the SC, which record the evidence of Middle Jurassic (170-175 Ma) and Late Cretaceous (69 Ma) collisional events, as well as the Late Jurassic (157 Ma) early subduction of an accretionary complex developed on the southern margin of the SC. Evidence of a Late Cretaceous (83 Ma) subduction-related magmatism preceding the last collisional event is recorded by the AG.

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Scales of equilibrium and disequilibrium in metamorphic rocks-Implications for phase equilibria modeling and pressure-temperature reconstructions

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Keywords: metamorphic petrology, equilibrium thermodynamics, disequilibrium textures, quantitative composition.

Metamorphic rocks evolve dynamically in response to deformation and changes in pressure (*P*) and temperature (*T*) conditions. In an attempt to minimize their Gibbs free energy, the rocks adjust their mineral assemblages, *i.e.*, the mode (abundance) and composition of locally coexisting minerals and fluid. Along a given *P*-*T* trajectory the evolution of a metamorphic rock is now readily modeled using the principle of Gibbs free energy minimization. Such a forward modeling technique requires a good approximation of the reactive bulk composition. Recent progress in the accuracy and efficiency of such techniques has had a major impact on the evolution of metamorphic petrology especially in our understanding of the physical conditions occurring in the crust. However, metamorphic rocks commonly preserve mineralogical and textural relics, such as compositionally zoned minerals. To petrologists, these archives are vitally important as they provide a (partial) record of the successive transformations and thus allow a sample's *P*-*T* history to be unraveled. However, relics also indicate that a rock-wide thermodynamic equilibrium clearly was not attained at all stages in the evolution of a rock. One might thus question the utility of equilibrium models to infer the petrogenetic conditions. *P*-*T* estimates must quantify compositional and textural effects and alternative modeling strategies are needed to account for the complexity of relic textures and mineral compositions.

In this contribution, we propose a new framework for alternative modeling and for deciphering the *P*-*T* history of metamorphic rocks. Essential software tools are presented to study and model the compositional variability of minerals, notably to link these to rock textures as documented in quantitative compositional maps. Thermodynamic models are specifically designed to be applicable to local domains. The goal is to test the equilibrium model at the appropriate scale, where one can reasonably expect that thermodynamic equilibrium has been achieved. For modeling to be realistic, mineral relics must be recognized, and fractional crystallization and resorption processes must be accounted for.

This new local modeling strategy has already been applied to various rock types, including amphibolite facies metapelites, migmatites, mafic and felsic eclogites. We will discuss typical results, for which compositional zoning of metamorphic minerals indicates a more complex record than initially expected. By applying a local modeling approach, it becomes possible to "read the rock" and to obtain rather detailed *P*-*T* paths from samples, for which traditional modeling techniques would provide only limited information, *e.g.*, peak metamorphic conditions. Such detail is particularly valuable in combination with *in situ* chronometry, to link spot dating to one or more specific stages of metamorphic evolution and their *P*-*T* conditions (petrochronology).

Microstructural, microchemical and geochronological investigation of two opposite, crustal-scale shear zones in the Garhwal Himalaya (NW India)

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Keywords: Himalaya, Main Central Thrust zone, Ar-Ar geochronology, South Tibetan Detachment System.

Constraining the timing of the activity of the Main Central Thrust zone (MCTz) and the South Tibetan Detachment System (STDS) is one of the major tasks to understand Himalayan tectonics. These shear zones are crustal scale ductile-to-brittle structures running all along the belt.

The MCTz and STDS are the lower and upper boundary, respectively, of the Greater Himalayan Sequence (GHS), the metamorphic core of the orogen. In some areas the MCTz is a km-wide shear zone, whereas in other areas it is bounded by two distinct thrusts. In Garhwal (NW India), the structurally lower and upper MCTz boundaries are the Munsiari and Vaikrita Thrusts (Valdiya, 1980), respectively.

We constrain the time of activity of the Vaikrita Thrust by ^{39}Ar-^{40}Ar dating of biotite and muscovite from two garnet-bearing mylonitic micaschists and one garnet-staurolite-bearing quartzite. Microstructural observations reveal at least three different mica growth stages with muscovite being larger and more abundant than biotite. Mica-1 highlights a relict foliation, only locally preserved, at high angle with respect to the main mylonitic one; mica-2 grew along the main mylonitic foliation; its small flakes are often shredded; mica-3 forms coronitic structures around garnet porphyroclasts. EPMA on muscovite shows restricted chemical variation, with Ti, Mg and Fe contents being systematically lower in muscovite-3. Biotite from micaschists shows no significant chemical variations, whereas in quartzite biotite-2 shows two distinct compositional clusters.

Rocks were crushed and sieved. Biotite and muscovite were separated by gravimetry and extensively handpicked. Biotite step ages range between 8.6 and > 12 Ma, and muscovite step ages between 3.6 and > 7 Ma. As all samples are from the same 10 m wide outcrop, "cooling ages" should be equal. Instead, their large variations are petrogenetically controlled. Since chloritization is pervasive in all samples, we use the Ca/K ratio to identify Ar released from mica *sensu stricto* from the intergrown alteration phases. Furthermore, the Cl/K ratio (Villa et al., 2014) allows us to distinguish mica-3 from mica-2. Handpicking enriched muscovite-3 over muscovite-2. The results are best explained by mica growth along the main foliation around 9 Ma. Coronites formed c. 3 Ma later during retrograde garnet breakdown, as shown by the lack of internal deformation in micas and by microchemical data.

The time span for the activity of the STDS is constrained by a little-deformed pegmatitic dyke close to it. Its white mica grew after the ductile deformation and gave a ^{39}Ar-^{40}Ar age > 16 Ma. Thus, the STDS froze c. 7 Ma earlier compared to the main movement phase of the Vaikrita Thrust.

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Kinematics and non-coaxial flow of the South Tibetan Detachment System (Himalaya)

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Keywords: Himalaya, non-coaxial flow, South Tibetan Detachment System (STDS).

The South Tibetan Detachment System (STDS) is a regional ductile-to-brittle top-to-the E and NE normal shear zone developed for more than 2000 km along the Himalaya strike. The STDS divide the very-low- to low-grade metamorphic rocks of the Tethyan Himalayan Sequence (THS), in the hanging-wall, from the medium to high-grade metamorphic rocks of the Greater Himalayan Sequence (GHS), in the footwall. We investigate, with a multidisciplinary approach, three different sections of the STDS cropping out in Lower Dolpo (western Nepal), Kali Gandaki Valley (central Nepal) and Dinggye area (south Tibet), where, due to the carbonate-rich nature of THS and GHS rocks, identifying and mapping the STDS is not a simple task (*e.g.*, Carosi et al., 2002).

Along all the studied structural sections, we densely sampled impure marble and calcsilicate from both tectonic units affected by the STDS related ductile-shearing.

Ductile heterogeneous deformation have been recognized, leading to the development of calcmylonites associated to a mylonitic foliation striking parallel to the STDS and dipping at low angle to the N and NE. Main kinematic indicators are asymmetric strain fringes around pyrite, polycristalline calcite or calcite/dolomite aggregates, foliation boudinage and asymmetric boudinage of calcite veins in low-grade metamorphic rocks of the THS, whereas mica fishes and S-C-C' fabric developed in GHS rocks. All kinematic indicators confirm a top-to-the N and NE sense of shear.

Microstructural and petrofabric analysis of calcite and quartz was carried out. Lattice preferred orientations (LPO) have been characterized through X-ray goniometer and U-stage on selected samples. Our investigation reveals the occurrence of shape (SPO) and LPO, in almost all samples, supporting intracrystalline creep and dynamic recrystallisation as the main deformation mechanisms.

Comparing both calcite and quartz pole figures we detected asymmetric distribution of **c** axis, pointing out coherent sense of shear as suggested also by kinematic indicators, observed at the mesoscale and at the microscale.

Vorticity of flow (Wk) estimated, through different types of vorticity gauges, highlight a non-coaxial deformation regime, with strong pure shear component, acting during the STDS activity both in high- and medium-temperature and low-temperatures mylonites.

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Quantitative microstructural analysis *vs.* numerical metamorphic petrology as a tool to investigate the *PTdX* evolution of orogenic process

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Keywords: geomatics, fabric analysis, effective reactant volume, metamorphic petrology information system.

The final aspect (*i.e.*, fabric arrangement and paragenesis) of the metamorphic rocks is the result of the counterbalancing factors controlled by deformation *vs.* recovery processes. For this reason, the quantification of the rheology properties by means of microstructural analysis, as well as of the definition of the thermodynamic equilibria by quantification of the effective bulk rock chemistries, represent two faces of the same medal. With this contribution, we would like to structure for the first time a unique Local Information System (LIS) platform in ArcGis® able to store and elaborate quantitative information from both microstructural and petrological points of view. The structure of our LIS starts from the acquisition of high resolution optical thin section scans, which are nowadays good input to extrapolate detailed grain boundary maps (*e.g.*, Li et al., 2008; De Vasto et al., 2012). These procedures adopt sequential stepwise controlled procedures consisting of filtering processes, followed by edge detection functions. These algorithms are able to automatically extrapolate polygonal features useful to obtain in turn microstructural derived parameter such as the grain size distribution as well as the shape preferred orientation of mineral grains. Yielded microstructurally derived results have been then integrated with the multivariate statistical image analysis of micro X-ray maps of the entire thin section (Ortolano et al., 2014a) in order to enrich the grain size distribution analysis with the mineral distribution map. This integration have led to structuration of a new local geodatabase where each detected mineral grain is accompanied by geometrical and compositional data features. The following classification of one or several microdomains per thin section, highlighted then in turn the sequence of recognized metamorphic equilibria, which can be used to a better definition of the effective bulk rocks chemistries, based on the objective interpretation of reaction-scale equilibration (*e.g.*, Fiannacca et al., 2012; Ortolano et al., 2014b).

Recently our procedure has been completed with the calibration of previously classified X-ray map *via* a multi-linear regression technique. This new analytical cycle permitted to obtain new image arrays, each of them representative of: a) the elemental concentration within a single phase expressed in a.p.f.u;.b) maps of the end members visualizing the potential zoning patterns of solid solution mineral phases. The latter can be then easily converted into *PT* maps integrating compositional data with thermodynamic modeling constraints.

Yielded results highlight as this new GIS-based workflow can be usefully applied in order to obtain an assisted semi-automated sequential image processing procedure, applicable in all the fields of petrological investigations, with particular focussing in the resolution of metamorphic petrology problems using a new numerical approach. This approach is able to minimize the subjectivity of the petrologists in the definition of the scale and composition of textural equilibria, storing at the same time in a unique LIS structure all the fundamental textural and petrological information of metamorphic rocks.

De Vasto, M.A., Czeck, D.M., Bhattacharyya, P. (2012): Using image analysis and ArcGIS ® to improve automatic grain boundary detection and quantify geological images. Comput. Geosci., 49, 38-45.

Fiannacca, P., Lo Pò, D., Ortolano, G., Cirrincione, R., Pezzino, A. (2012): Thermodynamic modeling assisted by multivariate statistical image analysis as a tool for unraveling metamorphic P T-d evolution: an example from ilmenite-garnet-bearing metapelite of the Peloritani Mountains, Southern Italy. Mineral. Petrol., 106, 151-171.

Li, Y., Onasch, C.M., Guo, Y. (2008): GIS-based detection of grain boundaries. J. Struct. Geol., 30, 431-443.

Ortolano, G., Zappalà, L., Mazzoleni, P. (2014a): X-Ray Map Analyzer: a new ArcGIS® based tool for the quantitative statistical data handling of X-ray maps (Geo- and material-science applications). Comput. Geosci., 72, 49-64.

Ortolano, G., Visalli, R., Cirrincione, R., Rebay, G. (2014b): PT-path reconstruction via unraveling of peculiar zoning pattern in atoll shaped garnets via image assisted analysis: an example from the Santa Lucia del Mela garnet mica schist (Northeastern Sicily-Italy). Per. Mineral., 83, 257-297.

Metamorphic timescale events constrained by diffusion in garnet overgrowth stages: the Late-Variscan static metamorphism of the Serre Massif (southern Calabria, Italy)

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Keywords: numerical petrology, image analysis, Calabria-Peloritani orogeny.

The tectono-metamorphic evolution of metamorphic basements reflects the dynamic journey of rocks, faced during their burial evolution into the deep crust up to exhumation upon surface, passing, potentially, through one or more static metamorphic stages due to local thermal rising. This implies a continuous changing in the intensive variables (*e.g.*, T, P, fO_2) through several types of dP/dT gradient for different precursor rocks, as highlighted by the peculiar continuous adjustment of the mineral assemblages as well as of the solid solution compositions. In the metapelite system, for instance, garnet is the solid solution mineral that best records these changes, since its forming porphyroblast textural characteristic and its slow cationic diffusion rates, making it one of the mineral most commonly used as a tracer of the P-T-t trajectories of metamorphic basements. In recent years, modeling concentration gradients modified by cationic diffusion processes has become an increasingly used geo-chronometry tool to constrain durations of thermal events, if temperature, pressure and element diffusion coefficients are known and if kinetic window condition is verified (Chakraborty, 2008).

In this work, we have investigated millimeter almandine-rich garnet crystals from garnet-micaschists of the Mammola Paragneiss Complex (Serre Massif-southern Calabria; Angì et al., 2010), highlighting a multistage metamorphic evolution consisting of an orogenic cycle partly overprinted by a thermal one, both of them ascribable to the Variscan orogenesis (Angì et al., 2010). In particular, we focused on the thermal cycle with the intent to estimate the timescale of the static event linked to the emplacement of Late-Variscan huge masses of granitoid bodies, by modeling compositional changes within garnet due to the high-temperature multi-component diffusive effects.

Obtained results highlighting a timescale for the Late-Variscan thermal event of about 1-3 Ma, suggesting a relatively rapid exhumation in this portion of the dismembered southern Hercynian European Belt, presently involved within the internal Alpine sector of the western Mediterranean geodynamics.

Angì, G., Cirrincione, R., Fazio, E., Fiannacca, P., Ortolano, G., Pezzino A. (2010): Metamorphic evolution of preserved Hercynian crustal section in the Serre Massif (Calabria- Peloritani Orogen, southern Italy). Lithos, 115, 237-262.

Chakraborty, S. (2008): Diffusion in solid silicates: a tool to track timescales of processes comes of age. Ann. Rev. Earth Planet. Sci., 36, 153-190.

Correlation between Maures Massif (France) and Sardinian Variscan basement: preliminary lithological, structural and metamorphic data from two sections of the European Variscan belt

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Keywords: Maures Massif, Corsica-Sardinia block, Variscan Belt.

The Maures-Tanneron Massif and the Corsica-Sardinia block are different segments of the southern Variscan Belt (Ricci & Sabatini, 1978; Matte, 2001; Corsini & Rolland, 2009), which during Miocene has suffered separation because of rotation of the Corsica-Sardinia block (Todesco & Vigliotti, 1993), that complicated the correlations between them. Lithological and metamorphic similarities between the two basements sections are numerous: a progressive increase of the Barrovian metamorphism can be recognized both in Sardinia (from SW to NE; Carmignani et al., 1994) and in the Maures-Tanneron Massif (from W to E; Corsini & Rolland, 2009; Schneider et al., 2014) and both sectors are divided in a medium-low grade complex and a migmatitic complex with granitic intrusions. From the structural point of view, till now, correlation between the two sectors is not so clear. This work aims to highlight similarities between these two segments of the Variscan Chain, focusing on structural correlations. Key areas of the western part of the Maures Massif were studied. Meso- and microstructural studies on field-oriented samples, collected along a W-E transect, allowed to recognize different deformation phases linked to the collisional stage followed by a transpressive deformation, mostly recorded approaching to the migmatitic zone of the massif. Structural evolution and kinematics of the shear zones resulted very similar to that outlined in the NE Sardinia (Carosi & Palmeri, 2002).

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Carosi, R. & Palmieri, R. (2002): Orogen-parallel tectonics transport in the Variscan belt of northeastern Sardinia (Italy): implications for the exhumation of medium-pressure metamorphic rocks. Geol. Mag., 139, 497-511.

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Matte, P. (2001): The Variscan collage and orogeny (480-90 Ma) and the tectonic definition of the Armorica microplate: a review. Terra Nova, 13, 122-128.

Ricci, C.A. & Sabatini, G. (1978): Petrogenetic affinity and geodynamic significance of metabasic rocks from Sardinia, Corsica and Provence. N. Jb. Geol. Paleont. Mh., 1978, 23-38.

Schneider, J., Corsini, M., Reverso-Peila, A., Lardeaux, J.M. (2014): Thermal and mechanical evolution of an orogenic wedge during Variscan collision: an example in the Maures-Tanneron massif (SE Fran-ce). Geol. Soc. Sp., 405, 313-331.

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New geological and structural characterization of Fornovolasco tectonic window (Alpi Apuane, Tuscany, Italy)

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Keywords: geological mapping, polydeformed structures, ore deposits, Fornovolasco, Apuan Alps.

The main results of a new geological-structural investigation performed from cartographic to microscale on the ore bodies exposed in the Fornovolasco area (Alpi Apuane Tuscany, Italy) are here presented.

In the area three main tectonic units were distinguished, from top to the bottom:

- The Tuscan Nappe including terms from the basal carbonatic cataclasites (cfr. Calcare Cavernoso *Auctt.*) to the uppermost Macigno Fm. The unit is characterized by large scale east-dipping monocline, with local excision of stratigraphic terms due to the presence of intra-unit low-angle normal faults (LANF). An early generation of intra-stratal decimetric to metric-scale tight to isoclinal folds (mainly observable within the Maiolica and Calcare Selcifero Fm.) and a later generation of open to tight folds associated with a crenulation cleavage mainly developed in pelitic units are common mesoscopic-scale deformation structures;
- The Panie unit, mainly represented by Norian-Rhaetian Grezzoni Fm.;
- The Apuane unit which appears subdivided in different tectonic subunits (Carmignani et al., 1976; Pandeli et al., 2004) including Paleozoic phyllites ("Scisti di Fornovolasco" *Auctt.*) and Mesozoic-Tertiary cover units mainly represented by Pseudomacigno Fm.

Within the Apuane unit, which shows cartographic to meso-scale structural features similar to those of the "Stazzemese zone", a new geological formation has been identified and mapped. This formation, hereafter indicated as "Fornovolasco Metarhyolite", is represented by acid metavolcanites characterized by the occurrence of tourmaline orbicules and dated, through zircon geochronology, to the middle-lower Permian (see Vezzoni et al., 2017, for details on mineralogical, geochemical and geochronological characterization). Moreover the siliciclastic and siliciclastic-carbonate deposits of Ladinian-Carnian age (Vinca Fm. and Tinello Metacarbonates of Pandeli et al.(2004) were analyzed in details, because the highest part of the magnetite mineralization present in the Fornovolasco mining area seems to show similar characters to Verrucano-like deposits with iron-oxides matrix.

Acknowledgements: this project has been supported by the MIUR-SIR grant "THALMIGEN" (RBSI14A1CV) granted to CB.

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Pandeli, E., Bagnoli, P., Negri, M. (2004): The Fornovolascoschists of the Apuan Alps (Northern Tuscany, Italy): a new hypothesis for their stratigraphic setting. Boll. Soc. Geol. It., 123, 53-66.

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The complex polymetamorphic history of the Southalpine realm: evolution of continental crustal slices from Variscan to Alpine time

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Keywords: petrology, structural geology, geochronology, rifting, Variscan orogeny.

Numerous polymetamorphic slices of basement crop out in the Alps. They are involved in the Alpine belt and partially overprinted by Alpine metamorphism which tends to delete the pre-Alpine history. Identification of pre-Alpine *vs*. Alpine events must be performed to avoid misunderstanding of the geological history. Pre-Alpine structures can be associated to two different geodynamic events: (1) Variscan structures related to Carboniferous collision, (2) Permo-Triassic rifting that overprints the Variscan history. Evidence for this Permo-Triassic event is poorly reported in the literature either because it was spatially localised or is particularly hard to recognize.

We investigate a portion of basement characterized by the absence of Alpine overprint: the basement of the southern Alps, which represent the former northern part of the Adriatic margin. Our goal is to clearly separate orogenic (Variscan) from rift-related (Permo-Triassic) structures. We target the Dervio-Olgiasca Zone (DOZ) and the Monte Muggio Zone (MMZ) that crop out along the northern part of Como lake. This basement records a Variscan history (Spalla et al., 2000) and it is cross cut by the Lugano-Val Grande normal fault (186-220 Ma; Bertotti et al., 1999).

Micaschists contain pseudomorphs composed of prismatic sillimanite and biotite after staurolite, as well as biotite and fibrolitic sillimanite aggregates after garnet, and muscovite after kyanite. Reconstructing the evolution of these rocks is fundamental to determine the pre-Alpine pressure and temperature conditions of the basement. Datable accessory mineral monazite and zircon are texturally correlated with the tectono-metamorphic evolution of the schist. Preliminary U-Th-Pb analyses on monazite provide evidence for a Late Carboniferous orogenic event followed by a possible Middle Triassic rift-related *HT* event.

The Dervio-Olgiasca-Zone (DOZ) and Monte Muggio Zone (MMZ) represent an example of well-preserved Variscan basement partially overprinted by a Triassic rift-related event. Across this study, we wish to highlight, that the Permo-Triassic metamorphism is well-developed only at the deepest structural level, it could easily be mistaken as Variscan and is only identified by careful micro-structural analysis.

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Spalla, M.I., Siletto, G.B., di Paola, S., Gosso, G. (2000): The role of structural and metamorphic memory in the distinction of tectono-metamorphic units: the basement of the Como lake in the Southern Alps. J. Geodynam., 30, 191-204.

Pre-Permian contrasting tectono-metamorphic evolutions in the Southern Steep Belt (Mortirolo area-Languard-Campo Unit – central Alps)

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Keywords: TMU, Permian, contrasting evolutions, extension.

Relicts of pre-Alpine continental crust are preserved in the Southern Steep Belt (Italian central Alps), between Valtellina and Val Camonica. A polymetamorphic rock association occurs, belonging to the Upper Austroalpine units, and includes lithotypes commonly attributed to the Languard-Campo nappe (LCN) and the Tonale Series (TS). Rocks belonging to LCN and TS are low to medium grade muscovite-, biotite- and minor staurolite-bearing gneisses and micaschists with interlayered garnet- and biotite-bearing amphibolites, marbles, quartzites and pegmatites, sillimanite-bearing gneisses and micaschists. The boundary between the two units is commonly recognised where large bodies of sillimanite-bearing gneisses (migmatitic) and amphibolites occur. Permian (260 ± 10 Ma) intrusive (granitoids, diorites and minor gabbros) also occur and crosscut the penetrative S2 foliation, developed between 260 and 280 Ma (zircon U-Pb geochronology). Two older contrasting tectono-metamorphic units (UTM), pre-dating Permian intrusives have been distinguished, one occurring at migmatitic conditions in metapelites, the other defined by staurolite-biotite-bearing assemblages. In this contribution we will discuss the geodynamic significance of these UTMs in the framework of the Variscan-Permian collision to extensional setting.

Garnet-rich nodules in ultramafic amphibolites from NE Sardinia

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Keywords: garnet nodules, ultramafic amphibolite, NE Sardinia, Variscan orogeny.

A lenticular-shaped body NE from Olbia is included in the Variscan migmatite of NE Sardinia. It consists of two-main lithological associations, *i.e.*, ultramafic amphibolites and plagioclase-rich amphibolites, that are considered genetically related as the result of a magmatic differentiation of an original tholeiitic magma (Ghezzo et al., 1979). The ultramafic amphibolites consists of three main compositional layers. The lower layer is dark-grey and reddish in color and it is made of olivine crystals, chlorite and amphibole; the middle layer is dark grey to greenish and consist mainly of greenish amphibole and large plagioclase crystals and the upper layer is made up of a dark-green, garnet rich amphibolite. This uppermost layer is characterized by the presence of porphyroblastic garnet, large amphibole grains (up to 4-5 cm) and minor pyroxene and plagioclase. This Layer is characterized by the occurrence of garnet nodules ranging in size from 1 to 15 cm. surrounded by a 1-2 mm thick amphibole-rich rim. At times the nodules are crosscutted by amphibole-rich veins. The garnet nodules are made up of garnet, amphibole, spinel and large amount of epidote. They are coarse-grained with a grain size similar to samples from the uppermost layer. Garnet occurs as anhedral crystals with several inclusions of epidote and green amphibole. Amphibole grains show a worm-like texture with spinel. Epidote often replaces garnet, or more rarely, amphibole. No relics of igneous minerals have been observed. In the garnet nodules SiO_2 ranges from 38 to 41 wt.%, MgO varies between 8-12 wt.%, $Fe_2O_{3(tot)}$ is comprised between 11 and 14 wt.%, CaO varies in the range 13-16 wt.%. TiO_2 content is lower than 0.27 wt.% whereas $Na_2O + K_2O$ is under 1.1 wt.%. The trace element abundance is comparable to that of the ultramafic amphibolites and plagioclase-banded amphibolites with Sr and Rb enrichment and P, Zr, Hf, Sm, Ti, Y, Yb depletion as compared to N-MORB. The *REE* pattern of the garnet nodules is moderately fractionated with marked positive Eu anomaly. Field data, mineral associations and chemical analyses suggest that garnet-rich nodules can not be considered as xenoliths because they show a strong affinity with the containing ultramafic amphibolites. It is more likely that they have an analogous origin shared in the magmatic chamber. The formation of these nodules can be due to magma drops fromed in the upper parts of the magma chamber, as the shape of the nodules suggests for plastic conditions at the time of their formation. These features suggest that the garnet nodules do not represent externally-derived xenoliths but rocks similar to those occurring in the magma chamber.

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Geochronology and deformation in the Ferriere-Mollières shear zone (Argentera Massif, western Alps): similarities and differences compared to other fragments of the Variscan chain in the Mediterranean area

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Keywords: Variscan shear zone, Argentera Massif, mylonites, East Variscan shear zone, monazite.

The architecture of the SE segment of the Variscan Chain is not entirely clear because of tectonic reworking during Alpine Orogenesis. Some authors proposed that the European Variscan belt is characterized by a composite orocline (Matte, 1986; Matte, 2001) made by two main branches: the western Ibero-Armorican arc and an eastern branch delimited by a system of regional-scale dextral transpressive shear zones known as the East Variscan Shear Zone (EVSZ; Corsini & Rolland, 2009; Carosi et al., 2012) extending from NE to SW involving the Alpine External Crystalline Massifs, the Maures Massif and the Corsica-Sardinia Block. The presence, the extension and the impact of this system of shear zones on the tectonic evolution of the chain is debated. To verify if shear deformation affecting the Alpine External Crystalline Massifs can be linked to the EVSZ is necessary to carefully investigate the kinematic of the flow and its age in order to check if there are similarities with other better-known contexts. We performed a kinematic vorticity analysis and an U-Th-Pb geochronological study on syn-kinematic monazites in the western Alps where a steeply dipping km-scale shear zone, the Ferriere-Mollières shear zone (FMSZ), cross-cuts Variscan migmatites in the Argentera External Crystalline Massif.

We recognized a high-temperature deformation associated to dextral transpression characterized by variation in the percentage of pure shear and simple shear along a deformation gradient. U-Th-Pb analyses on syn-kinematic monazites were performed on selected mylonites from different structural position in the shear zone. The oldest ~ 340 Ma ages were obtained in protomylonites whereas ages of ~ 320 Ma were found in mylonites from the core of the shear zone. These ages indicate that the FMSZ is a preserved Variscan shear zone. Ages of ~ 320 Ma obtained in this work are in agreement with ages of the dextral transpressional shear zones in the Maures-Tanneron Massif and Corsica-Sardinia. However transpression in the Argentera Massif started earlier than in other sectors of the southern Variscan Chain. This is possibly caused by the curvature changing of the belt leading to the progressive change of orientation of the belt with respect to the regional stress field.

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The "Fornovolasco meta-rhyolite": an Early Permian magmatic event recorded in the Apuan Alps basement

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Keywords: Apuan Alps, "Fornovolasco meta-rhyolite", U-Pb zircon geochronology, Permian magmatism.

The Apuan Alps are the main tectonic window of the northern Apennines thrust-and-fold belt, showing wide outcrops of the Paleozoic basement unconformably overlain by a Triassic to Oligocene meta-sedimentary cover. The basement consists of a Late Cambrian to Devonian siliciclastic succession associated with Middle Ordovician felsic igneous rocks and their weathering and erosion products (Porphyroids and Porphyritic schists Fm.). This latter formation has been recently dated at 457 ± 3 Ma (Paoli et al., 2017).

In the southern Apuan Alps, the occurrence of massive tourmaline-rich porphyritic rocks has been known for more than a century. Notwithstanding some previous studies (*e.g.*, Bonatti, 1933; Pandeli et al., 2004), their interpretation remained debatable. The finding of new outcrops, mainly located close to the Fornovolasco hamlet, showing peculiar textural features mainly represented by tourmaline orbicules, promoted a new investigation of this rock (hereafter "Fornovolasco meta-rhyolite").

The "Fornovolasco meta-rhyolite" is a white to dark grey porphyritic rock, variably dotted with bluish-black orbicules composed by schorlitic tourmaline, quartz and minor plagioclase. The primary mineralogy was partly obliterated with the development of a pervasive schistosity, more pronounced toward the contact with the host-rock. Textural features (*e.g.*, porphyritic structure, embayed quartz, occurrence of tourmaline orbicules) suggest a sub-volcanic nature of the protolith. Euhedral zircon crystals with oscillatory zoning have been analyzed by LA-ICP-MS to determine the crystallization age of the protolith. The U-Pb geochronology points to an Early Permian age.

This work reports the first evidence of a Permian magmatism in the Apuan Alps, highlighting the occurrence of two different magmatic cycles recorded in the Apuan Alps basement, *i.e.*, a Middle Ordovician one related to the Porphyroids and an Early Permian one related to the "Fornovolasco meta-rhyolite". The identification of a Permian felsic magmatism opens new scenarios for the post-Variscan evolution of the basement and for the ore genesis in the Apuan Alps, and it allows the comparison with other European localities.

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Garnet chemical and oxygen isotope zoning and accessory mineral investigation to constrain the evolution of subducted continental crust (Sesia Zone, Italy)

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Keywords: oxygen isotopes, subduction, garnet, zircon.

Garnet is a key mineral in metamorphic petrology for constraining pressure and temperature (*P*-*T*) paths. Garnet can preserve multiple growth stages due to its wide *P*-*T* stability field and the relatively slow diffusivity for major and trace elements at sub-solidus temperatures. *P*-*T*-*t*-fluid paths of the host rock may be reconstructed by combining metamorphic petrology with microscale trace element and oxygen isotope measurements in garnet and accessory mineral *in situ* dating.

Subduction zones represent relevant geological settings for geochemical investigation of element exchanges during aqueous fluid-rock interactions. The Sesia Zone consists of a continental sequence containing a variety of mono- and poly-metamorphic lithologies such as metagranitoids, sediments and mafic boudins. The Variscan-Permian granulite to amphibolite-facies basement (6-9 kbar, 650-850°C; Lardeaux & Spalla, 1991) experienced *HP* metamorphism (15-22 kbar, 500-550°C; Regis et al., 2014) during Alpine subduction. In different lithologies of the Internal Complex (Giuntoli & Engi, 2016), including metabasites from Ivozio Complex, Ti-rich metasediments from Val Malone, micaschists from Lys Valley and pre-Alpine Mn-quartzites associated to metagabbros from Cima Bonze, garnet is abundant and shows a variety of textures that can be related to resorption, replacement and possible metasomatism. Internal zoning in zircon in these samples preserves information about the age of the protolith (*ca.* 350 Ma gabbro at Ivozio), Permian (Val Malone) and Alpine metamorphism (Ivozio and Lys Valley).

In situ microscale oxygen isotopes analysis of garnet zones was performed by ion microprobe with the SwissSIMS Cameca at University of Lausanne and SHRIMP-SI at the Australian National University. Each sample has a distinct $\delta^{18}O$ composition and shows different degrees of variation between domains. Homogeneously values of < 5 ‰ are measured in the garnets from Ivozio metagabbro. Intragrain variations up to ~ 3.5 ‰ in the porphyroblasts from Val Malone metasediments and up to ~ 6.5 ‰ in Cima Bonze garnets suggest significant metasomatic replacement from external fluids.

The combination of oxygen isotopes, trace element geochemistry and geochronology, and *P*-*T* modelling allows reconstructing the major stages of metasomatism, as well as identifying the nature of the fluid interacting with the rock at each metamorphic stage.

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Pre-alpine history of the Sassa gabbro complex, Dent Blanche nappe, western Austroalpine

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Keywords: Permian gabbro, lithosphere thinning, western Alps.

Within the European Alps, post-Variscan gabbro complexes are well documented only all over the Austroalpine and Southalpine domains. Their emplacement is assessed at the Permian-Triassic times and heralded the opening of the Alpine Tethys. The peculiar distribution has been interpreted as the effect of an active asymmetric rifting in which the future northern Adria passive margin (Austroalpine and Southalpine) was the hangingwall (Spalla et al., 2014; Marotta et al., 2016 and references therein). In this contribution we focus on the Sassa gabbro complex that is part of the Permian gabbro bodies of the Collon–Matterhorn group (Dal Piaz et al., 1977; Monjoie et al., 2007) and is intruded in the Arolla Series meta-intrusives of the Austroalpine Dent Blanche nappe. Despite the Alpine structural and metamorphic reworking affecting the Dent Blanche nappe, the Sassa gabbro complex clearly preserves primary magmatic features (Baletti et al., 2012). The Sassa gabbro complex consists of meso-gabbro, leucogabbro, melagabbro, and anorthosite that are intruded by porphyritic, plagiogranitic, and aplitic dykes. Primary structures consist of cumulitic fabric and magmatic layering and foliation. Magmatic mineral relicts are pyroxene, plagioclase, biotite, spinel, and amphibole. Two following pre-Alpine coronitic assemblages overprint the magmatic minerals. The two post-magmatic assemblages are characteristic of amphibolite and greeschist facies, respectively and are interpreted as the metamorphic re-equilibration during the progressive exhumation of the gabbro, within an extensional lithospheric context. In conclusion the pre-Alpine evolution of the Sassa gabbro is similar to that of other Permian-Triassic gabbro complexes of the Alps and characterised by high T/P ratio.

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Session S19:

Geochronology and geochemistry of accessory minerals: timing of petrogenetic processes and deformation

Conveners:

Deborah Lo Pò (Univ. di Bologna)

Antonio Langone (CNR, Pavia)

Leonardo Casini (Univ. di Sassari)

Matteo Maino (Univ. di Pavia)

U-Pb dating of zircons from a dyke of the Finero Mafic Complex (Ivrea-Verbano Zone, Italian Alps): when a simple case become a paradox

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Keywords: microstructures, zircon U-Pb dating, trace elements, mafic dyke, Ivrea-Verbano Zone.

The section of lower continental crust, Ivrea–Verbano Zone (IVZ) is under large debate because of the unknown timing of under- and intra-plating of the mafic melts. These melts have been essentially dated as Early Permian in the central part of the IVZ (Peressini et al., 2007) and Middle Triassic in the northeastern sector (Zanetti et al., 2013).

To unravel this controversy we performed a study on zircon grains from plagioclase-rich dioritic dykes discordantly intruded within metadiorites/gabbros forming the External Gabbro unit of the Finero Mafic Complex (IVZ- Type Finero).

The diorites dykes consist mainly of plagioclase (An_{18-24}) with subordinate amounts of biotite and spinel defining melanocratic layers. Zircon and corundum are common accessory phases.

The zircon grains can be subdivided in two populations: i) zircon from the leucocratic layer and ii) zircon from the melanocratic layers.

Morphology, internal features (cathodoluminesce zoning, crystallographic preferential orientation, fractures, cracks), chemistry and U/Pb dating distribution of the zircon grains coupled with textural information allowed us to track the multi-stage evolution of the dyke-system.

Zircons from the leucocratic layers show a large variation of ages (Late Carboniferous to Early Jurassic) if compared with the grains from the melanocratic layers that resulted to be always younger than Late Permian.

For the zircons from the leucocratic layers the younger ages were obtained from inner bands/sectors oriented parallel to fractures and the mylonitic foliation. the ages distribution is coherent with trace element variations (*e.g.*, the younger domains are generally associated with enrichments of Nb, Ce, Ta, Pb, Th, U and *HREE*).

While the zircons from melanocratic layers are the result of a Triassic metasomatic event promoting deformation, chemical variation and modification of the mineral assemblage of the pre-existing (Permian?) dykes.

These results on the zircons allowed us to retrieve information on the dykes intrusion which experienced a multi-stage evolution with a crystallization of the leucocratic domains at first (Late Carboniferous – Early Permian) followed by annealing and reorganization of zircon grains during a (K-rich) metasomatic event with injection and crystallization of the melanocratic layers (biotite + oxides). As a consequence, the intrusion of the External Gabbro unit must have occurred before the Triassic (probably during Late Carboniferous-Early Permian), synchronous with the other mafic bodies of the Ivrea-Verbano Zone.

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Geochronology of late Variscan magmatism of Sardinia: a review

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Keywords: Sardinia-Corsica batholith, Variscan granites, plutons emplacement, lithospheric delamination.

Sardinia represents a southern transect of the Variscan Belt and is classically divided from SW to NE into a fold and thrust belt Foreland, Nappe zone and Axial zone. This latter high-grade domain is separated from the Nappe zone by the so-called Posada-Asinara Line. The whole metamorphic basement is intruded by many calc-alkaline coalescent plutons forming the Corsica-Sardinia Batholith. The timing of magmatism, in Sardinia, is broadly referable to a large interval in the range of 320-280 Ma. Recent geological maps coupled to several chronological systematics, point out to recognize two main post-collisional magmatic peaks clustered at about 305 Ma (Older Magmatic Peak, OMP) and at 285 Ma (Young Magmatic Peak, YMP), respectively.

Plutons intruding different parts of the Sardinian basement show different geological styles. Among the OMP, main differences regard: (a) the granodiorite/granite volume ratio in the main plutons; (b) the abundance of peraluminous rock-types; (c) the occurrence of mafic intrusions; (d) the abundance of late-magmatic dyke swarms. The Axial zone is dominated by monzogranites and subordinate granodiorites and leucogranites (320-307 Ma); tonalites and granodiorites (305-300 Ma), along with peraluminous granites, characterize the inner Nappe zone (*i.e.*, Goceano, Baronie, Barbagia). Remarkably, the oldest intrusions (*i.e.*, Barrabisa and Santa Maria: 320 Ma) are foliated and may represent a pre-batholith magmatic phase. Plutons occurring in the external Nappe zone and the Foreland are generally dominated by granodiorites (*e.g.*, Arbus, Ogliastra, Sàrrabus: 305-300 Ma) associated to small gabbronoritic bodies. The YMP is marked in the Axial zone by large leucogranite intrusions (Monte Lerno); gabbroic intrusions are present at 285-280 Ma. The YMP is dominant in the external Nappe zone and in the Foreland. This peak include monzogranites and leucogranites with minor granodiorites; specific characters are: (a) common occurrence of F-bearing, ferroan, ilmenite-series granitoids; (b) slightly peraluminous character; (c) very shallow emplacement levels, with common greisen alteration; (d) presence of Sn-W-Mo and F ores; (e) association to swarms of tholeiitic mafic dikes. The timing and distribution of Sardinian intrusive magmatism are tentatively framed during the post-collisional evolution of the chain, in response to progressive lithospheric delamination along a N-S direction. In this model, the passive upwelling of hot astenosphere triggered dehydration melting at lower to intermediate crustal levels, associated with minor melting of the lithospheric mantle. Several major issues emerge from this schematic picture, including (a) the precise timing of the magmatic peaks, (b) the significance of the gap between them, (c) the difference in volumes and spatial distribution of the main rock-suites, (d) the geological and petrological frame at the district- to single pluton-, up to regional scale, and (e) the age of mafic dyke swarms.

Advantages and limitations of zircon U/Pb dating of granites – an example from the Corsica-Sardinia Batholith

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Keywords: Variscan, magmatic systems, pluton, Carboniferous-Permian transition.

U/Pb zircon dating is perhaps the best established method to constrain the age of granitic plutons and, broadly speaking, magmatic systems.

Despite the robustness of the method and the possibility to achieve high-precision, the results obtained might sometimes do not represent the crystallization age of the rock as inherited zircons can occur. Moreover, a number of processes such as igneous and metamorphic overgrowth, annealing after radiation damage, hydrothermal alteration, and grain-scale diffusion of Pb, U and Th can severely affect the isotopic composition of zircon, leading to analytically correct, tough geologically meaningless, ages. Therefore, optimization of the sampling strategy is crucial to obtain the age one is looking for.

A good example of unexpected limitations relevant to the zircon system is offered by the Tempio Pausania pluton (TPp), a late Variscan intrusion belonging to the Corsica-Sardinia Batholith (340-280 Ma). The pluton is a large monzogranitic massif composed of three main magmatic batches: a) coarse grained monzogranite with megacrysts cumulates; b) strongly porphyritic monzogranite; c) fine grained leuco-monzogranite. The pluton has an elliptic shape oriented about N120°, and is intruded sideways by discordant bimodal plutons dominated by leuco-monzogranites and more mafic, mantle derived, stocks.

Only the western termination of TPp is emplaced within the metamorphic basement developing a thick chilled margin. Samples of TPp were picked up away from major post-Variscan faults and choosing the less weathered, fine-grained rocks. The first two samples retain a huge population of zircons with Permian ages undistinguishable from those of the surrounding, apparently younger, plutons, whereas a few crystals show Carboniferous ages. Only one sample collected inner part of the pluton yielded a statistically meaningful population of Pennsylvianian zircons that can be interpreted as the true crystallization age of TPp (316.8 ± 2.3 Ma).

Constraints on metamorphic evolution from *REE* minerals, rutile and zircon in pelitic rocks of the central Alps

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Keywords: *HP* metamorphism, monazite, rutile, zircon, central Alps.

The Cima Lunga-Adula unit in the central Alps is constituted by pre-Mesozoic continental basement rocks (orthogneisses, paragneisses and metapelites) and Mesozoic cover rocks, enclosing minor boudins of mafic and ultramafic rocks. The Variscan *HP* mineral assemblages were pervasively deformed and overprinted during Alpine orogeny. Since their discovery, metabasics and ultrabasics have been the main object of the researchers as they preserve (*U*)*HP* eclogite-facies assemblages (peak metamorphic conditions up to 3.0 GPa and 840°C; Nimis & Trommsdorff, 2001). Relatively few information is available for the metamorphism of the gneiss complex constituting the country rocks, for which a limited number of study indicates considerably lower peak metamorphic conditions (up to 0.8 Gpa and 660°C; Grond et al., 1995).

Here, we present some petrographic and geochemical data to partially fill the lack of consistent data about conditions of the Alpine and Variscan metamorphic stages developed by the metapelitic rocks. We focus on kyanite and garnet-bearing paragneiss closely involved together with the mafic *HP* rocks during the Alpine deformation. We present pressure-temperature-deformation path based on mineral assemblages (both in matrix and inclusions within garnet) and geo-barometry and thermometry on rutile and zircon coupled with meso- and micro-structural characterization. U-bearing accessory minerals are also investigated in order to perform geochronological characterization.

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U–Pb thermochronology of rutile to constrain the exhumation history of the lower crust: an example from Alpine Corsica

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Keywords: rutile, U-Pb geochronology, Zr-in-rutile thermometry, Corsica, Belli Piani, rifting.

U–Pb geochronology of rutile is an ideal tool to constrain the thermal evolution of the lower crust during rifting and exhumation, given its moderate closure temperature and the occurrence of rutile in a variety of lower crustal lithologies. U–Pb geochronology of rutile is particularly powerful when coupled with Zr-in-rutile thermometry, which can independently constrain the temperature of growth and/or last recrystallisation of rutile. This allows testing of the common assumption that U–Pb ages record the time of cooling through the closure temperature, which can be invalidated by growth or recrystallisation of the mineral below its closure temperature.

In this study we apply U–Pb geochronology and Zr thermometry of rutile to a lower crustal section in Alpine Corsica, to provide constraints on the thermal evolution of the distal European margin during the Jurassic continental rifting that culminated in the opening of the Tethys. We focus on the Belli Piani unit of the Santa Lucia nappe, which preserves a section of Permian lower crust that experienced a minimal Alpine overprint, and bears a striking resemblance to the renowned Ivrea Zone lower crustal section (Italy). At the base of the Belli Piani unit, a 2–4 km thick mafic magmatic complex contains slivers of entrained granulite facies metapelite. We analysed rutile from three of these metapelitic slivers, sampled from the uppermost to lowermost Mafic Complex. Textural evidence for rutile formation during Permian granulite facies metamorphism is corroborated by high Zr-in-rutile temperatures of dominantly 850–950°C. Lower Zr-in-rutile temperatures of 750–800°C in a few grains are partly associated with elongate strings of rutile within quartz ribbons, interpreted to record recrystallisation of some rutiles during high-temperature shearing. The high Zr-in-rutile temperatures demonstrate that both crystallisation and re-crystallisation of rutile occurred above the closure temperature of Pb in rutile (~ 550–650°C). U–Pb ages of rutile can thus reliably be expected to record cooling through this temperature, providing a *T-t* point uncomplicated by effects such as later re-crystallisation.

Rutile U–Pb ages are extremely reproducible both within and between samples, with sample ages ranging from 160 ± 2 Ma to 161 ± 2 Ma. No other age populations were detected in any sample. These data indicate that the Santa Lucia lower crust last cooled through ~ 550-650°C at ~ 160 Ma, coeval with the first formation of oceanic crust in the Tethys. The new data will be integrated with published data from the Ivrea zone to compare the thermal evolution of the opposing European (Santa Lucia) and Adriatic (Ivrea) continental margins created by rifting associated with the opening of the Tethys.

Petrogenesis of the two-mica Larderello-Travale plutonic system by assembly of non-contemporaneous, isolated and isotopically distinct magma batches

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Keywords: CA-ID-TIMS, zircon high-precision dating, oxygen isotopes, granites.

The Larderello-Travale plutonic system in southern Tuscany (Italy) is formed by high-silica (68-78% SiO_2) peraluminous two-mica and tourmaline-bearing granites with marked crustal isotopic signature (*e.g.*, $^{87}Sr/^{86}Sr = 0.715$-0.721). In this study, zircon crystals from rock samples cored at 3.0-4.5 km depth were investigated by combining cathodoluminescence imaging of growth textures, *in situ* oxygen isotopic data and high-precision U-Pb dates determined by chemical abrasion isotope dilution–thermal ionization mass spectrometry.

Magmatic zircon crystals from the six rock samples analysed exhibit an overall range in $\delta^{18}O$ of *ca.* 5 ‰, with values ranging from 8.6 to 13.5 ‰. Crystals from individual samples exhibit inter-grain oxygen isotope variability exceeding 3 ‰. Moreover, intra-grains $\delta^{18}O$ heterogeneity is also observed in 75% of the magmatic core-rim pairs. Zircon crystals from individual rock samples are characterized by a large scatter in $^{206}Pb/^{238}U$ ages that cannot be explained by analytical uncertainties alone. Therefore, the age of emplacement of the granites has been determined based on the youngest assemblages of zircon grains which overlap within analytical error. The first granite was emplaced in the north-eastern part of the plutonic system at 3.637 ± 0.008 Ma. Zircon grains from this rock yield all the same age within error and display the highest mean zircon oxygen isotope composition ($\delta^{18}O = 11.8$‰). A second composite magmatic pulse was emplaced in the eastern area of the plutonic system where four samples give emplacement ages spanning from 2.605 ± 0.010 to 3.177 ± 0.020 Ma. Zircon grains from each of these four samples display a spread in dates of *ca.* 200-400 ky and extremely variable $\delta^{18}O$. Finally, the youngest granite was emplaced at 1.671 ± 0.004 Ma. This granite is characterized by an age spread of 300 ky as well as by zircon having the lowest mean oxygen isotope composition in the plutonic system ($\delta^{18}O = 9.3$ ‰).

We propose a model in which isolated and isotopically distinct magma batches were generated by partial melting of different metasedimentary crustal sources. In our model, different fertile crustal domains undergo partial melting at different times, with the time of melting depending on the interplay between the evolution of the thermal anomaly in the crust and the composition of the source rock. The non-simultaneous melting of the different crustal sources reflects on their cooling paths and thus on the timing of zircon crystallization (*i.e.*, on the U-Pb zircon ages). Finally, these isotopically diverse zircon-bearing magma batches were assembled into single shallow-level intrusions generated during the three major magma pulses mentioned above.

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Lower crustal metapelites: an ideal case for microstructural and geochronological characterization. An example from migmatitic metapelites of the Serre Massif (Calabria, southern Italy)

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Keywords: migmatitic metapelites, giant garnets, CPOs of quartz, LA-ICP-MS U-Th-Pb.

In the northern Serre Massif (Calabria, southern Italy) a 8 km thick amphibolite-granulite facies Hercynian continental crust is exposed and shows a metamorphic gradient increasing from S toward N. This lower crustal section shares several similarities with well studied Palaeozoic crustal sections exposed in the southern Alps, *i.e.*, the Ivrea-Verbano Zone. The lowermost level (the "granulite-pyriclasite unit") consists of 1 km thick layer of mafic granulites followed by about 2 km thick layer of felsic granulites. Toward the higher structural levels, migmatitic metapelites (the "metapelite unit") define a 5 km thick belt.

So far it was believed that such a Palaeozoic lower continental crust is vertically continuous and tectonically undisturbed. However, our detailed fieldwork has revealed that the felsic granulites and the migmatitic gneisses are juxtaposed by a *ca.* 600 m thick high temperature shear zone. The shear zone developed at the base of the metapelite unit, where the mylonitic migmatitic gneisses are characterized by several centimetre to decimetre long ellipsoidal garnet porphyroclasts surrounded by an anastomosing matrix made up of elongated sillimanite prisms and biotite flakes. Garnet contributes to a strong strain partitioning in the mylonitic migmatites, and where garnet together with K-feldspar crystals forms a stress sustaining framework, we observe interbedded quartz layers with large recrystallized grains. Within the mylonitic matrix the grain size and abundance of quartz were strongly reduced and the crystals are primarily characterized by phase-boundaries with sillimanite prisms, biotite flakes and minor plagioclase grains. The main stretching lineation, well traced by the preferred alignment of sillimanite prisms. Locally, some decimetre-thick felsic dykes crosscut the main mylonitic foliation.

Field structural data and CPOs of quartz, measured with EBSD within the different microstructural sites, testify that the shear zone developed along the flat of a normal fault, at temperatures exceeding 650°C.

Preliminary microstructural investigation on accessory minerals reveals the presence of monazite, zircon and rutile within the mylonitic metapelites and zircon within the felsic dykes. LA-ICP-MS U-Th-Pb dating will be performed in order to reconstruct the *T-t* evolution of this lower crustal sector of the Palaeozoic continental crust. The coupling of different geochronometers will provide useful information on the timing of the evolution of the lower continental crust. Possibly, a comparison with the other well-known lower crustal section (*i.e.*, the Ivrea-Verbano Zone) will be also presented.

U-Pb LA-ICP-MS data on zircons from paragneisses and augen gneisses of Castagna unit in Catena costiera and Sila piccola (Calabria)

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Keywords: U-Pb zircon ages, paragneiss, augen gneiss, Castagna Unit, Calabria.

The aim of this paper was the U-Pb zircon dating in paragneiss of the Castagna Unit outcropping in Catena Costiera (CC) and Sila Piccola and in augen gneiss of the same Unit outcropping in CC to evaluate the similarities or the differences of the geological evolution of the continental crust portions belonging to the same unit and dislocated along the Alpine Chain in Calabria.

The measured ages in the paragneiss from Sila Piccola form clusters at 2700 Ma, 2100 Ma, 1700 Ma, 1031-722 Ma, 637 Ma, 559-515 Ma and 499-421 Ma. These ages are comparable with those measured in augen gneisses of Sila Piccola (Fornelli et al., 2014). The magmatic protoliths of augen gneisses intruded an older metamorphic basement (paragneiss) at about 540 Ma and the whole sector was involved by Ordovician-Silurian tectonic. Both meta-sedimentary rocks and augen gneisses record the same geological events.

In the paragneiss from CC the measured age clusters are 2700 Ma, 2100 Ma and 1025-864 Ma and only one age at 638 Ma. In the two samples of augen gneisses from this area, the whole measured ages form clusters at: 1612 Ma, 975-758 Ma, 583-512 Ma, 508-495 Ma and one age at 327 Ma. The revealed ages in augen gneisses from CC, are comparable with the ages measured in other augen gneisses both from Calabria and Sicily, except the record of Variscan metamorphism (327 Ma) emerged only in CC area. A different geological history, instead, results by paragneisses from CC considered as host basement of Neoproterozoic-Cambrian acidic magmatism (Fornelli et al., 2014). In these paragneisses are missing the records of: 1) Ediacarian magmatism (540 Ma, intrusion ages of protoliths of augen gneisses); 2) Ordovician-Silurian tectono-thermal event (495-420 Ma); 3) Variscan metamorfism (327 Ma).

The missing of these ages in the paragneiss of CC represents a problem. Two hypotheses can be made: 1) the data ages are scarce, more determinations must be performed on other samples; 2) a different geological history was followed by the two sectors of continental crust, in particular, the paragneisses from CC could not represent the basement in which the protoliths of augen gneisses were intruded and, in addition, the augen gneisses outcropping in CC were involved by Variscan metamorphism resetting the zircon age, that for the first time emerges in these rock types. In fact the augen gneisses in Calabria and Sicily display a comparable spectrum of zircon ages comprised between 3242 Ma (Williams et al., 2012) and 421 Ma without Variscan ages.

Fornelli, A., Piccarreta, G., Micheletti, F. (2014): In situ U-Pb dating combined with SEM imaging on zircon – An analytical bond for effective geological reconstructions. In: "Geochronology methods and case studies", N.A. Mörner, ed. Intech, Rijeka, 109-139.

Williams, I.S., Fiannacca, P., Cirrincione, R., Pezzino, A. (2012): Peri-Gondwanian origin and early geodynamic history of NE Sicily: A zircon tale from the basement of the Peloritani Mountains. Gondwana Res., 22, 855-865.

Contamination evidence of the Tonian Goias Stratiform Complex (Brazil) from *in situ* Lu-Hf zircon analyses

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Keywords: zircon, Lu-Hf, U-Pb, stratiform complex, contamination, Brazil.

The large layered Goiás complexes are three mafic-ultramafic layered intrusions that outcrop in a ~ 350 km, NNE-trend belt within the Brasilia Belt (central Brazil). From N to S, they are: Cana Brava, Niquelândia and Barro Alto.

We present new U-Pb SHRIMP-II zircon analyses and identify a coeval Neoproterozoic intrusion age of the three complexes at ~ 790 Ma, and demonstrate that the Goiás complexes are fragments of a single intrusion, the Tonian Goias Stratiform Complex, which intruded during the Neoproterozoic and was disrupted during its tectonical exhumation.

Inherited zircons with Mesoproterozoic ages are consistent with the formation age of the metavolcanic-metasedimentary sequences in magmatic contact with these three intrusions and suggest some degree of contamination of the complexes. This contamination in Niquelândia and Cana Brava is well known in the literature as previously revealed by bulk-rock Rb-Sr and Sm-Nd systematics. The two complexes show contamination in their gabbroic sequence with local chemical enrichment and more abundant crustal xenoliths. Conversely, the upper part of Niquelândia, mainly formed by anorthosite, is almost or totally uncontaminated.

In situ Lu-Hf analyses on zircons from the Goiás complexes were run during instrument calibration of the Lu-Hf methodology at the Centro Interdipartimentale Grandi Strumenti of the Università di Modena e Reggio Emilia. The measurements were carried out using a Neptune MC-ICP-MS coupled with a New Wave UP-213 laser ablation. The instrument was first calibrated on a standard solution and, following, *in situ* analyses were carried out together with CZ3 and TEMORA2 zircon standards and a new in-house standard MRD-42. Mass bias and isobaric interference were corrected offline using the Hf-INATOR free software of Giovanardi & Lugli (2017).

In situ Lu-Hf zircon data from the gabbroic sequences show negative εHf(t) values, which are consistent with crustal contamination of the parental melts, according also to the Rb-Sr and Sm-Nd systematics. Zircons from the upper anorthosites range from slightly positive to slightly negative εHf(t) values, thus suggesting some contamination also in the upper part of the sequence. Inherited zircons commonly show positive εHf(t) values, which indicate a mantle-derived melt origin for the magmatism of the metavolcanic-metasedimentary sequence. The εHf(t) values of inherited zircons recalculated to the age of the intrusion suggest that the anorthosites might have been contaminated from these time-evolved mantle-derived melts.

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Giovanardi, T. & Lugli, F. (2017): The Hf-INATOR: A free data reduction spreadsheet for Lu/Hf isotope analysis. Earth Sci. Inform., DOI 10.1007/s12145-017-0303-9.

Nature and ages of supposed tuffaceous layers in the Triassic carbonate platform of the Strona-Ceneri zone and their geodynamic consequences

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Keywords: tuffites, Triassic magmatism, southern Alps, terrigeneous deposits.

Layers considered made by tuffaceous material are occasionally found in Triassic carbonate platform sequences in the western sector of the southern Alps. Their nature, age and the geodynamic setting of the putative magmatism are still matter of debate. In fact, it cannot be presently excluded that such levels are the product of erosion and re-deposition of the Permian acid volcanics located at the base of the Mesozoic sedimentary cover or terrigenous deposites. Recently, similar deposits have been related to the erosion of craters produced by meteorite impact. The few available geochronological data on these levels (M. San Giorgio area, Lugano, CH) yield Triassic ages (245 ± 1 Ma; U-Pb zircon, Mundil et al., 1996), which are slightly older than that estimated based on their stratigraphic position.

To shed light on all the open questions, we have investigated supposed tuffaceous layers occurring within a late Anisian-Ladinian succession in the Mesozoic sedimentary cover of the Strona-Ceneri Zone, in the Borgosesia area, as well as those occurring at the same stratigraphic position in wells of the Villafortuna-Trecate oil system field (western Po Plain, NW Italy).

All these deposits are constituted by a variable mixture of carbonate and silicate components. The results of XRD analysis allows us to recognise two different types of layers. The first is characterised by the presence of low-*T* alteration minerals of both mafic and sialic mineral phases, associated with dioctahedral or trioctahedral micas. Conversely, the second group is characterised by abundant quartz, associated to sanidine, muscovite, hematite and sometime diopside.

Zircons have been separated with conventional methods from two samples of the first group (Lembo di Stegno and Lembo di Crevacuore), and two from the second group (Lembo di Monte Fenera and Villafortuna-Trecate). Based on colour, morphology and internal structure, zircons have been divided in two populations. One group is constituted by light-pink coloured zircons with prismatic habits and tight oscillatory zoning suggesting growth under magmatic conditions. Zircons from the second group are colourless, rounded in shape and with only relics of magmatic zoning. They most likely suffered metamorphic recrystallization.

Ages obtained from the two quartz-free samples point to a volcanic activity in the time interval of ~ 231-238 Ma, resulting concomitant to tectono-magmatic events recorded by the Finero Complex (NE Ivrea-Verbano Zone; Zanetti et al., 2013; Langone et al., 2017) and the Triassic magmatism of the Dolomites area.

Conversely, the zircons from the “Lembo di Monte Fenera” and Villafortuna-Trecate oil field produce a very large range of crystallisation-recrystallization ages, which span from Proterozoic to the Permian-Triassic boundary, thus indicating a dominant contribution from the crystalline basement to the zircon population and identifying these deposits as terrigenous layers.

Langone, A., Padrón-Navarta, J.-A., Ji, W.-Q., Zanetti, A., Mazzucchelli, M., Tiepolo, M., Giovanardi, T., Bonazzi, M. (2017): Ductile-brittle deformation effects on crystal-chemistry and U–Pb ages of magmatic and metasomatic zircons from a dyke of the Finero Mafic Complex (Ivrea-Verbano Zone, Italian Alps). Lithos, 284-285, 493-511.

Mundil, R., Brack, P., Meier, M., Rieber, H., Oberli, F. (1996): High resolution U-Pb dating of Middle Triassic volcaniclastics: Time-scale calibration and verification of tuning parameters for carbonate sedimentation. Earth Planet. Sci. Letters, 141, 137-151.

Zanetti, A., Mazzucchelli, M., Sinigoi, S., Giovanardi, T., Peressini, G., Fanning, M. (2013): SHRIMP U-Pb zircon Triassic intrusion age of the Finero mafic complex (Ivrea-Verbano Zone, Western Alps) and its geodynamic implications. J. Petrol., 54, 2225-2265.

T-t **evolution of the continental lower crust exposed in Val Cannobina (Ivrea-Verbano Zone): new insight from U-bearing accessory minerals**

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Keywords: geochronology, monazite, rutile, Ivrea-Verbano Zone.

The Ivrea-Verbano Zone (IVZ) represents an uplifted section of the pre–Alpine intermediate–lower continental crust. It has been traditionally subdivided in three main lithological units: i) Kinzigite Formation (supracrustal metamorphic rocks), ii) Mafic Complex (intrusive mafic rocks) and iii) mantle peridotite. The Kinzigite Formation consists of siliciclastic metasediments with intercalation of metabasic rocks, minor calcsilicate rocks and marbles. A broad metamorphic gradient increasing from amphibolite to granulite facies is recognized in the Kinzigite Formation from SE towards NW. In the northernmost sector of the IVZ, from the Val Cannobina to Brissago, the Kinzigite Formation is in contact with the metagabbro/diorite of the External Gabbro Unit that records Carboniferous to Triassic ages (Zanetti et al., 2013; Langone et al., 2017). Here, migmatitic metapelites and amphibolites are abundant whereas granulites occur mostly as septa within the External Gabbro Unit.

In order to better constrain the *T-t* evolution of the continental lower crust in the northernmost sector of IVZ we carried out LA-ICP-MS dating of monazite and rutile from migmatitic metapelites and mafic granulite (septa), respectively. U–Pb concordant dates from monazite define a major cluster at about 280 Ma and a minor cluster at about 230 Ma. Remarkably, the younger data were obtained from samples close to the contact with the External Gabbro Unit. Rutile from the mafic granulitic septa provided Upper-Middle Jurassic ^{206}Pb/^{238}U ages.

Results suggest that the studied lower crustal sequence experienced during Mesozoic multiple thermal perturbation events. As already reported for the central IVZ (Ewing et al., 2015) these events were likely related to the extensional tectonic that promoted the Triassic-Jurassic exhumation of the western paleo-margin of Adria (*e.g.*, Beltrando et al., 2015). In conclusion, data from this study support the evidence that the *T-t* evolution of the continental lower crust in the northernmost sector of IVZ is analogous to that of the central and southern sections.

Beltrando, M., Stockli, D. F., Decarlis, A., Manatschal, G. (2015): A crustal-scale view at rift localization along the fossil Adriatic margin of the Alpine Tethys preserved in NW Italy, Tectonics, 34, 1927-1951

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Zanetti, A., Mazzucchelli, M., Sinigoi, S., Giovanardi, T., Peressini, G., Fanning, M. (2013): SHRIMP U-Pb zircon Triassic intrusion age of the Finero mafic complex (Ivrea–Verbano Zone, Western Alps) and its geodynamic implications, J. Petrol., 54, 2235-2265.

Zircon U-Pb dating of high-temperature lower crustal deformation within mafic granulites: the lucky case from the Val Cannobina (Ivrea-Verbano Zone, southern Alps, Italy)

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Keywords: high-temperature deformation, mafic granulites, lower crust, Ivrea-Verbano Zone.

The Ivrea-Verbano Zone (IVZ) represents an uplifted part of the pre–Alpine intermediate–lower continental crust located in the southern Alps of northwest Italy. The lowermost crustal sectors are affected by several high-temperature (*HT*) shear zones (*e.g.*, Rutter et al., 1993); the timing of this *HT* deformation is still poorly constrained. A geochronological study was performed on zircon grains from a middle-lower crustal shear zone exposed in the northern sector of the IVZ. The shear zone developed in mafic/ultramafic rocks of the External Gabbro Unit and marks the contact with ultramafic rocks of the Amphibole-Peridotite Unit. It can be followed for several km and consists of an anastomosing network of mylonites/ultramylonites. Ductile deformation occurred at $T \geq 650°C$ and $P \geq 0.6–0.4$ GPa (Degli Alessandrini et al., 2016), and continued under retrograde conditions at $T = 650–500°C$ and $P = 0.6–0.4$ GPa (Kenkmann, 2000). The timing of deformation is poorly constrained; Ar-Ar dating of amphibole suggest that mylonitization of hornblendite and gabbro of the External Gabbro unit took place from 220 to 180 Ma (Boriani & Villa, 1997).

Zircon grains were studied both directly on rock thin section and as separates from three representative outcrops along the shear zone. Zircons are abundant (up to 30 grains per thin section), generally rounded to sub-rounded and with dimensions up to 500 µm.

U–Pb data are mainly discordant and the apparent $^{206}Pb/^{238}U$ ages show a large variation from Carboniferous to Jurassic. Isotopic data, combined with microstructural, morphological and internal features of zircon reveal a large component of inheritance and suggest recrystallization under *HT* conditions during the Late Triassic – Early Jurassic. *HT* deformation in the shear zone, at lower crustal levels, was coeval with lower temperature mylonitic deformation at upper crustal levels, and is inferred to be related to Mesozoic rifting processes at the Adriatic margin (*e.g.*, Beltrando et al., 2015).

Beltrando, M., Stockli, D.F., Decarlis, A., Manatschal, G. (2015): A crustal-scale view at rift localization along the fossil Adriatic margin of the Alpine Tethys preserved in NW Italy. Tectonics, 34, 1927-1951

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Monazite dissolution-reprecipitation in medium-grade metasedimentary rocks from the northern Apennines, Italy

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Keywords: monazite, dissolution-reprecipitation, thermodynamic modelling, medium-grade metamorphism, northern Apennines.

Fluid-induced dissolution of parent phases and precipitation of products is a fundamental process in metamorphism (Putnis & Austrheim, 2010). Here we present the dissolution-reprecipitation behaviour of monazite, one of the main rare-earth element (*REE*)-bearing accessory minerals useful for obtaining geochronological and geochemical information from a wide range of Ca-poor crustal rocks. The reactions involving monazite were studied in a micaschist recovered from the Pontremoli 1 well (Tuscany) and the implications of fluid-controlled monazite breakdown on age dating were discussed (Lo Pò et al., 2016). The micaschist belongs to the Variscan basement of the Northern Apennines. In this rock monazite, either disseminated in the matrix or included in white mica and chlorite partially replacing garnet, is surrounded by coronitic microstructures consisting of concentric shells of apatite + Th-silicate, allanite, epidote. Studies of the element partitioning between garnet and accessory minerals and the garnet inclusion mineralogy suggest that monazite was partially dissolved and replaced by apatite, allanite and epidote during garnet breakdown to chlorite and muscovite. This stage was associated with the retrograde and decompressional evolution of the micaschist at fluid-present conditions. Through thermodynamic modelling, we determined the *P*-*T* conditions of the monazite partial dissolution and replacement process at 510 ± 35°C, during a nearly isothermal decompression path from 8 kbar to 2-3 kbar. Fluid-induced alteration of monazite also resulted in a partial resetting of the monazite ages, which were determined to be between 294 and 19 Ma. The maximum extent of the alteration process occurred in monazite located within retrogressed garnet rims. In this microstructural site, Pb in the Variscan monazite was lost.

Lo Pò, D., Braga, R., Massonne, H.-J., Molli, G., Montanini, A., Theye, T. (2016): Fluid-induced breakdown of monazite in medium-grade metasedimentary rocks of the Pontremoli basement (Northern Apennines, Italy). J. Metamorph. Geol., 34, 63-84.
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A tentative chronological scheme for the Variscan metallogenic peaks in Sardinia

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Keywords: Sardinia, Variscan metallogenic peaks, intrusion-hosted/related ores, structurally-controlled ores.

The Variscan metallogenesis of Sardinia is still debated. Main unsolved problems regard the nature of ore deposits, chronology and relationships with the structural and magmatic framework of the Variscan chain. Recent studies, which focused the magmatism/metallogenesis relationships allow to bracket mineralizing events in two fundamental groups of ore deposits: (1) intrusion hosted/related; (2) structurally-controlled. The regional distribution of deposits is not homogeneous; the main districts occur in the frontal part of the Variscan nappe building. The type-(1) ore deposits are related to post-collisional calc-alkaline intrusive suites, clustered around an early 310-300 Ma *older magmatic peak* (*OMP*), and a 290-285 Ma *younger magmatic peak* (*YMP*). Typical *OMP*-related ores are the hydrothermal Pb-Zn (Ag, Cu, Ni-Co) vein fields of Montevecchio (SW Sardinia) and Sos Enattos (NE Sardinia), and the Cu-Zn-Pb (Ag, Au) skarns of central Sardinia. *OMP*-related hydrothermal ores resulted from polyphasic, long-lasting fluid circulations at shallow crustal levels; a distinctive feature is their sideritic gangue. Pb and S isotope data confirm the genetic linkage of hydrothermal ores with *OMP* granitoids; fluid inclusions indicate that the bulk of ore minerals precipitated during low-temperature stages. *YMP*-related deposits include Sn ± W ± Mo hypo- and meso-thermal veins, Mo greisens, Sn ± W skarns, F-Pb-Zn ± Ag ± Cu ± Ba veins associated to different suites of F-bearing, ilmenite-series ferroan granites. Fluorite ± topaz are distinctive gangue or ore (Silius district) minerals in this phase. The type-(2) ores are less easily interpretable; in the past they were considered *stratabound* SEDEX deposits. Structurally-controlled, mesothermal vein systems are typical of SE Sardinia. They are associated with cataclastic/mylonitic zones developed between tectonic units stacked in regional antiforms (*e.g.*, Flumendosa Antiform). Ores show an initial As ± W mineralizing stage, followed by a Sb ± (Pb-Zn-Cu) and Au ± (Ag) stage. Pb and S isotopes and fluid inclusions data suggest multiple sources of fluids, including metamorphic and Variscan magmatic sources. Timing of mineralization is controversial, but geological evidences indicate that: (a) large-scale fluid circulations and mineralization started with the extensional tectonic phases in southern Sardinia; (b) ores are hosted in the low-grade metamorphic basement without clear spatial relations with intrusives; (c) structurally-controlled vein systems are always intersected by *YMP*-related F ± Ba ± Pb veins; (d) locally, As – W – Sb-Au veins are eroded and covered by Early Permian (295 Ma) sediments. According with these constraints, an age after the beginning of the Flumendosa Antiform tectonic collapse and before the emplacement of *YMP* intrusions (307-295 Ma) is proposed for the structurally-controlled ores. Overall, the framework of Variscan mineralizing events in Sardinia point to multiple metallogenic peaks bracketed in the 307-285 Ma interval.

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The plutonic-subvolcanic-volcanic connection in the long-lived Campiglia Marittima igneous system (Tuscany, Italy): a zircon CA-ID-TIMS dating study

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Keywords: CA-ID-TIMS, zircon dating, long-lived system, Campiglia Marittima.

Understanding the timescales of magmatic processes in the continental crust is critical to answer to key questions regarding timing of petrogenetic processes at different levels of the plumbing system. Geochronological methods using the common accessory mineral zircon reach high-precision with the implementation of single-zircon CA-ID-TIMS U–Pb procedures. Recent high-precision geochronological data highlight that the processes leading to the accumulation of large volumes of evolved magma in the upper crust occurred over an extended period of time.

The Campiglia Marittima system offers a suitable scenario for studying the duration of processes at different levels of the plumbing system and the connection existing between felsic and mafic magma batches. Uplift and erosional processes have exposed plutonic, subvolcanic, and volcanic rocks (both of mantle and crustal origin), as well as hydrothermal products. U–Pb dating revealed the protracted crystallization of zircon in all studied samples, lasting between 100 and 700 ka. The dispersion of zircon ages is at odds with what could be expected. Indeed, it is shortest for the Botro ai Marmi pluton (100 ka), intermediate for the subvolcanic mafic Temperino porphyry (450 ka), and longest for the volcanic San Vincenzo rhyolite (700 ka). The youngest zircons from the Botro ai Marmi granite have ages identical to ^{40}Ar-^{39}Ar ages of granite biotite and metasomatic phlogopite from skarn crosscutting the granite. The Temperino mafic porphyry and the San Vincenzo rhyolite show younger sanidine ages (emplacement/eruption age). The youngest zircon age from the pluton is therefore assumed to approximate the age of emplacement and final crystallization of the melt, whereas the zircons from the Temperino mafic porphyry and the San Vincenzo rhyolite are considered antecrystic, derived from re-mobilised earlier magma extracted from a deeper reservoir at the emplacement age.

The new documentation of an extended period of crystallization for the Campiglia igneous system (about 1000 ka) matches with observations for the long-lived magmatic systems of Larderello and Elba Island. These data support the existence of multiple crustal reservoirs far larger than outcropping igneous products. The observed mantle signature of metasomatic fluids suggest the presence of hidden mantle-derived reservoir able to activate episodically crustal melting and magma transfer to shallow levels. This sequential magmatic activity (both from mantle and crust) could be controlled by multiple, small batches of mafic magma, that did not lead to the formation of a single, homogeneous, hybrid pluton at the emplacement level.

A new approach to the interpretation of low temperature thermochronology data

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Keywords: low temperature thermochronology, geothermal gradient, rock conductivity, central Britain.

Constraining the timing and rate of formation of first order topography is crucial for unravelling the interplay between deep and surface processes. Low temperature thermochronology is used to determine cooling histories of rocks in the upper crust (usually < 10 km), but quantifying the amount of denudation requires an estimation of the geothermal gradient. Although efforts have been made to predict the effect of changes in the basal heat flow and fluid circulation on the upper crust geothermal gradient, little attention has been paid to the role of the crustal heat production and the thermal conductivity of the rocks that are being denuded. Also overlooked is the influence of density variation on the isostatic response of the crust to denudation and, therefore, total rock uplift.

Here we present a case study from central Britain where, despite many efforts, reconstructing the Cenozoic evolution of topography remains highly controversial, hampering the possibility of understanding the influence that the proto-Icelandic plume and North Atlantic rift had in this region and, more generally, the effect of plumes and rifting on continental margins. The pattern of strategically sampled new apatite fission track, and apatite and zircon He ages extend the resolution of the thermal histories, and provide more precise constraints on the syn-rift (early Cenozoic) geographical distribution of palaeotemperatures than it was previously available. We have used a numerical model to constrain the thermal effect of heat producing granite batholiths in central Britain beneath blanketing layers of low thermal conductivity sedimentary rocks and constrain the amount of denudation under variable geothermal conditions. The new, more accurate estimates of denudation allow insights into the geological history of the area. Using numerical modeling, we have determined that the low temperature thermochronology-derived amounts and spatial distribution of denudations can be explained by a combination of thermal and underplating-driven uplift, without invoking any other causes, such as intra-plate stresses, as it has been suggested.

This study demonstrates that a careful use of multi-thermochronometers, combined with information about the thermal structure of the eroded crust permit to derive robust constraints on the geological history of an area.

Combining *in situ* U-Pb geochronology in zircons and geological data to investigate nappe formation in the central Alps

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Keywords: SHRIMP II U-Pb dating, Nappe formation, central Alps.

The pre-Alpine Variscan gneissic crust was intensely intruded by several generations of granitoids forming laccoliths and dikes of different shapes and sizes within paragneisses, augengneisses and amphibolites. During the Alpine orogenic cycle this initial and complex geological architecture was reshaped into a fold and thrust belt. Nevertheless, distinguishing within a nappe pile of gneisses a major tectonic contact from a reactivated magmatic contact is not trivial. In the Lepontine dome (central Alps), these gneissic nappes are subdivided into, from bottom-to-top, Leventina, Simano, Adula/Cima-Lunga and Maggia. In particular, the boundary between the Leventina and the Simano gneisses is not clear. The boundary was traced within leucogneisses by joining lenses of metasediments of unknown age but assumed to be Mesozoic.

Magmatic Early Permian U-Pb SHRIMP zircon ages from a folded granitic dike discordant within paragneisses that separate the Leventina and the Simano units attest moderate deformation along the boundary during the Alpine orogen. Furthermore, Devonian-Silurian U-Pb SHRIMP ages in detrital zircon cores of the same paragneisses suggest that the deposition was older than Mesozoic. Hence, those sediments can not be used as Alpine nappe divider. Therefore, the combined geochronological and geological results bring evidence (i) of moderate strain localization between the Leventina and the Simano, questioning the allochthonous character of the Simano unit, (ii) of a top-to-the-foreland deformation gradient between the Leventina and the Adula/Cima-Lunga units, and (iii) of non-coaxial ductile deformation along inherited rheological heterogeneities within the units, complicating the tectonic understanding.

Precise hematite (U-Th)/He age determinations using a multi-aliquot method

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Keywords: ore dating, (U-Th)/He method, Elba Island, Apennines.

Dating of iron oxides holds potential determining ore deposit formation, regional climate histories and transient hydrothermal events associated with faulting.The (U+Th)/He method is developing as useful chronometer of iron oxide formation, but may be hampered by natural diffusive and recoil loss of ^{4}He and the partial loss of U and/or Th during the He analysis process.We have used a multi-aliquot method to obtain precise (U+Th)/He ages of hematite from Cenozoic hydrothermal systems where cogenetic adularia Ar/Ar ages can be determined. The technique relies on the separate measurement of ^{4}He and ^{238}U + ^{232}Th concentrations in 3-6 aliquots of ~ 5 mg of homogenized hematite. Average He and (U+Th) concentrations vary at the ± 2-3% level, consequently the (U+Th)/He ages of each sample is typically ± 5%. Six samples of specular hematite from the Rio Marina mine, Elba, yield an average age of 5.26 ± 0.20 Ma (2σ). The isochron age (5.30 ± 0.03 Ma; 2σ) is considerably more precise, and demonstrates that the hematites contain no significant trapped non-radiogenic He. These ages are consistent with the K/Ar age of cogenetic adularia (5.32 ± 0.11 Ma; Lippolt et al., 1995) providing a good indication that He loss from Cenozoic hematite is insignificant and the (U-Th)/He method may prove to be a high precision dating tool for hydrothermal and supergene processes.

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U-Th-Pb dating of hydrothermal ore deposits from electron probe micro-analysis of uraninite: the cases of Cogne, Val Vedello and Novazza (Italian Alps)

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Keywords: U-Th-Pb dating, uraninite, EPMA, Western Alps, Orobic Alps, Cogne, Val Vedello, Novazza.

Uraninite (UO_2) is an uncommon accessory mineral in some magmatic, metamorphic and sedimentary rocks. Chemical analyses of uraninite performed by electron probe micro-analyzer (EPMA) can be profitably used for U-Th-Pb dating. We employed this technique to constrain the age of formation of two types of hydrothermal deposits from the Italian Alps, namely an ophiolite-hosted magnetite deposit (Cogne, western Alps) and two uranium deposits (Novazza and Val Vedello, Orobic Alps). In the first case, we aimed to establish whether the Cogne magnetite deposit, a relatively uncommon type of ophiolite-hosted deposit, was Alpine or pre-Alpine. In the second case, we used uraninite to date the hydrothermal events responsible for widespread siderite occurrences in the Southalpine domain.

At Cogne uraninite occurs as rare inclusions in magnetite and forms anhedral to euhedral crystals, ranging in size from 1 to 40 μm. Textural evidence suggests that uraninite formed contemporaneously with magnetite, thus uraninite was used to date the magnetite mineralization. Based on all the radiometric age determinations (n = 53), we calculated a weighted average age of 152.8 ± 1.3 Ma (mean square weighted deviation, MSWD = 1.3), which is consistent with a pre-Alpine genesis of the ore, related to an oceanic seafloor hydrothermal system.

At the two uranium deposits of Novazza and Val Vedello (Orobic Alps), abundant carbonate minerals (mainly siderite and Fe-rich dolomite) are associated with sulfides (dominant sphalerite, pyrite and galena) and uraninite, and form disseminations, veins and impregnations in the volcanoclastic facies of the Early Permian Collio Formation. At both sites, uraninite shows textural equilibrium with siderite and Fe-rich dolomite, but widespread alteration and recrystallization complicate the scenario. Therefore, we only analyzed apparently unaltered uraninite grains, which are a few-micron large at Novazza and submicron- to micron-sized at Val Vedello. Radiometric ages for the Novazza deposit range from ~ 290 to ~ 130 Ma (n = 20). The uraninite ages for the Val Vedello deposit (n = 62) are scattered between ~ 270 and ~ 50 Ma, but one large (20 μm) uraninite grain has a plateau age of 169 ± 3 Ma (MSWD = 1.4; n =13). By averaging the oldest ages obtained for Novazza and Val Vedello, we obtained a best-estimate formation age for siderite-uraninite mineralization of 275 ± 13 Ma (MSWD = 3.2; n = 6). Younger ages are interpreted to reflect protracted interaction with hydrothermal fluids and/or deformation/recrystallization during Jurassic rifting and successive Alpine orogenesis.

Our examples confirm that uraninite EPMA chemical U-Th-Pb dating can be a valuable tool in solving some geological issues, having also the advantage of being more affordable and rapid, compared to other analytical techniques. Moreover, the improvement of EPMA resolution (spot size << 1 μm) in modern instruments may enlarge the range of potentially analyzable samples.

Session S20:

Computational geochemistry and mineral sciences: new developments and future directions

Conveners:

Donato Belmonte (Univ. di Genova)

Mauro Prencipe (Univ. di Torino)

A new computational approach to the study of epitaxy: the calcite/dolomite case

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Keywords: adhesion energy, interfacial energy, epitaxy.

A new way to analyze the theoretical and computational aspects related to the determination of the adhesion and interfacial energies in epitaxial systems is presented. Then, we studied the epitaxial phenomena in calcite (Cc) – dolomite (Dol) systems by adopting the recent computational strategy designed by our research group. Specifically, we investigated at empirical level the (10.4)Cc/(10.4)Dol, (10.0)Cc/(10.0)Dol and (11.0)Cc/(11.0)Dol epitaxial interfaces determining their structures and thermodynamic properties. Moreover, we showed how the energy distribution is modified in layers of calcite and dolomite at the epitaxial interface. These results are used to gain some insights on the epitaxial growth of dolomite above calcite. In particular, we found that the (10.0)Cc/(100)Dol interface shows the minor structural modifications, as well as the highest adhesion energy. This implies that the probability to have epitaxy between calcite and dolomite is higher for the (10.0)Cc/(10.0)Dol interface with respect to (11.0)Cc/(11.0)Dol and (10.4)Cc/(10.4)Dol.

A revised thermodynamic model for the crystal surfaces

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Keywords: surface segregation, thermodynamic model, surface energy.

A revised thermodynamic model to explain the deviation of the surface composition from that of the bulk (*i.e.*, segregation) is proposed. This phenomenological model is based both on the multilayer approach (*i.e.*, the crystal is treated as an infinite set of layers of formula units (f.u.) and each layer potentially has a different composition) and on the recent findings on the behaviour of the free energy per f.u. in proximity of a crystal surface (Bruno & Prencipe, 2013; Bruno, 2015; Bruno et al., 2016). The model is developed for a binary solid solution, but it is extendible to any number of endmembers. The effect of the different parameters of the model on the surface composition is successively evaluated. We also investigate how sensitive is the surface composition to variations of that of the bulk crystal.

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Manganese under pressure: thermodynamic modelling of phase relations in blueschist manganesiferous quartzites of Voltri Massif (Varenna Valley, Ligurian Alps)

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Keywords: Mn-ores, thermodynamics, sursassite, phase relations.

Manganese ores are widespread in different geological settings of the Alps and Apennines. Nevertheless, chemical features and phase stability relations of Mn-bearing minerals are not so frequently used to obtain informations on their genesis and evolution. In this work we studied a high-pressure manganese mineralization located in the Varenna Valley (Voltri Massif, Italy). This is the first Mn-ore described so far in Ligurian Alps which, differently from the low-grade Mn-ore hosted in the Jurassic cherts of eastern Liguria (Graveglia Valley), underwent a diffuse requilibration at blueschist-facies metamorphic conditions.

The outcrops are characterized by quartzitic rock lenses of few meters in size with peculiar structural and mineralogical features. The manganesiferous quartzites experienced intense deformation and recrystallization processes which produced a compositional banding given by alternating quartz-rich and Fe-Mn oxide-rich layers. Spessartine and sursassite are rock-forming minerals. A suite of unusual accessories minerals, such as ardennite, pyrophanite, calderitic garnet and kanonaite, are also present.

The aim of this work is to address the conditions of formation of the *HP* mineral parageneses by pseudosection thermodynamic modelling. However, the lack of calorimetric data for some rare Mn-minerals forced us to use empirical methods to obtain their thermodynamic properties. As first approximation, we used for sursassite [$Mn_4Al_6Si_6O_{22}(OH)_6$] the crystal structure data of Mellini et al. (1984), the exchange reaction approach of Helgeson et al. (1978) and the polyhedral model of Van Hinsberg et al. (2005). The dataset of Tumiati et al. (2015) was adopted for the other Mn-bearing phases. A value of $G° = -13231,19$ kJ/mol is thus obtained for sursassite. However, we found an additional $\Delta G° = -218$ kJ/mol is necessary to have this phase stable in our calculated pseudosection. This energy difference is about 2% of the total value, within the experimental uncertainty for this kind of minerals. P-T and T-fO_2 pseudosections in the model system SiO_2-Al_2O_3-Fe_2O_3-MnO-Mn_2O_3-CaO-H_2O were calculated by Gibbs free energy minimization with the PerpleX package (Connolly & Kerrick, 1987) adding the thermodynamic parameters optimized for sursassite. The calculated phase relations are in good agreement with petrographic observations and previous semi-quantitative estimates made on analogue occurrences (Reinecke, 1986) and allow to constrain the sursassite stability field below $T = 400°C$ and between 8-10 kbar. A strong control of oxygen fugacity on phase equilibria is also evident.

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***Ab-initio* calculation of NMR spectra of tobermorite and jennite: decoding the microscopic structure of cement**

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Keywords: density functional theory, solid state NMR, jennite, tobermorite, cement.

Calcium silicate hydrate (CSH) is an important hydration product of Portland cement and controls the setting and strength of concrete. The atomistic structure of CSH has been a major focus of research in cement since the past four decades but remains poorly understood.

In this work, we report an *ab-initio* study of the atomistic structure of CSH models (jennite and tobermorite), with C/S ratios between 0.6 and 1.4. Based on the best crystallographic data available, we have simulated the ^{29}Si, ^{17}O, ^{1}H and ^{43}Ca NMR spectra from first principles, and we compared to existing experimental data.

Our results compare reasonably well to NMR experiments, except in the case of anomalous tobermorite, where the experimental NMR spectrum show a large amount of defects (Q^1) and cross-links (Q^3), not present in the idealized structure of tobermorite. Our simulated ^{43}Ca NMR spectrum is in good agreement with a recent challenging experiment by Kirkpatrick and can help the assignment of the experimental NMR peaks.

Thermoelastic properties of *bcc*-Fe from first-principles and classical molecular dynamics

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Keywords: density functional theory, elastic constant, lattice dynamics, molecular dynamics, iron.

We calculated the thermomechanical properties, the isothermal and adiabatic elastic constants of *bcc* iron, by two different methods.

The first is based on first-principles total-energy and lattice-dynamics calculations, using the plane wave psueudopotential packages Quantum-Espresso (Giannozzi et al., 2009). In particular we obtained the isothermal and adiabatic elastic constants by minimizing the quasi-harmonic (QH) vibrational free energy under finite strain deformations. This method requires to pay special care in the fitting procedure for the static and temperature-dependent contributions to the free energy, and in the verification and validation of our pseudopotential *vs*. all-electron calculations. We also discuss the error propagation for the two free-energy contributions separately, and we provide error bounds for the calculated properties.

We found that the zero-temperature mechanical properties are sensitive to the details of the calculation strategy employed, and common GGA exchange-correlation functionals provide only fair to good agreement with the experimental elastic constants. On the contrary, their temperature dependence is in excellent agreement with experiments in a wide range of temperature almost up to the Curie transition.

Next, we performed a comprehensive, critical study of the vibrational, thermodynamic and thermoelastic properties of *bcc* iron by classical molecular dynamics with using well established embedded-atom method (EAM) interatomic potentials. Molecular dynamics simulations are used to address anharmonic effects, where dynamical matrices are constructed as a time average of the second moment of the atomic displacements, as a function of temperature. The elastic constants are then obtained from the sound velocities along high symmetry directions in reciprocal space.

The comparison of our results to ultrasonic measurements highlight that first-principles calculations reproduce extremely well the elastic constant softening as a function of temperature, while existing EAM potentials present several limitations in describing the thermoelastic properties of iron.

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Bader's topological analysis coupled with catastrophe theory: getting insight a mineral phase transition

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Keywords: instability in minerals, *ab-initio* calculations, catastrophe theory, electron density.

The Bader topological analysis of the electron density from *ab-inito* calculations is used in combination with the catastrophe theory to herald appearance of instability that may lead to transformations of minerals, as a function of pressure/temperature. In particular, we focus on the evolution of non-degenerate critical points towards degenerate critical points. The catastrophe theory formalism provides the mathematical tool to model the electron density in the neighbouring of the critical point, and to rationalise the occurrence of instability in terms of electron density topology and Gibbs energy. The phase transitions that rutile, periclase and corundum undergo because of pressure and/or temperature are here discussed in the light of the catastrophe theory. The aim of this investigation is to boost a use of the bare electron density topologic analysis to foresee appearance of instability through the evolution of critical points towards degeneracy.

How does quartz respond to deviatoric stresses? *Ab initio* calculations on SiO_2 tectosilicate

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Keywords: *ab initio* calculations, quartz, deviatoric stress.

Most high-pressure crystallographic studies aim to understand the behavior of crystals under hydrostatic pressure by immersing the sample in a fluid pressure medium and describing its volume behavior by conventional equations of state with Reuss bulk moduli. However, mineral inclusions trapped inside cubic host minerals provide another case because they are subjected to isotropic strain. If the inclusion is isotropic, it will still exhibit isotropic stress from the isotropic strain, and the behavior will be the same as for a crystal in a fluid pressure medium. But, if an elastically anisotropic inclusion, such as quartz, is entrapped in an isotropic host, it must develop anisotropic (*i.e.*, deviatoric) stress and thus both its stress state and its structural changes are different from the hydrostatic case. Moreover, deviatoric stresses may also produce changes in the Raman shifts (Briggs & Ramdas, 1977; Korsakov et al., 2009).

To investigate how quartz responds to deviatoric stresses, we performed *ab initio* HF/DFT (Hartree-Fock/Density Functional Theory) calculations at static conditions to determine its crystal structure and Raman shifts under isotropic strain conditions (*i.e.*, a quartz grain inside a garnet host), to be compared with those obtained by experiments and DFT simulations under hydrostatic pressure. Our results show that the changes in the lattice parameters under isotropic strains (obtained by applying equal linear strains in all directions) are significantly different from those obtained under isotropic stress (obtained by imposing hydrostatic pressure). Also, the Raman shift changes as a function of mean normal stress show small differences (*i.e.*, few cm^{-1}), mostly for the frequency band at 128 cm^{-1}, with respect to those calculated under isotropic strain. Therefore, the measurement of the wavenumber of a single Raman-active phonon mode cannot yield information about the stress state of an inclusion crystal, nor should it be interpreted by means of the hydrostatic calibration as a measure of the average normal stress in an anisotropic inclusion. This assumption may lead to large errors in pressure estimates when applied to anisotropic inclusion phases.

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Silicate melts as polarized continua

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Keywords: *ab-initio*, polarized continuum model, melts, thermodynamics.

The reactive properties of silicate melts (intrinsic and extrinsic stability with respect to glassy and crystalline aggregates) and some low-medium range structural features may be investigated through first principles in the framework of the Integral Equation Formalism of the Polarized Continuum Model (Tomasi & Persico, 1994). In this presentation we will briefly treat the following points:

1) vibrational properties of the glassy and liquid state and the nature of the glass transition in SiO_2 and Al_2O_3 (Ottonello et al., 2010; Belmonte et al., 2013);

2) stabilizing effect of counter-ions on zeolitic rings and existence of the Pauling Double Bond (Gatti et al., 2012);

3) electrostatic solvent radius and solvation energy in terms of the Pierotti-Reiss Scaled Particle Theory (Ottonello & Richet, 2014; Ottonello et al., 2015)

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Ab initio modelling of thermal-IR spectra of olivine and orthopyroxenes: application on remote sensing for Mercury

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Keywords: *ab initio*, modelling, olivine, pyroxenes, TIR spectra, Mercury.

Modelling is a common practice to interpret to a more fundamental level the information acquired in laboratory. Though concerning spectroscopic techniques, spectral modelling is still an unfamiliar field, especially within spectroscopy applied to planetary science.

This study aims to enhance the application of quantum mechanical calculations for the simulation of thermal-infrared spectra at high temperature with an innovative approach: calculations of vibrational frequencies and modelling of emissivity spectra at room ad at high temperature of olivine and orthopyroxenes, which are supposed to be components of Mercury surface (Sprague et al., 2007), by means of *ab initio* quantum mechanics calculations.

The approach is carried out employing hybrid HF/DFT approach for its accuracy in calculating vibrational frequencies by means of the computer code CRYSTAL14 (Dovesi et al., 2014), which enable a reliable simulation of a full vibrational pattern. The simulations are compared with the measurements thermal emissivity spectra obtained experimentally of the same minerals at different steps of temperature from 320 to 900 K.

The aim to verify the reliably of this simulations and if it can be foreseen the trend of spectral features due to temperature. Moreover since spectral signatures of minerals are intimately related to the crystal structure, the emissivity bands measurement represent a remote sensing mode, to determine planetary surface composition (*i.e.*, Mercury). In fact, the investigation is mostly focused on the possibility to develop an application of the method on the data that will be acquired by MERTIS, the Mercury Radiometer and Thermal Infrared Spectrometer (MERTIS) on board of the ESA BepiColombo Mercury Planetary Orbiter spacecraft due in 2018 (Helbert et al., 2010). This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement No 714936) to M. Alvaro and has also been supported by the MIUR-SIR grant "MILE DEEp" (RBSI140351).

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Ab-initio study of sulfosalts: difficulties and perspectives

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Keywords: sulfosalts, semiconductors, chalcostibite, *ab-initio* calculations.

Sulfosalts have attracted great interest during the last decades. Looking for a sustainable world, coupled with a growing global energy demand, alternatives energy technologies are needed (Bell, 2008) and sufosalts are very good candidates for these purpose. Sulfosalts, with their intrinsically low lattice thermal conductivity, are widely used as thermoelectric and photovoltaic devices (Zhang et al., 2016). Despite their importance, just a few studies have been performed on sulfosalts and their physico-chemical characteristics at ambient and non-ambient conditions. In the present project, chalcostibite is studied. It is the end-member of the $CuSbS_2$-$CuBiS_2$ (chalcostibite-emplectite) solid solution. The unique electronic structure of these minerals, having lone pairs isolated on the square pyramids occupied by the Sb, and its evolution with pressure, might be well characterized by *ab-initio* calculations. So far, Density Functional Theory (DFT) is the most commonly used method to calculate the asymmetric distribution of charge in crystal structures containing atoms with half filled *s*-orbitals in the last valence shell (*e.g.*, Sn^{2+}, Sb^{3+}, Tl^{+}, Pb^{2+} and Bi^{3+}; Olsen et al., 2010). The aim of the present project is to investigate the crystal structure and its evolution at ambient and non ambient conditions of chalcostibite by using the hybrid Hartree–Fock/Density Functional Theory (HF/DFT) approach as implemented in CRYSTAL14 (Dovesi et al., 2014). Electron Core Pseudopotentials (ECP) and Linear-Combination-of-Atomic-Orbitals (LCAO) are used for core electrons and valence shell electrons, respectively, for Sb. This approach and its performance were extensively checked by Causà et al. (1991) and, even if non-negligible, the contribution of ECP on the bias between HF-ECP-LCAO calculations and both experiments and pure LCAO calculations might be minimized down to approximately +2.5% for the lattice parameters and 6% for force constants (Causà et al., 1991). We are able to analyse the crystal structure of sulfosalts at ambient and non-ambient conditions, enhancing the knowledges on their stability and structural evolution.

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Session S21:

Natural and model systems to unravel the volatiles cycle in the deep Earth

Conveners:

Nadia Malaspina (Univ. di Milano-Bicocca)

Simone Tumiati (Univ. di Milano)

Mo isotopes as tracers for deep recycling of subducted C-rich, anoxic sediments in the mantle source of the Roman magmatic province

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Keywords: molybdenum isotopes, subduction, anoxic sediments, ultrapotassic rocks.

Understanding the role of recycled sedimentary material into the convecting mantle is a key aspect to provide new constraints on the chemical budget of subduction zones. Mo isotopes have been shown to fractionate in the oceans during the incorporation into sediments, being perceptive to redox conditions. The variable composition of Mo isotopes recorded in different geochemical reservoirs offers the opportunity to use these isotopes as tracers of recycled material into the mantle. This is particularly true for sediment formed under anoxic conditions, which inherited from the seawater specifically heavy isotopic compositions.

The potassic and ultrapotassic igneous rocks of the Roman magmatic province (Italy) show extremely variable and well distinct geochemical and radiogenic isotopic signatures, which are referred to a strong but variable involvement of a subduction-recycled component in their genesis, hence they represent an interesting case study for tackling the role of different subduction-related metasomatic agents using Mo stable isotopes.

We performed Mo isotopes on magmatic rocks and sedimentary end-members as proxy of the recycled component. Roman igneous rocks display variable Mo isotope compositions, which are significantly heavier compared to any sediment-dominated subduction-related magmatic rocks measured so far (*e.g.*, Lesser Antilles). Such heavy Mo isotopic signatures, reveal a sort of "Mo anomaly", which is not observed in the nearby subduction-related magmatic regions. The heavy isotope composition, along with the pronounced sediment-dominated character, suggests the presence of an isotopically heavy component in the subducted material that is likely to derive from subducted, anoxic organic-rich sediments. In this context, the application of Mo isotopes to complex subduction settings show the potential of Mo isotopes as tracers of recycled anoxic sediment, and thus the fate of organic carbon, in subduction zones.

Raman and FTIR studies of hydrous natural olivine and synthetic forsterite at 1100°C and up to 4 GPa

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Keywords: Raman spectroscopy, IR spectroscopy, NAMs.

Water distribution in the deep Earth represents one of the most important topics in the field of geodynamics, because it has a large impact on the physical and chemical properties of the Earth's mantle, such as electrical conductivity, seismic anisotropy, diffusion and rheology.

Water content in the mantle could very likely be regulated by mineralogical phases called DHMS Dense Hydrous Magnesium Silicates, which are thermodynamically stable within certain ranges of temperature and pressure but, at greater mantle depths, undergo a series of phase transitions to a more stable structure, releasing large quantities of water in the mantle.

Regarding water storage capacity, major phases in both the upper and lower mantle have limited H_2O solubilities (< 0.2 wt%) whereas those of the transition zone are very high (up to 3.3 wt%) which may imply strong chemical and physical heterogeneities with depth.

High P and T tools allow us to simulate mantle conditions in the laboratory, with particular attention to H_2O.

Syntheses were carried out using Piston Cylinder and Multi Anvil apparatus at 1100°C and up to 4 GPa, with polycrystalline samples of natural olivine and synthetic forsterite and H_2O liquid, respectively, as starting materials and hydrogen source. FTIR spectroscopy was used, as it is particularly sensitive to the presence and concentration of hydrogen in crystal lattices. Some experiments involved the dissolution of D_2O rather than H_2O to observe modes involving H- and D-displacements and for eventual isotopic exchange experiments to determine self diffusivities of hydrogen.

In addition to quantitative analyses (H_2O concentrations ranges between 100 and 400 ppm wt%), fitting processes allowed us to identify the positions of the major absorption bands, attributable mainly to "silicate defect" and "interstitial position" mechanisms of hydrogen incorporation. We also investigated the relative intensities between the peaks near 1000 and 3600 cm^{-1}, in order to improve the calculation of total water content.

Raman spectroscopy was primarily used to understand how water may influence crystal structure of olivine, giving us important information about the strength of Si-O bonds in olivine's isolated tetrahedral structure and the interactions between tetrahedral and octahedral cations. H^+ protons tend to bond to the apical oxygens of SiO_4 structure, leading to a weakening of the entire lattice, shown mainly in terms of frequency and relative intensity in peaks of the internal modes.

The incorporation of hydrogen led also to the identification of new peaks both in lower and higher frequency region associated with vibrational modes involving the motion of OH groups.

Our combined FTIR and Raman investigation provides important links between the speciation and solubility of water in this nominally anhydrous mineral and the strong influence of small concentrations of dissolved H_2O on its transport properties.

Deep Earth carbon reservoirs: an experimental study on carbide systems under high pressures

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Keywords: carbon reservoirs, carbides, high pressure experiments.

The active processes occurring at the early stage of evolution of the Earth (*i.e.*, Hadean period) have the potential to determine the actual distribution of carbon, and played a fundamental role in the thermal and dynamic evolution of the early planet. However, we still have a relative very limited knowledge regarding the fate of the original Earth's carbon and the processes in which is involved. Processes such as the devolatilisation during planetary accretion might have depleted carbon in the mantle, while ingassing from a C-rich atmosphere, late bombardment of C-rich materials, or entrapment of C-bearing metallic liquid in silicate mantle phases might have increased it (Dasgupta & Hirschmann, 2010). To decipher the fate of this carbon fluxes and balances, the key is to understand how the element is partitioned in deep Earth reservoirs, and which is the storage capacity of different carbon bearing phases. Lately together with diamond, graphite and carbonate, whose behaviour at extreme conditions have been extensively investigated (*e.g.*, Hazen & Schiffries, 2013; Boulard et al., 2015) also carbides started to be taken into account. Little is known about the properties of simple carbides such as SiC, and more complex carbon bearing systems (*i.e.*, Fe – Si – C) and many open questions are still seeking for an answer: what are the melting relations that characterise these systems? What is the role of carbon rich phases in the global carbon cycle? To address these questions, we performed ultra-high pressure (*UHP*) and temperature (*T*) experiments on carbon bearing alloys, to evaluate the behaviour of carbon and the subsolidus and melting relations between different phases. Experiments were performed coupling double side laser heating with diamond anvil cells. *In situ* synchrotron X-ray diffraction, and *ex situ* analyses on recovered samples were combined to obtain a better characterisation of the run products (*e.g.*, Mao & Boulard, 2013). Samples, micrometer thick deposition, ensure better performances during laser heating and guarantee reproducibility of the experimental conditions. The investigated *P-T* field cover pressures up to 150 GPa and temperature up to 3500 K. We will show the results on the behaviour of C in the complex ternary Fe-Si-C system, including phase diagram and melting curve. Furthermore, the stability of carbon on binary system (*i.e.*, SiC) will be discussed. The results of this study open new scenarios on the behaviour of carbon in deep reservoirs with potentially important impacts on the Earth's mantle geodynamics.

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Evidence for mantle metasomatism by slab-derived fluids in garnet peridotites of Monte Duria, central Alps, N Italy

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Keywords: mantle metasomatism, garnet peridotite, Adula Nappe, Monte Duria.

The Adula-Cima Lunga nappe represents the highest of the Lower Penninic units of the central Alps. It consists of orthogneiss and paragneiss of pre-Mesozoic origin hosting lenses of metacarbonates, partly retrogressed eclogites and garnet/chlorite peridotites. The garnet peridotite bodies cropping out in the southern area of the nappe complex (Alpe Arami, Cima di Gagnone and Monte Duria) record the highest metamorphic conditions ($P > 3.0$ GPa, $T = 800\text{-}850°C$). In the study area garnet peridotite lenses are in contact with biotite-bearing migmatites or hosted in amphibole-bearing migmatites and K-feldspar gneisses.

Petrographic and minerochemical data indicate a previously unknown *HT* stage during peridotite and eclogite exhumation. Peridotites show orthopyroxene with symplectites of tiny crystals of baddeleyite (ZrO_2) and srilankite ($ZrTi_2O_6$), whereas only zircon was found in the symplectites after garnet.

Bulk rock analyses of peridotites show *REE* content 3 to 5 times lower than PM but with a clear selective enrichment in *LREE* (spoon-like pattern), and with a Eu positive anomaly. The same “spoon like” pattern in the *LREE* field is displayed also by eclogites, shifted to values 2 to 5 times higher than PM. Due to the similarities of the *REE* patterns of peridotite and eclogite and the occurrence of the Eu positive anomaly in most of the peridotite analyses that points to a contamination by a “basaltic” source, we suggest that eclogites are the source of the metasomatic agent that enriched the original garnet peridotite.

The Monte Duria area thus represents a natural laboratory where is possible to study *in situ* the mantle-crust interaction. Metasomatic agents and processes, relationships between *UHP-UHT* metamorphism and metasomatism, and mechanisms of emplacement of mantle rocks into crustal slab can be here addressed and framed in the context of the well known geological background of the Alps.

High-pressure rock carbonation: implications for the reactivity of C-bearing fluids and the magnitude of fluid flow in the subducting slab

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Keywords: carbon cycling, subduction, metasomatism, fluid fluxes.

Fluid fluxes in subducted oceanic crust can be very large and transfer massive quantities of volatile species from the slab to the shallow crust and hydrosphere. High-pressure rock carbonation is a newly discovered fluid-mediated process that may play a pivotal role in the subduction zones C cycling (Piccoli et al., 2016; Scambelluri et al., 2016). Defining the fluid source and the magnitude of fluid flow responsible for rock carbonation is essential to better understand the reactivity of C-bearing fluids with the slab-forming rocks. This study focuses on the *HP* carbonate bearing metasomatic system in the lawsonite-eclogite terrains of Alpine Corsica (France). Metasomatic carbonates are found along lithological boundaries juxtaposing the serpentinite basement with the cover units. We performed a petrological and Sr-Nd isotopic study of these metasomatic carbonates. All the analyzed samples display very homogenous εNd_i signature (~ -8), but $^{87}Sr/^{86}Sr_i$ values plot along a mixing curve between serpentinite/metasediments/ continental crust ($0.708 < {}^{87}Sr/^{86}Sr_i < 0.709$), suggesting that metasomatic carbonates precipitate from a multi-source metamorphic fluid. We therefore use quantitative mass balance approach to evaluate element mobility, and calculate time integrated fluid fluxes responsible for *HP* rock carbonation. Our results show that massive Ca and CO_2 mass gain occurred during open system fluid-rock interactions. Moreover, all samples display significant Na mass gain, whereas the gain in Mn, Cr and Ni may vary from one sample to another. The overall trace element budget does not change during rock carbonation, with the exception of a slight enrichment in the most incompatible elements (Gd, Td, Dy, Y, Ho). These results suggest that fluids were mainly aqueous and very diluted. A conservative estimation of time integrated fluid fluxes gives a minimum value of 10^4-10^5 m^3_{fluid} m^{-2}_{rock}. It is concluded that carbonate metasomatism is spawn by regional-scale advective Ca-C mass transfer by means of extremely channelized fluid flow along lithological boundaries.

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Hydrous carbonatitic liquids generated by subducted pelagic carbonates

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Keywords: subduction, carbonatite, calcite, aragonite.

Pelagic limestones, hundred meters in thickness, are subducted today in a variety of subduction zones worldwide (Colombia, New Zealand, Vanuatu). Impure marbles constitute large tectonometamorphic units in mountain belts (*e.g.*, Alps) testifying to their lithological and geochemical identity throughout the orogenic cycle. Despite the geochemical relevance of systems enriched in $CaCO_3$, experimental investigation mostly focused on carbonated pelites, characterized by low Ca/(Ca+Mg+Fe) ratio.

Here we model the composition and the condition of formation of liquids, formed from subducted impure limestones, in the system $CaO-Al_2O_3-SiO_2-H_2O-CO_2$, profiting of phase relationships in the subsystem $CaO-H_2O-CO_2$ (CHC) where a continuous transition between a high-density "vapor" and a carbonated hydrous "melt" was suggested to occur above a second critical endpoint located approximately at 4 GPa (Wyllie & Boettcher, 1969).

Multianvil experiments were performed at 4.2 and 6.0 GPa on three bulk compositions, where zoisite and/or Al_2SiO_5 saturation prevents the formation of portlandite and dellaite, experimentally recorded on eutectic melting in CHC, but barely found in nature. H_2O contents was varied from 6 to 21 wt%.

Aragonite + kyanite + fluid, and minor lawsonite form at 700°C, replaced by zoisite at 800°C. Between 850 and 950°C, a complex sequence of textural features is observed upon quenching of single volatile-rich liquid phase formed at run conditions. Precipitates include dendritic $CaCO_3$, silicate glass and Al-rich whiskers. The bulk composition of such hydrous carbonatitic liquids is retrieved by image analysis on X-ray maps, showing Ca:Al:Si ratios up to 6:1:3.

Hydrous Ca-carbonatitic liquids are efficient media for scavenging volatiles from subducted crustal material and for metasomatizing the mantle wedge. Thermodynamic modelling suggests that reactive percolation in a harzburgitic matrix generates carbonated wehrlite bodies, containing 15–20 wt.% clinopyroxene and 5–10 wt.% garnet.

Wyllie, P.J. & Boettcher, A.L. (1969): Liquidus phase relationships in the system CaO-CO2-H2O to 40 kilobars pressure with petrological applications. Am. J. Sci., 267-A, 489-508.

The speciation of carbon within eclogite rocks as function of pressure, temperature and oxygen fugacity. Implications for the origin of carbonatitic melts and diamonds

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Keywords: carbonatitic melts, diamonds, redox mantle, eclogite, high pressure.

The speciation of volatile elements within mantle rocks is strongly controlled by the local redox conditions buffered by the surrounding abundant Fe-bearing minerals. The application of an oxy-thermobarometer proposed for eclogite rocks (Stagno et al., 2015) allows thermodynamic predictions of the redox state for a subducting oceanic crust as function of pressure and temperature. In contrast, the speciation of carbon during subduction can only be inferred if the fO_2 at which carbon (graphite or diamond) and carbonate (solid/melt) coexist is known. This fO_2 can be calculated using a thermodynamic dataset for the subsolidus end-member mineral equilibrium as dolomite + coesite = diopside + carbon + oxygen (DCDG/D; Luth, 1993). However, an experimental calibration of this oxygen buffer at temperatures and pressures at which CO_2-rich melts can form is still missing.

We performed experiments at pressures between 3 and 6 GPa and temperatures between 900 and 1300°C using the Voggenreiter 840 t, Walker-type multi anvil press available at *HP*/*HT* Lab at National Institute of Geophysics and Volcanology (INGV, Rome). The starting material employed for all the experiments is a mixture of synthetic omphacitic glass, quartz, dolomite and graphite representative of the Dolomite-Coesite-Diopside-Graphite buffering assemblage [DCDG/D] loaded in a graphite capsule wrapped by a metal foil. The synthetic eclogite mixture is, then, sandwiched between layers of ilmenite + rutile (1:1 ratio) and ~ 3 wt% iridium used as redox sensor (Taylor et al., 1992). The recovered quenched samples were polished for textural and chemical characterization of the mineral phases using FE-SEM and the electron microprobe.

Preliminary results shows that with increasing temperature a carbonatitic melt forms with ~5 wt% SiO_2 at 900°C. At 1100°C, the melt is carbonate-silicate with 25 wt% SiO_2, that increases to ~ 32 wt% SiO_2 at 1200°C. The experimentally measured fO_2 plotted as a function of pressure and temperature appears lower than thermodynamic predictions, and show a gradual decrease as the silica content of the melt increases.

The results from this study show that magmas with compositions from carbonatitic to carbonate-silicate (hybrid) melts can form in eclogite rocks within less than 1 log unit of fO_2 interval. Our results are, then, integrated with additional experiments performed at lower mantle conditions to model the origin of diamonds from CO_2-bearing fluids by redox reactions involving Fe-bearing minerals.

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The potential role of amphibole in fixing carbon in the lower crust

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Keywords: amphibole, carbon, deep crust.

Carbon (C) cycle and fluxes between mantle and exosphere are critical processes for the Earth's atmosphere and climate on short to long time scales (Dasgupta &Hirshmann, 2010). Recent estimates of C fluxes suggest that most of the subducted C is recycled through subduction, even if there is an apparent imbalance between the amount of C released from the subducting slab and the amount returned to the atmosphere at volcanic arcs (Kelemen & Manning, 2015). Current knowledge on C solubility in volatile-free major mantle minerals suggests their minor role in fixing C, especially at low pressure (Shcheka et al., 2006). Yet no specific studies have been never carried out on amphibole, one of the most important repository minerals in the lower crust-upper mantle system for volatile elements (F, Cl, and H_2O). Compared to the other common mantle minerals amphibole has a more versatile crystal structure which could favor the incorporation of C or its compounds. Carbon was measured in amphibole crystals from the crustal amphibole-rich peridotite of the Finero Complex (Ivrea-Verbano; Italy) with Thermo Scientific Flash Elemental Analyzer on different mineral fractions (63, 125 and 250 µm) and through different sample preparation approaches (*e.g.*, with and without HCl leaching). Data corrected for blank contamination suggest several hundreds of ppm of C in the analyzed amphiboles, while bulk rock data reveal significantly lower C contents (up to four times). Data carried out on amphibole from lower crustal rocks from Himalaya also reveal similar high C concentrations. Spectroscopic methods (Raman and FT-IR) were employed on Finero amphiboles in order to verify C speciation and its structural environment. FT-IR did not provide any evidence for the presence of structural C in amphibole, while the Raman spectrum showed the presence of a weak peak at 1055-1060 cm^{-1}. It was not possible to clearly assign it to CO_3^{2-} vibrations due to overlapping between the carbonate peak position and the silicate network bands. Molecular CO_2 bands were not observed. The measured C in the studied amphibole seems to be unrelated to mineral structure. The inspection of the amphiboles surface by SEM show the presence of (sub)micro-inclusions potentially being a source of C signal. These preliminary results and related issues are promising and suggest to go ahead with the working hypothesis that amphibole-rich rocks, constituting a significant part of the lower crust, may represent a significant C reservoir that is presently neglected in the global mass balance.

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Kelemen, P.B. & Manning, C.E. (2015): Reevaluating carbon fluxes in subduction zones, what goes down, mostly comes up 2015. Proc. Nat. Acad. Sci., 12, E3997-E4006

Shcheka, S.S., Wiedenbeck, M., Frost, D.J., Keppler, H. (2006): Carbon solubility in mantle minerals. Earth Planet. Sci. Letters, 245, 730-742.

Deep abiotic hydrocarbons: subduction zones are undisclosed reservoirs

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Keywords: abiotic hydrocarbons, deep C cycling, subduction zones.

Abiotic hydrocarbons play a fundamental role in the evolution of the Earth and other planetary bodies inside and outside the Solar System. They participate into the C and H cycles and exert a major effect on redox processes controlling the physics, the evolution and the habitability of our planet, the production of pre-biotic C compounds and nutriments for living organisms, and the understanding and exploration of other planets. Redox reactions related to serpentinization of ultramafic rocks are considered as a key geological process generating abiotic hydrocarbons, and have been focusing a great effort during the last decades. However, our current vision of serpentinization and abiotic hydrocarbon genesis is limited to shallow terrestrial environments in the biosphere or shallow sub-biosphere, whereas the potential of equivalent processes at high-pressure conditions is largely overlooked. New results from the study of high-pressure serpentinizing systems from fossil subduction zones reveal that large amounts of highly reduced species, dominantly H_2 and CH_4 can be produced abiotically at temperature and pressure conditions that largely exceed the present limits of life (Vitale Brovarone et al. 2017). This discovery points subduction zones as new, large reservoirs for these species and provides a new perspective on the deep C cycling at convergent margins, including the generation of deep pre-biotic C compounds. This presentation aims at summarizing this discovery and discussing its potential implications at a global scale.

Vitale Brovarone, A., Martinez, I., Elmaleh, A., Compagnoni, R., Chaduteau, C., Ferraris, C., Esteve, I. (2017): Massive production of abiotic methane during subduction evidenced in metamorphosed ophicarbonates from the Italian Alps. Nature Commun. , DOI:10.1038/ncomms14134.

Session S22:
Innovative methods and techniques for soil and water characterization and the definition of natural background values

Conveners:

Giovanna Armiento (ENEA, Roma)
Marino Vetuschi Zuccolini (Univ. di Genova)

Radium isotopes and their decay products to assess the age of a NAPL-spill

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Keywords: radium isotopes, NAPL, dating, gamma-spectroscopy.

Radium isotopes and their decay products are used to estimate the time since the accumulation of radium in impacted soils and sediments from crude oil and gas wastewater spills (Lauer & Vengosh, 2016). The retention of unsupported ^{226}Ra and ^{228}Ra from spill water to soil and the ingrowth of Ra progeny result in three independent age dating methods using the ^{228}Th/^{228}Ra, ^{210}Pb/^{226}Ra, and ^{228}Ra/^{226}Ra activity ratios. Here, we present an original method based on the accumulation of the alpha-recoiled ^{228}Ra and ^{224}Ra atoms from soil and sediments to a spilled Non-Aqueous Phase Liquid (NAPL), initially not containing radium. In order to test this method, two different experiments were carried out. About 35 g of monazite sand was left to react with 11 mL of white petroleum distributed by PIC S.r.l., (test 1) or distilled water (test 2) for a period of 6 months. Periodically, about 2 mL aliquots of reagent solutions were sampled, counted by gamma spectrometry and then reinjected into the glass vials. ^{228}Ra and ^{224}Ra activity concentrations were indirectly determined using their gamma-emitting daughter products, ^{228}Ac peaks at 338/911 k*e*V and ^{212}Pb peak at 238 k*e*V, respectively. As expected, ^{228}Ra accumulation in the liquid phase is not detectable at the beginning, while that of ^{224}Ra is. Since its abundance is inferred from ^{212}Pb, we expect that other processes besides ^{224}Ra recoil affects ^{212}Pb activity, because ^{212}Pb derives from the decay of ^{220}Rn (thoron) which is a gas and thus have a higher mobility. Actually, ^{220}Rn budget in the liquid phase also depends on thoron recoil and diffusion from the sand to the liquid phase, counterbalanced by ^{220}Rn decay and escape to the air phase in the glass vial. In order to quantify these thoron fluxes, proper experiments are in progress. From these data, proper equations to describe radium accumulation curves were obtained and compared with the theoretical ones. By resolving these equations with respect to time, the age of a spill can be obtained and applied to natural systems. A further observation is that ^{212}Pb activity in white petroleum is 2.6 times that measured in distilled water. This may be due to a different solubility either of radium or radon in the NAPL. Since radon distribution coefficient between white petroleum and water at ambient temperature is known (De Simone et al., 2017) and that of radium is not, *ad-hoc* testing in a large range of *p*H is in progress to assess this. The final step will be to apply this new information to a real case-study.

De Simone, G., Lucchetti, C., Pompilj, F., Galli G., Tuccimei, P. (2017): Laboratory simulation of recent NAPL spills to investigate radon partition among NAPL vapours and soil air. Appl. Radiat. Isotop., 120, 106-110.

Lauer, N., & Vengosh, A. (2016): Age Dating Oil and Gas Wastewater Spills Using Radium Isotopes and Their Decay Products in Impacted Soil and Sediment. Environ. Sci. Technol. Letters, 3, 205-209.

Hydrogeochemistry and threshold values of Cl^-, SO_4^{2-} and F^- in groundwater

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Keywords: hydrogeochemistry, hierarchical clustering analysis, background range, threshold value, Sardinia.

For any environmental geochemical investigation, the knowledge of geochemical background of dissolved substances and hydrochemical conditions is a prerequisite (Edmunds & Shand, 2008). From a regulatory point of view, the definition of threshold values, *i.e.*, the upper limits of background variation, is mandatory for the regional authorities that have to address a sustainable management of water resources (European Dir. 2000/60/CE, 2006/118/CE, 2014/80/EU and Italian Legislative Decrees 152/2006 and 30/2009).

The Sardinia island (Italy) is one of the European areas least affected by potentially anthropogenic impacts, such as spreading urbanization, intensive agriculture and regional atmospheric contamination. Such characteristics allow to consider Sardinia a good site for testing an approach that integrates geochemical tools, hierarchical cluster and geographical information system, aimed at estimating background concentrations of chloride, sulfate and fluoride at the regional scale. The GIS method was used for mapping and spatial visualization.

Analytical data of groundwater samples were obtained from several hydrogeochemical surveys and the groundwater-monitoring program established by the Sardinian Regional Government. The water chemistry was investigated on the basis of dissolved components Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_3^-, Cl^-, SO_4^{2-}, NO_3^- and F^-. Based on hierarchical cluster analysis, four principal clusters and eight sub-clusters of groundwater samples were identified. Background concentrations of chloride, sulfate and fluoride were estimated for each cluster using different estimators, which provide more reliable background and threshold estimates (Matschullat et al., 2000). Values of total dissolved solids (TDS) were a major distinguishing factor in principal clusters, whereas relative proportions of major cations and anions distinguished the sub-clusters. Chloride threshold values above regulations were observed in water bodies hosted in sediments and volcanic rocks, sulfate threshold values above regulations were associated with water interacting either with sulfide minerals or gypsum. Fluoride and nitrate showed distinct signatures in some sub-clusters; specifically, the highest threshold value of fluoride were observed in saline groundwater interacting with mineralized rocks; the highest threshold of nitrate was observed in groundwater samples located in areas where agricultural activities are diffused. The results of this study indicate that the integration of hierarchical clustering analysis with the geochemical characteristics of groundwater, also taking into account the geological context, allow the repartition of groundwater samples in distinct hydrogeochemical groups, which in turn allowed to calculate the background ranges and reliable threshold values in groundwater.

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Matschullat, J., Ottenstein, R., Reimann, C. (2000): Geochemical background-Can we calculate it? Env. Geol., 39, 990-1000.

Cr, Ni, and other Potentially Toxic Elements (PTEs) in serpentine soils from different ophiolite complexes (Liguria, Italy)

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Keywords: natural background, potentially toxic elements, serpentine soils.

Serpentine soils, formed from ultramafic bedrocks, play a primary environmental role due to low content of essential elements (P, K, and N), high content of ecotoxic metals (Cr, Co, Ni), and low Ca/Mg ratio. In this multidisciplinary study, we combine mineralogical, petrological and chemical investigations on several soil profiles deriving from ultramafic bedrocks with different degree of serpentinization and deformation. In particular, we determine the concentrations and distributions of PTEs (Potentially Toxic Elements) in serpentine soil profiles from the high pressure-low temperature metaophiolite of the Voltri Unit (Ligurian Alps) and from the low-grade ophiolite of the Val di Vara Supergroup (northern Apennine).

Major, minor, and trace element concentrations were analysed *in situ* and in laboratory via Field Portable X-Ray Fluorescence spectrometer and by means of ICP-EOS and ICP-MS. All the data-set was inserted in a GIS database and used to produce contour maps for the evaluation of the spatial distribution of selected PTEs.

All the studied soils are litho soils to brown ranker, characterized by a poor evolution (primitive soils) from 10 to 70 cm in thickness. Along the studied soil profiles, the most abundant minerals are derived from the bedrock (*e.g.*, serpentine, magnetite, chlorite, olivines and pyroxenes) with various degree of supergenic alteration. In general, the authigenic phases are subordinated and mainly represented by Fe-oxyhydroxides and oxides, with minor amount of clay minerals.

More than 90% of the PTEs in the soils is represented by: Cr, Ni, Co, Cu, Zn, and V. The soils are generally depleted in Cr, Ni, and Co and enriched in Cu, Zn and V with respect to the bedrocks,. Moreover, with some minor exceptions, Cr and Ni show a bottom to top systematic decrease in concentration whereas Co and V tend to concentrate toward the superficial horizons.

As expected in such primitive soils, both the mineralogy and the chemistry is compatible with the bedrock, and seems controlled mainly by the serpentinization degree and metamorphic re-equilibration, as much as by the rock texture and proximity with other lithologies.

From the environmental point of view, all the studied soils systematically exceed (more than one order of magnitude) the commercial and industrial concentration limit for Cr, Ni, and Co, according to Italian law (D.M. 471/1999; D.Lgs 152/2006).

Our investigations show that these critical concentrations of PTEs in serpentine soils are related to geogenic sources since these elements are linked to the bedrock-forming minerals or to their alteration products.

The use of a GIS database with mineralogical, petrological and chemical data linked to geological maps is proved to be a valuable tool to produce contour maps for the preliminary evaluation of the spatial distribution of potentially harmful elements and thus to define their natural background concentrations.

Thallium distribution in rocks from the Sant'Anna tectonic window (Apuan Alps, Italy)

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Keywords: thallium, environmental hazards, geodatabase, Apuan Alps.

The high concentration of thallium (Tl) in some pyrite ore deposits from southern Apuan Alps (Tuscany, Italy), with Tl contents up to 1100 µg/g (D'Orazio et al., 2017) represents an important environmental hazard owing to the geographical location of this area, facing the densely populated Versilia coastal plain, as proved by the severe thallium contamination of the drinkable water distribution system in the Pietrasanta area (Campanella et al., 2016; Biagioni et al., 2017).

Usually, the passage of thallium, as well as other toxic elements, from the litosphere to the hydrosphere and potentially to biosphere, is ascribed to human activities (*e.g.*, mining activities); however, in addition to anthropogenic sources, natural sources for thallium pollution should not be neglected and the contribution of Nature should be taken into account when looking for sources of problems involving metal contamination.

From this perspective, sixty samples of rocks belonging to the Paleozoic basement cropping out in the Sant'Anna tectonic window, upstream of Pietrasanta, were collected in order to determine their major- and trace-element contents. The studied area was divided into square cells with 150 m of size. Each cell was characterized by at least one sampling site. Samples were collected orthogonally to the main foliation of the rocks, along a 50 cm-long logline, after the removal of the altered portions of the rock surfaces. Rock samples were then powdered and their geochemistry was determined through X-ray fluorescence (for major elements) and Inductively Coupled Plasma-Mass Spectrometry (for trace elements). Geochemical data were stored in a geodatabase implemented in ArcGIS and the evaluation of basic statistical parameters for Tl was performed through the R software. The concentration map of Tl was obtained using the multivariate adaptive regression splines method implemented in R "earth" package.

The thallium average concentration, in the studied area, is 13 µg/g, ranging between 2 and 71 µg/g. The element concentration increases considerably close to the ore deposits. The results of the present study represent a useful tool for the estimation of the background concentration of Tl (and other potentially toxic elements) in the studied area, representing a reference for remediation actions and for general management purposes.

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Micro-Raman Spectroscopy: a useful tool for COPR soils characterization

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Keywords: hexavalent chromium, micro-Raman spectroscopy, COPR, mineralogical control.

This work is part of a much wider project aimed at the determination of the role of the mineralogical control on the release of toxic metals in soils and waters. Preliminary, but very promising, results on the mineralogical characterization of chromite ore processing residue (COPR) soils by means of Raman Spectroscopy are shown.

Raman Spectroscopy could be a powerful tool for studying COPR soil because of minimal sample requirement and the possibility to analyze untreated soil.

Toxic metal pollution has become a severe problem in industrialization process at regional scale. Among the toxic metals, hexavalent chromium (Cr(VI)) is considered as a serious pollutant. The Stoppani S.p.A. industry located in the Cogoleto and Arenzano area (Genova, Italy), transformed Cr(III) from chromite mineral ($FeCr_2O_4$) (Piccardo et al., 1989) to Cr(VI). It ceased the activity at the beginning of 2003, and since 2001, the site has been included, with DM n.468, into the national program of environmental remediation and restoration.

The total Cr concentration in factory area soils is 15,000 mg/kg compared to a regulatory threshold for industrial areas of 800 mg/kg (D.lgs. 152/2006).

The mineralogical and minero-chemical characterization of soil samples, performed by means of X-ray powder diffraction (XRPD) and scanning electron microscopy (SEM), indicate that they are characterized by: a) residual roasting chromite ranging in composition from $MgCr_2O_4$ at core and $MgFe_2O_4$ at rim; b) trona ($Na_3(CO_3)(HCO_3)\cdot 2(H_2O)$) and brownmillerite ($Ca_2(Al,Fe^{3+})_2O_5$) high temperature industrial products; c) gypsum ($CaSO_4\cdot 2(H_2O)$), calcite ($CaCO_3$) and ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26(H_2O)$) as result of subsequent weathering (Hillier et al., 2003; Chrysochoou & Dermatas, 2006).

It is noteworthy that no Cr^{VI}-phases (*i.e.*, $PbCrO_4$ and Na_2CrO_4) are found; this could be due to different causes: leaching processes in the soil, or solubilization of these phases during sample preparation.

Only micro-Raman analysis of untreated COPR samples, after granulometric separation (71, 50, 20 μm), have revealed the presence of chromate phases such as sodium chromate (Na_2CrO_4) and crocoite ($PbCrO_4$).

These are very promising results for COPR soils characterization in order to assess the mineralogical control for the release of hexavalent chromium in percolating waters.

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Monitoring soil organic matter content in croplands through Vis-NIR-SWIR spectroscopy

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Keywords: soil organic matter, Vis-NIR-SWIR spectroscopy, tillage erosion.

Organic matter is the most active and vital component of the soil because of its role in the chemical, physical and biological processes. Increasing soil organic matter (SOM) generally results in increasing soil productivity and reducing the atmospheric CO_2 content that contributes to climate change. Therefore, preservation and restoring of SOM through appropriate crop practices and minimum tillage are fundamental.

In hilly landscapes, erosion is responsible of SOM depletion in topsoils. Tillage erosion has been recognized as one of the main erosive processes affecting croplands in hilly terrains and can be evidenced from differences in soil properties along a hill slope (van Oost et al., 2006). Intensive tillage erosion results in substantial soil truncation and within field redistribution of soil and its constituents, including SOM.

Due to the large variability of SOM in the 3*D* space, monitoring actions to assess SOM variations are time consuming, expensive and affected by high levels of uncertainty. However, the mapping of SOM spatial distribution at the national, regional and local scales has been tentatively carried out in Italy (Costantini & Dazzi, 2013).

In the present study, we attempt to predict the SOM content in topsoils in order to estimate the tillage erosion rate, using VIS-NIR-SWIR spectroscopy and standard soil analyses (Conforti et al., 2013, 2015; Stenberg et al., 2010). However, soil texture, structure, moisture, and mineralogy also influence the appearance of the weak features diagnostic of SOM. The overall shape in the visible region of the spectra proved to vary with the SOM content and field- or farm-scale calibrations have demonstrated to be promising in estimating SOM abundance. Target crops are vineyards and olive groves in hilly terrains. Laboratory analyses of topsoil samples include SOM, *p*H, conductivity, cationic exchange capacity, texture, and XRD mineralogy determination.

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Sustainability of aquifers in Mali: Sr and Pb isotopic signatures and tritium age

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Keywords: aquifer isotope geochemistry, Pb isotopes, Sr isotopes, tritium dating.

An exploratory assessment of the sustainability and vulnerability of water wells in aquifers in northern Mali can be attempted on the basis of two criteria: the connectivity of aquifers and their recharge age. The former can be addressed using Sr-Pb isotopic signatures, as isotope ratios are dependent on the isotope geochemistry of the bedrock but not on saturation/precipitation reactions. The latter can be addressed using tritium activity measurements, which are most sensitive to recharges that occurred between 1950 and 1965.

A total of 11 water samples from wells already in operation and from wells being constructed were collected over 700 km E-W distance between the Kayes and Mopty regions. Typical sample sizes were 100 mL. Sr and Pb were separated from the other dissolved ions by cation-exchange resin chromatography. Isotopic compositions of Pb and Sr were measured my multicollector ICP mass spectrometry.

Results show that each well has a different Sr-Pb isotopic signature. A first-order conclusion appears to be that aquifers have very limited areal extents and each well taps a separate aquifer. In principle it would be possible to model water interactions with the bedrock in such a way that neighbouring wells can be matched pairwise, by assuming *ad-hoc* Sr and Pb concentrations and isotopic compositions; however, even in this highly artificial scenario it is impossible to fit more than two wells at the time. The robust conclusion is that no aquifer extends for the entire 700 km in E-W direction. A likely, and more strict, conclusion is that the E-W extensions of aquifers are smaller than 50 km or even less in some cases.

Tritium measurements were performed on small (10 mL) sample aliquots. Detection limits and uncertainties are therefore very high. Five wells (irregularly scattered in the sampling area) have detectable tritium anomalies; calculated recharge and residence ages range between 30 and 60 a.

Sustainability requires achieving a steady state between withdrawal and recharge. Considering the very long recharge times, this puts strict limits on the pumping speed. The vulnerability is a function both of total water mass and of connectivity: pollution of a small aquifer can occur as an effect of even a small pollutant mass, but its effects are likely to be restricted to the area covered by the aquifer if it is indeed unconnected to neighbouring ones.

Preliminary geochemical and geological characterization of the thermal sites of Galatro and Antonimina (south Calabria, Italy)

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Keywords: Galatro, Antonimina, thermal waters.

A preliminary geochemical characterization of Galatro and Antonimina thermal waters was performed following the approach proposed by Vespasiano et al.(2015) and Apollaro et al.(2016). The thermal sites are located in a back-arc and fore-arc basins between the Serre and Aspromonte Massifs, in a very complex geological setting. This sector of the Calabrian orogen is characterized by series of NNE-SSW and NNW-SSE strike normal kinematic faults displacing the crystalline-metamorphic units and their sedimentary successions of several hundred meters (Tripodi et al., 2013). Close by, the Aspromonte unit, made up of Variscan metamorphic rocks intruded by peraluminous granites, is overlaid by the Phyllites with intercalations of metarenites and metalimestones of the Stilo unit intruded by late Variscan plutonites. Mesozoic sedimentary successions of conglomerates, sandstones and yellow shallow water dolostones and limestones rest on the basement of the Stilo Unit.

Waters sampled from Galatro Spa have shown basic *p*H value of 7.94, outlet temperatures of 37.7°C, negative redox potentials (–266 m*V*) and total dissolved solids of 1173 ppm. Waters from Antonimina reported a *p*H value of 7.5, outlet temperatures of 35.2°C, redox potentials of 66 m*V* and total dissolved solids of 11,510 ppm. Both heat up thanks to the reservoir rocks through conductive transfer during prolonged circulation into the deep aquifer at temperatures close to 55°C. Waters attain thermo-chemical equilibrium rising relatively quickly to the surface, along sub-vertical faults and fractures, preserving part of their physical and chemical characteristics. The water chemistry is analysed by means of the triangular diagrams of the major anionic/cationic constituents and correlation plots. Triangular diagrams show a Na-Cl and Na-Cl(SO_4) composition for Galatro and Antonimina respectively. Further geochemical and isotopic analyses are currently planned to reconstruct the main recharge areas, residence times and reservoirs characteristics.

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Mo isotopic fractionation in Tso Morari lake waters

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Keywords: Mo isotopic composition, evaporation effect, Tso Morari lake, India.

One unsolved question in the Mo isotope systematics is the variability of river water Mo when a river enters a lake. We report here a simple case study on the Tso Morari (Lha.mo.la.tso), Ladakh, NW India, at an elevation of 4500 m. The lake has one larger and one smaller inflow and no outflow. As a result of evaporation its waters are brackish. Its depth is shallow and its redox condition is oxic.

During the 2008 HKT field trip we collected water from the larger, northern river inflow 100 m upstream of the lake (sample R) and from the lake *ca.* 20 m from the coastline (sample L), and solids from the upper few cm of sediment mud in the same near-coast locality (sample S). Samples were analysed in 2008 in preparation for the paper by Neubert et al. (2011) but never published. The results are shown in the Table; δ^{98}Mo is referred to the same reference material used by Neubert et al. (2011).

The results show a rather large isotope fractionation between river input and lake water. They also underline the preponderance of evaporation in controlling the Mo element budget, as the lake water has a 12 times higher Mo concentration than the inflow, despite an active and abundant removal of Mo into the sediment. The Mo isotopic composition of lake water is not a mixture between the inflowing Mo and the precipitated sediment, because of the absence of any correlation between the isotopic composition of Mo and its concentration. The isotopically heavy Mo of lake water requires an equilibrium fractionation between dissolved and precipitated Mo. The preferential partition of the light isotopes into the sediment matches that observed in oxic sedimentation on the ocean floor (Siebert et al., 2003).

In conclusion, the "lake effect" shown by Tso Morari is capable of shifting the Mo isotopic signature of river waters towards heavier values. The disproportionation of a part of the dissolved Mo into an isotopically light sediment drives the residual dissolved Mo towards a higher δ^{98}Mo.

Sample	Mo concentration (ppb)	Isotopic composition (δ^{98}Mo)
R (river inflow)	1.62±0.02	1.44±0.06
L (lake water)	19.6±0.3	1.81±0.04
S (sediment)	44±1	0.05±0.07

Neubert, N., Heri, A.R., Voegelin, A.R., Nägler, T.F., Schlunegger, F., Villa, I.M. (2011): The molybdenum isotopic composition in river water: Constraints from small catchments. Earth Planet. Sci. Letters, 304, 180-190.

Siebert, C., Nägler, T.F., von Blanckenburg, F., Kramers, J.D. (2003): Molybdenum isotope records as a potential new proxy for paleoceanography. Earth Planet. Sci. Letters, 211, 159-171.

Session S23:

Geochemistry and isotope-geochemistry in food traceability: state of the art and new perspectives

Conveners:

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Relationships between Sr isotopic composition of mineral waters and deciduous human teeth: a contribution to human mobility and food traceability studies in Italy

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Keywords: isotope geochemistry, human mobility, food traceability.

In recent years, isotopic studies have provided a huge contribution to archaeology. Several studies, carried out in variable localities of the world, have focused their attention on human mobility, to identify non local individuals from ancient burials and reconstruct their migrations, by measuring the strontium isotope ratios ($^{87}Sr/^{86}Sr$) of their teeth enamel. This method is based on the premise that rocks display variable $^{87}Sr/^{86}Sr$ ratios depending on several factors associated with the geological characteristics of the site, *i.e.*, age and type of the parent rocks (*e.g.*, Price & Gestsdóttir, 2006; Kenoyer et al., 2013), and original rubidium (Rb) content. The bioavailable Sr present in soil and groundwater is incorporated into local plants and, through the food chain, enters the human body. On this basis, $^{87}Sr/^{86}Sr$ signatures in human tissue mirror the $^{87}Sr/^{86}Sr$ values of water, plants and consumed food, which in turn reflect that of bedrock of a given region (Ericson, 1985).

In this study, Sr isotope ratios were measured on commercial mineral waters from variable Italian water springs, on soils and plants from the Neapolitan area, and on teeth enamel of children. The latter were born and still live in the Neapolitan area (south Italy), so that constraints on their childhood diet are available. The aim was to discriminate among the contributions of soil, water, food etc., and identify the main one affecting the isotopic signature of teeth enamel. The results of this investigation will be important for human mobility studies because they will allow understanding to which extent Sr isotopes can be effectively used for i) discriminating non-local from local individuals, and ii) assessing the effects on the modern society of a diet based on food from different geographic areas.

Ericson, J.E. (1985): Strontium isotope characterization in the study of prehistoric human ecology. J. Hum. Evol., 14, 503-514.

Kenoyer, J.M, Price, T.D., Burton, J.H. (2013): A new approach to tracking connections between the Indus Valley and Mesopotamia: initial results of Strontium isotope analyses from Harappa and Ur. J. Archaeol. Sci., 40, 2286-2297.

Price, T.D. & Gestsdóttir, H. (2006): The first settlers of Iceland: an isotopic approach to colonisation. Antiquity, 80, 130-144.

$^{87}Sr/^{86}Sr$ in wines, grapevine sap, soils, and bedrocks: an experimental study on geologic and pedologic characterisation using radiogenic isotope of heavy elements

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Keywords: Tuscany, Chianti Classico, Sr-isotope, wines, micro-vinification, geologic traceability.

An experimental study to define the Sr-isotope from bedrocks to soil and its uptake by the vine roots to the biological live of the plant then to the wine, was made on micro-vinifications of grape-bunches from one of the main high quality wine area of Chianti Classico Consortium (the Barone Ricasoli Winery).

The experimental work was carried out with a deep control of the boundary conditions (*i.e.*, type of geological substratum, soil, and ground water supply etc.) on 11 sampling points distributed on a relatively small but geo-pedologically variegated area. From each sampling point, grape-bunches were harvested from single vine-plant over a period of four consecutive harvest years. Sr-isotope was also determined on grapevine sap, on the bio-available fraction of the soil, on bulk soil and on the rocks of the substratum.

No significant Sr-isotope variability was observed among wines obtained through micro-vinification from different harvest years, suggesting that the Sr uptake process from the grapevine roots to its final product is time independent even at a very small scale (single vine). A significant Sr-isotope variability is detectable among wines obtained by micro-vinifications of grapes growing on vine plants from different soils type. Each harvest point is characterised by a specific Sr-isotopic value related to its substrata. The Sr-isotopes of each single wine batch matches those obtained from the sap of the corresponding grapevine plant. In addition these data correlate with the bioavailable fraction of soils collected on which the plant grown. All Sr-isotopic data obtained fall well within the range found for bedrock. A mismatch was observed, however, between the Sr-isotope signature of micro-vinifications and the corresponding whole soil. Decoupling of Sr-isotopes between soils and bedrocks has also been found, and attributed to differential behaviour of minerals in response to pedogenetic and weathering processes, which are controlled essentially by the mineralogy of bedrock.

The findings of our experiments confirm the evidence that the biological activity of the vine is not able to change the original $^{87}Sr/^{86}Sr$ up-taken from the bio-available fraction of the soil, and that the $^{87}Sr/^{86}Sr$ signature of wines is thus an unadulterated feature of the inorganic Sr component achieved by the *terroir*. Eventually, the recurrent small-scale $^{87}Sr/^{86}Sr$ value differences may support the possibility to typify the cultivation suitability of single *cru* apt to yield wines of the best quality by isotopic monitoring, combined with other important parameters such as best exposure, less water stress etc.

Inter-measure determination of the isotopic composition of strontium

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Keywords: Thermal Ionization Mass Spectrometry, instrumental fractionation, Rayleigh's distillation.

In thermal ionization mass spectrometry instrumental fractionation produces bias which preclude direct measurements of the values of the isotopic ratios of the element in analysis. Cavazzini (2009; 2012) has shown that the empirical laws of fractionation, as power law and exponential law (Russel et al., 1978) can be interpreted in terms of a process of distillation in the ion source of the mass spectrometer, according to Rayleigh's (1902) distillation theory. This interpretation predicts linear paths of evolution in x *vs.* y and in x *vs.* x/z diagrams where x, y and z are measured values of isotopic ratios.

Analytic representations of these paths of evolution show that the slope and the y-intercept of the linear paths are functions of the true values of the isotopic ratios involved, x_0, y_0, z_0 and of a quantity, which we here call a, which is a function of the masses of the isotopes which define the isotopic ratios. Due to particular structure of slope and y-intercept, if we know the values of the masses of the isotopes involved we can calculate the true values of the isotopic ratios.

If a number of x *vs.* y distributions are obtained from different measurements of a sample, however, it is observed that the slope and the intercept of the straight line which best fits the distribution change. These changes can be interpreted as due to a not-exact equivalence of the fractionation factors of the isotopic ratios involved, which turns quantity a to parameter a' that does not depend only on the masses of the isotopes. This fact can be related to irreproducibility in loading the sample on the filament, to irreproducible behavior of the acceleration voltage, of voltages of the collimators in the ion source, of the current through the filament(s) etc. which determine the value of a' to change randomly. Since the values of the true isotopic ratios are sensible functions of these parameters, the calculated values may significantly differ, resulting in the impossibility to calculate the true values of the isotopic ratios by a single measurement of the sample.

In this case, however, due to particular structure of slope and y-intercept of the theoretical lines which represents the distributions, it can be shown that parameter a' can be eliminated, and the slopes of distributions obtained from different measurements of a sample are expected to be linearly correlated with the respective intercept values, the slope and the intercept of this linear correlation being the true values of the isotopic ratios.

The values of slope and intercept of the straight lines which best-fit the distributions we obtained from different measurements of the worldwide used NIST SRM 987 have been observed to be linearly correlated. The linear best-fit of this correlation suggests for this standard material $^{88}Sr/^{86}Sr = 8.29 \pm 0.01$ and $^{87}Sr/^{86}Sr = 0.70705 \pm 0.00045$ (1σ errors), values which are significantly lower than those presently assumed in the literature.

Cavazzini, G.(2009): Rayleigh's distillation law and linear hypothesis of isotope fractionation fractionation in thermal ionization mass spectrometry. Int. J. Mass Spectr., 288, 84-91.

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Rayleigh, J.W.S. (1902): On the distillation of binary mixtures. Philos. Mag., 42, 521-537.

Russell, W.A., Papanastassiou, D.A., Tombrello, T.A. (1978): Ca isotope fractionation on the Earth and other solar system materials. Geochim. Cosmochim. Acta, 42, 1075-1090.

New analytical methodologies for geographical and varietal traceability of enological products

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Keywords: food traceability, isotope, secondary indicators, chemometrics.

Notwithstanding urbanization and globalization, the strengthening consumers interests towards food with a well-defined geographical origin has been kept constant and features such as food authenticity and traceability are becoming peculiar to the entire mankind. This work summarizes the results of a long term research project [supported by AGER, Agroalimentare e Ricerca, cooperative project between grant-making foundations under the section 'wine growing and producing'] focused on the development of geographical and varietal traceability models of two typical Italian oenological products, Lambrusco PDO and TRENTODOC, by means of primary and secondary indicators. In particular, this work reviews the adopted strategy and the obtained results as regard the potentiality of primary geographical tracers, *i.e.*, strontium isotopic ratio, $^{87}Sr/^{86}Sr$ and elemental content and secondary indicators (aromatic-, DNA- and NMR-profiles). The innovation of the adopted strategy lies in the use of a systematic approach for developing a geographical traceability model, which requires a deep knowledge of the whole matrices that characterised the investigated systems, namely soils, vine branches, grape juices, intermediate products and wines. For these reasons, a statistically representative sampling for Modena and Trento districts was performed and the investigated indicators were monitored in all the investigated matrices obtaining (i) isotopic maps able to highlight the geographical link between the investigated wines and their territory of provenance, (ii) varietal traceability models based on aromatic and DNA-profile, and (iii) classification model based on the combination of NMR signals and chemometrics.

Development of geographical traceability model of oenological products by means of strontium isotope ratio $^{87}Sr/^{86}Sr$

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Keywords: strontium isotope ratio, geographical traceability, food.

The possibility to assess the link between a food and its territory of origin (its 'terroir') surely represents a peculiar added value for consumers and producers and it is useful for the enhancement of the product itself. Hence, the definition of analytical/objective criteria for supporting a 'papery' geographical traceability of food, with a particular attention to those awarded with quality marks such as PDO, PGI, can represent a real important and challenging task.

The provenance of investigated food can be investigated by means of several proper analytical indicators. Among the different primary indicators, isotopic ratio of strontium, 87 on 86, has provided optimum results in the development of models of geographical traceability for different types of food. However, when this indicator is used, it requires a deep knowledge of the geological properties of the investigated territory and more in general of the whole matrices that characterised the analysed systems. In the case of oenological products, these matrices are soils, vine branches, grape juices, intermediate products and wines. Therefore, it is important to follow a systematic approach which includes several aspects: (i) a statistically representative sampling, (ii) accurate and precise measurements, (iii) optimization of the analytical methodologies for the determination of the investigated parameter, (iv) an a priori systematic study of the performance of the Sr isotope ratios within the whole "production cycle" of a food, soil-water-plant-fruit-raw-food, (v) the development of geographical traceability model, and (vi) validation of the obtained model. All these aspects are peculiar for the development of isotopic maps able to characterize a food/territory and they will be deeply handle in the present communication. Finally, the performance as geographical tracer of the investigated indicator will be highlighted in three different cases of study, namely Lambrusco of Modena PDO, Barolo PDO and Chianti DOCG wines, respectively.

Determination of trace elements and strontium isotope ratio in grape musts of the northern Piedmont region (Italy) by mass spectrometry based techniques

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Keywords: wine traceability, trace elements, Sr-isotopes, Nebbiolo.

Isotopic tracers are often combined with elemental analysis in wine traceability, origin assessment and quality control. In particular, the $^{87}Sr/^{86}Sr$ isotope-ratio systematics applied to must and wine has proven to be effective in reflecting the geological and pedological features of the provenance area (Marchionni et al., 2013; Petrini et al., 2015) due to the lack of fractionation processes in the soil-plant system, even if an adequate Sr-isotope data-base for wine sample authentication is still lacking.

In the present work the analysis of trace metals and metalloids and the Sr-isotopic systematics were applied to 16 must samples from vines growing in the Valsesia-Supervolcano Geopark in the Piedmont region (northwest Italy), a land famous for the production of quality Nebbiolo-based red wines. In particular twenty-six trace elements (Li, Be, Sc, Ti, V, Cr, Fe, Mn, Co, Ni, Cu, Zn, Ga, As, Rb, Sr, Y, Mo, Cd, Sn, Sb, Cs, Ba, Ce, Tl and Pb) were measured in each sample by inductively coupled plasma mass spectrometry (ICP-MS). The results indicate a wide variability in trace element concentration in musts from the different vineyards, always below the European legal limits for wine consumption. The analysis of the data suggests that the concentration of trace elements in these musts is attributable to natural sources, being a reflection of the volcanic signature of the ground where the vineyards grow.

Isotopic analyses were carried out by thermal ionization mass spectrometry (TIMS). The $^{87}Sr/^{86}Sr$ ratio of musts is in the wide range 0.71161-0.71816, showing a highly radiogenic nature which is consistent with the peculiar Sr-isotopic features of soil bedrocks that reflects the age and geochemical nature of magmatic protolith. In some of the samples the $^{87}Sr/^{86}Sr$ ratio correlates with the $^{87}Rb/^{86}Sr$ ratio, indicating that musts inherited the parent-daughter isotopic relationships of rock-soils and assuming importance for authenticity purposes.

Marchionni, S., Braschi, E., Tommasini, S., Bollati, A., Cifelli, F., Mulinacci, N., Mattei, M., Conticelli, S. (2013): High-precision $^{87}Sr/^{86}Sr$ analyses in wines and their use as a geological fingerprint for tracing geographic provenance. J. Agr. Food Chem., 61, 6822-6831.

Petrini R., Sansone L., Slejko, F.F., Buccianti, A., Marcuzzo, P., Tomasi, D. (2015): The $^{87}Sr/^{86}Sr$ strontium isotopic systematics applied to Glera vineyards: a tracer for the geographical origin of the Prosecco. Food. Chem., 170, 138-144.

Geological and geochemical fingerprints of the Bosa Geopark-Farm vineyards (Apuan Alps, Italy). Preliminary results

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Keywords: wine traceability, geochemistry, Sr-isotopes, Apuan Alps; Bosa Geopark-Farm.

The ability to trace the area of production for a wine is a priority for both consumers and producers, since the wine quality and characteristics are essentially due to the geographical and geological environment where vines grow. In particular, mountain and hillside vineyards distinguish from their flatland counterparts for the exposure to climate contrasts, temperature shifts (even diurnal), higher solar radiation and light intensity which affect the development of grape berries. How the different elevation of production directly contributes to the distinct aromas and flavors in wine, for example by developing a more favorable phenolic profile, remains a much debated topic. The Bosa vineyard is located in the Farm of the Apuan Alps UNESCO Global Geopark, few hundred meters north-east from the Careggine village (Garfagnana, Lucca) at an altitude of about 850 m a.s.l. It hence lies within the highest-altitude areas for wine production in Italy and Europe, such as vineyards in the Lombardia region (Valtellina), Valle D'Aosta (Morgex), Alto Adige, Sicily (Valledolmo, Etna), in the Valais (Switzerland) and Pyrenees mountain range (France).

The small experimental vineyard at Bosa grows on a mountain slope with a southwestern exposure, where the geological bedrock is formed by varicoloured shales interbedded with decimetric-thick calcarenite and siliceous calcilutite beds (Dudda member, Late Cretaceous-Paleogene), which characterize the uppermost part of the Scaglia Toscana Formation belonging to the Tuscan Nappe, the unmetamorphic tectonic unit which is tectonically superimposed on the metamorphic core of the Apuan Alps. Wine and grape juice (Merlot) from the 2014 and 2015 Bosa vintages and topsoil from two Bosa vineyards were studied by Sr-isotopic composition and trace element analysis. The preliminary results indicate a close correspondence between the $^{87}Sr/^{86}Sr$ ratio in wine (0.70843) and the Sr labile component in soil (0.70847), while the grape juice shows a slightly higher Sr isotopic composition (0.70872). Wine is characterized by relatively high Fe content (about 100 mg/L) and significant Mn and Ni content (about 1400 µg/L and 120 µg/L, respectively). The relatively high $^{87}Rb/^{86}Sr$ ratio measured in wine (12.7) is not coupled with a correspondingly radiogenic-Sr signature, as expected on the basis of the geological age of the bedrocks, suggesting that these features are inherited by soils, must and wine. These data contribute to explore the possibility of quality-wine production in high altitude vineyards and in the particular microclimate of Apuan Alps.

A comparative $^{87}Sr/^{86}Sr$ study on Red and White wines to validate its use as geochemical tracer for the geographical origin of wine

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Keywords: Red wine, White wine, geographical origin, strontium, food traceability, $^{87}Sr/^{86}Sr$.

The wine geographical traceability has gained importance in the modern society producing the need of valid scientific protocols able to trace geographic provenance of wines. A strict correlation does exist between the wine and its *terroir*. Stable isotopes of light elements are nowadays widely used to detect aroma and flavor sophistications in wines, but it now is clear their little reliability for defining exactly and directly the geographic traceability of wines because of their strong dependence upon local climatic and anthropic factors. In the last decades, isotopic ratios of heavy elements of geological interest, such as $^{87}Sr/^{86}Sr$, have gained interest in tracking regional provenance of foods and especially of wine. Recently high precision $^{87}Sr/^{86}Sr$ analyses have shown that Red wines keep the isotopic values of the vineyard substratum. Indeed, neither biological nor winemaking and aging processes are able to change the $^{87}Sr/^{86}Sr$ values through the oenological food chain from grapes to Red wine. In addition, $^{87}Sr/^{86}Sr$ of Red wines and those of rocks from the geological substratum of their vineyards correlate directly. Little isotopic studies were performed on white wines that might show minor sensibility to geographic traceability using $^{87}Sr/^{86}Sr$ due to their more complex wine-making procedure in which some geological additives are used to stabilize and clarify the final product. To fill this experimental gap $^{87}Sr/^{86}Sr$ has been determined for the entire production chain, from terroir to final product, of Red and White wines from the same winery. Sr-isotope data were also determined for the young pyroclastic rocks of the geological substratum, and the soil of the vineyards to disambiguate the original contribution to the $^{87}Sr/^{86}Sr$ values of wines. Further Sr-isotope data have been determined on additives used for fining the White wine. Our data further confirm that Sr-isotopic ratios of Red wines i) are constant through the different harvest years; ii) are not influenced by winemaking processes; iii) are strongly related to those of the geological substratum. The $^{87}Sr/^{86}Sr$ on White wines is showed, analogously to Red wines, that the winemaking process and the use of geologic additives, like bentonite, in the wine stabilization, and chalk in wine clarification and fining do not alter the Sr isotopic ratio acquired from the soil, confirming the applicability of the technique also on White wines.

$^{87}Sr/^{86}Sr$ isotopes in grapes of different cultivars used as a geochemical tool for geographic traceability of agriculture products

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Keywords: Sr isotopes, grapes, soil, traceability.

The increasing demand of high quality food products promoted the development of rigid regulations for certification of authenticity and protection from frauds. This is leading to an increasing request of suitable scientific protocols able to confirm the authenticity of food products by tracking their geographical origin. Respect to stable isotopic composition of light elements (H, C, O, N, B), the isotopes of heavy elements (Sr, Pb) have the advantage to correlate directly with the geological and pedological substrata of farms with no effects related with climatic variations. In the last decades, among the different food products, radiogenic heavy isotopes for tracing geographic provenance of wine was heavily investigated. These studies focused on finding relationships between the final product and their area of provenance, but none of them investigated in detail the possible differences in ^{87}Sr absorption from the bioavailable fraction of the soil by the different cultivars and vine genotypes. Here we present a detailed study on an extensive grape inter-varietal and site-specific study to implement the knowledge about vine geographical identification with Sr isotopes. $^{87}Sr/^{86}Sr$ of fresh red and white grapes, soils and rocks from three selected vineyards with similar but isotopically distinct geological substrata were determined. The research was performed on fruits from four consecutive harvest years on grapes of various genotypes from vineyards developing on three different geologic substrata. Results show that $^{87}Sr/^{86}Sr$ does not change through the years and reflects the one of the soil of production bioavailable fraction. Moreover its absorption from the soil is not influenced by the vine genotype/isotopic fractionation induced by the different vine genotype. These findings further demonstrate the reliability of this tool, even at a very small scale, for food products geographic origin assessment, being the strontium isotopic signature in grape exclusively acquired from the soil, and then strictly related to the local geology.

Session S24:

Emerging pollutants in the environment: a challenge for geochemistry and isotope-geochemistry

Conveners:

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Integrated approach to the assessment of Campania Plain water vulnerability

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Keywords: groundwater, hydrogeochemistry, modeling, pollution, radon, Campania Plain.

The desire of knowledge of what we drink and the growing awareness of what we eat, has more than ever put light on environmental issues related to the human health.

The Campania Plain (CP), the notorious land of fires, has been analysed through a new approach to the vulnerability that combines hydrogeology and environmental geochemistry tools to identify areas where safeguards and prevention measures are being implemented.

The CP represents a structural depression defined as a wide coastal belt that extends from the Volturno river plain to the Sarno river basin.

Its lithology consists in alluvial and pyroclastic deposits, deriving from stretching tectonics activity, that are based on deepest sedimentary units composed of carbonate sediments. CP deposits are interested by two distinct aquifer units, separated by the Campanian ignimbrite layer.

The deeper CP aquifer acts as a confined or semi-confined aquifer depending on the local continuity of ignimbrite layer and tectonic structures.

Instead, the shallow aquifer consists of unconfined and poorly sorted sand, clay and peat *(*Cuoco et al., 2015). To evaluate rock-water interrelation in aquifer have been realized 2,5*D* cross sections of CP in ArcScene software.

The CP can be considered as a natural laboratory to validate hydrogeochemical methods and models for its diffuse anthropogenic and geogenic pollution due to the interaction processes between natural water and rock.

The aim of this work is to evaluate CP groundwater quality through the application of a new model of integrated vulnerability assessment that incorporates hydrogeological and geochemical methods.

The interrelation between the two aspects is finalized to obtain a geomedic approach to the evaluation of CP contamination to have a relation between pathologies and contamination. Vulnerability charts have been realized through the application of modified Susceptibility Index (SI) method, implemented by introduction of parameters related to the class contamination and the demographic pressure. The next step of this work is to switch from vulnerability assessment to large scale risk assessment.

This work arises from a collaboration between the hydrogeochemical group of University of Sannio, the geochemistry group of University of Naples and the ABC Naples who manages the Neapolitan aqueduct. One of the aim of this collaboration is monitoring Radon gas in Neapolitan aqueduct waters. Radon contamination in Neapolitan water is due to geogenic factors; in fact numerous storage aqueduct tanks are located in volcanic rocks such as tuffs. The anomalous radon concentration founded in the water could be a human health problem, also considering the last 2013/59/EURATOM.

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Lead isotopes as tracers of toxic elements transfer from the environment to humans. A case of study in the Sarno river basin, south Italy

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Keywords: toxic metal, Pb isotopes, soil, human hair, stream sediment, water, lettuce.

Exposure to environmental pollution remains a major source of human health risk throughout the world, with children being the most vulnerable group. Associations between environmental pollution and health are complex and often poorly characterized. Levels of exposure are often uncertain or unknown as a result of the lack of detailed monitoring studies. Long latency times, the effects of cumulative exposures, and multiple exposures to different pollutants, which may act synergistically, together cause considerable difficulty in fully understanding the links between environmental pollution and human health.

The present study shows how a large detailed geochemical survey assesses pollutants in different environmental media and links that to levels in biological material. The use of Pb isotope ratios is valuable to assist with the identification of the main sources of contamination, and especially to discover whether and as such pollutants are transferred to humans.

This study was performed on various environmental media of the Sarno river basin (soil, stream sediment, groundwater, surface water, lettuce) and human hair.

The results show the distribution of potentially toxic elements is undoubtedly influenced by human activities. However, in many cases, the natural component for some elements seems to prevail compared to the anthropogenic component, due to the volcanic nature of the investigated area. The numerous industrial activities (mainly tanneries) have caused environmental contamination of especially Cr and Hg in soil and sediment samples. Such contamination is also evident in lettuce and hair of the resident population, which shows particularly high values for both Cr and Hg. This could cause serious problems for human health, especially for the inhabitants of the northeastern part of the basin. The high concentrations of Be and Sn are instead related mostly to the volcanic nature of the terrains of the investigated area. High concentrations of As and Cu are in part related to the volcanic nature of the study area; this is especially true for Cu, although they are undoubtedly also caused by intense agricultural activity. In fact vineyards, widespread along the slopes of Mt. Somma–Vesuvius, use Cu, Cr and As mixtures, to treat wooden posts, and could represent an additional source of metal contamination due to the leaching of metals from the posts to the ground. The high Sb, Pb and Zn values are certainly related to human activities (traffic, agriculture and industry), as demonstrated by the Pb isotope ratios, which demonstrate that most of the Pb present in the various environmental media, especially in lettuce and hair, is influenced by anthropic sources. The most important exposure risks within the study area are associated with Cr, Cu, Hg, Zn and Pb levels in topsoil and stream sediment, and the ingestion of locally grown lettuce. The high concentrations of these elements in hair are a further confirmation of this exposure pathway.

Potentially toxic elements distribution in the soil of Salerno urban area (Italy)

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Keywords: urban soils, background, baseline, toxic elements, geochemical maps, additive logratio (alr) transformation.

Among the most dangerous pollutants for human health, potentially toxic elements (PTEs) are certainly the most widespread and abundant in urban areas. Italian legislation set trigger and action levels, in addition to organic substances and compounds, for only a restricted number of inorganic elements (As, Be, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sb, Se, Sn, Tl, V and Zn). However, a geochemical survey cannot ignore other elements, even if national legislation does not consider them to be harmful. Hence, we analysed a much wider set of inorganic elements in order to properly assess and monitor the quality of the environment.

The paper discusses the results arising from a geochemical survey conducted in the Salerno urban area, where a total of 151 topsoil samples were collected and analyzed for 42 elements by ICP-MS and ICP-AES. Geostatistical analyses were carried out in order to show the single element geochemical distribution and the distribution of factor scores elemental associations from R-mode factor analysis. In performing factor analysis, the additive logratio (alr) transformation was applied to the whole dataset in order to deal with the closure effects of the investigated geochemical data.

In carrying out this survey, mapping of contaminant distribution was used to allow immediate appraisal of PTEs variability and to enable rapid identification of areas that may contain hazardous concentrations. This has been possible by means of the application of a mathematical approaches (multifractal-IDW, C-A and S-A methods) that allowed us to produce a more effective geochemical visualization cartography and to determine natural backgrounds and anomalies, proving their value in the field of environmental geochemistry.

The study revealed that major and minor elements (Al, Ca, Fe, K, Mg, Na, P, S, Ti) have a perfectly natural distribution with no discernible association to any human activity or presence. In contrast, many trace and ultra-trace elements (Ag, As, Au, Ba, Be, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Pd, Pt, Rh, Sb, Sn, Tl, V, Zn) show anomalous concentration values almost exclusively in the most inhabited areas, industrial sites and along high traffic roads, while others (B, Bi, Ga, La, Sc, Se, Sr, Te, Th, Tl, U, W) show concentrations compatible with the natural background levels.

The use of alr-trasformed data instead of the normal data in the factor analysis allowed a better interpretation of the distribution patterns having returned five factor models which, once mapped, were easier to interpret. The investigation allowed to determine, for each element, the distribution of concentration values on the territory and to define the natural background values for environmental purposes that will consent the adjustment of the existing legislation to the local situation, at least in terms of soil pollution levels. In fact the D.L. 152/06 states that trigger and action levels can be modified as a function of local known natural backgrounds.

Minor and trace elements distribution in hypothermal groundwater of north-western Sardinia: an environmental challenge

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Keywords: minor and trace elements, geochemical survey, hypothermal groundwater, north-western Sardinia, thermodynamic calculations, environmental challenge.

Concentrations of 25 minor and trace elements were determined in 15 groundwater collected throughout the north-western Sardinia island (Italy, western Mediterranean) with the aim to evaluate the element distribution and the origin of probable inorganic micro-pollutants. Sardinia island is part of the south European Variscan basement that during its geodynamic evolution was affected by variable degrees of metamorphism and intrusion of Carboniferous–Permian orogenic granites. The basement is overlain by Permian to Neogene sedimentary (mostly carbonate) and volcanic rocks mostly confined in basinal areas (Cuccuru et al., 2015). In north-western Sardinia basinal, as much as granitic areas, are affected by a well documented heat flow anomaly (Della Vedova et al., 1995) that gives rise to widespread hypothermal manifestations (T = 18-42°C). Two water groups were identified: the first one, associated with volcanic-dominated basins (VW), includes cold to hypothermal Na–HCO_3 waters characterised by high EC, CO_2, Na^+, Ca^{2+}, SO_4^{2-} contents; the second one, associated with the granitic basement (GW), comprises hot NaCl-rich waters with low EC values. Thermodynamic calculations performed using the geochemical modeling program Geochemist's Workbench® GWB® 8.0 (Betke, 2010), coupled with the thermodynamic database thermoddem (Blanc et al., 2007), show that, depending on temperature and log ($aCa^{2+}/a2H^+$) values, cold to hypothermal Na–HCO_3 water is in equilibrium with kaolinite whereas hot NaCl-rich water is in equilibrium with minerals of the zeolite group. Further, and in some cases, hypothermal Na–HCO_3 water may exceed the maximum admissible concentration for elements of some environmental concern including As, Fe, and Mn suggesting that a proper and detailed geochemical survey in the area is needed.

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Della Vedova, B., Lucazeau, F., Pasquale, V., Pellis, G., Verdoja, M. (1995): Heat flow in the tectonic provinces crossed by the southern segment of the European Geotraverse. Tectonophys., 244, 57-74.

Residues of chlorinated pesticides in the soils of the Campanian Plain (southern Italy) and health implications

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Keywords: chlorinated pesticides, soils, risk assessment, Campania Plain.

The environmental behavior and fate of organochlorine pesticides (OCPs) have recently become an area of focus because of their ubiquity, persistence, and bioaccumulation in the environment, as well as their high toxicity to humans and non-target organisms. A systematic grid sampling method and geostatistics were employed to investigate the spatial distribution, inventory, and potential ecological and human health risks of the residues of hexachlorobenzene (HCB) and chlorinated cyclodiene pesticides in soils of the Campanian Plain, Italy, and explore their relationship with the soils properties. One hundred and nineteen soil samples were collected between April and May 2011. The geometric mean (Gmean) concentrations of HCB and cyclodiene compounds followed the order CHLs (0.82 ng/g, sum of heptachlor, heptachlor epoxide, trans-chlordane, and cis-chlordane) > DRINs (0.62 ng/g, sum of aldrin, dieldrin, and endrin) > SULPHs (0.57 ng/g, sum of α-endosulfan, β-endosulfan, and endosulfan sulfate) > HCB (0.22 ng/g). The residual levels of most cyclodienes in agricultural soils were generally higher than those of corresponding counterparts in the other land uses. Agriculture is a significant source of chlorinated cyclodiene pesticides. Significant differences in the concentration of HCB and cyclodienes in the soils across the region are observed, and the Acerra-Marigliano conurbation and Sarno river basin areas exhibit particularly high residual concentrations. Some legacy cyclodienes in the Campanian Plain may be attributed to a secondary distribution. The Gmean inventory of HCB, SULPHs, CHLs, and DRINs in the soil is estimated to be 0.081, 0.41, 0.36, and 0.41 metric tons, respectively. The non-cancer and cancer risks of HCB and cyclodienes for exposed populations are deemed essentially negligible. The Italian environmental law D. Lgs.152/06 does not involve endosulfan, however, we identified a potential ecological risk caused by endosulfan in soil, which, when considered along with the continued localized use of endosulfan, should attract attention from authorities.

Geochemical and Pb isotopic characterization of the Domizio Flegreo and Agro Aversano area (Campania region, Italy)

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Keywords: environmental geochemistry, pollution, potentially toxic metals, isotopic analysis, lead.

The Domizio Flegreo Littoral and Agro Aversano area covers 1287 km^2 and includes 90 municipalities. Nowadays, the total population is about 1,300,000. Morphologically, it includes part of Campania Plain which is surrounded by the Mesozoic limestones of the southern Apennines (N and E), the Roccamonfina volcano (N), the Somma-Vesuvius volcano (SE), the Phlegrean Fields volcanic area (SW) and the Tyrrhenian Sea (S and W). Across this area, agriculture (tobacco, potatoes, corn) and farming represent one of the most important economic activities. Moreover, many industries are also present such as a production branch of FIAT (a worldwide famous automotive industry) and the Montefibre plant (producing polyester fibers) within the administrative boundaries of the Acerra municipality. In the same municipality an urban waste treatment incinerator operates since 2009, as well. In the whole territory, unfortunately, illegal waste disposal and burning practices are also quite diffuse. A thorough geochemical environmental study focused on topsoil, groundwater, vegetable (corn) and human hair samples has been carried out in this area. The research is based on 1064 topsoil samples, 27 groundwater samples, 24 samples of human hair and 13 corn samples taken across the study area. Although samples were analysed for 53 elements at Berau Veritas Analytical Laboratories (Vancouver, Canada) by means of ICP-MS and ICP-ES after an aqua regia digestion, we focused on 15 key elements (As, Be, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sb, Se, Sn, Tl, V and Zn). All the data have been statistically treated and dot, interpolated and hazard maps have been produced by means of the GeoDAS, a geochemical oriented GIS software. In general, Cu, Pb, Hg, Sb and Zn resulted to be the most critical pollutants for the area. Furthermore isotopic analyses have been carried out at the Radiogenic Isotope Laboratory of U.S. Geological Survey (Reston, VA, USA) on a selection of the available samples. They were analysed using an HR-ICP-MS and a FinniganMat (Spectromat) spectrometers and the results show that Pb in our samples comes mostly from anthropogenic activities (aerosols, fly ash and gasoline) with a geogenic influence due to Mts. Vesuvius and Roccamonfina volcanics and aerosols.

The role of atmospheric pollutants in the assessment of Air Quality Index in the middle of Irpinia (Campania, Italy)

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Keywords: air pollutants, air quality index, tropospheric ozone, Irpinia, Italy.

In the framework of the project “SOS Climate" performed by a class of students attending the Aeclanum High School in Mirabella Eclano (Italy), a daily pollutant survey was conducted by processing the data from monitoring stations available on web. This performance has been driven in the data collection phase as well as in the preliminary processing by researchers of the Sannio University. Subsequently these researchers have been checked data and discussed in depth the results in order to establish the rule of atmospheric pollutants in the assessment of Air Quality Index (AQI) of the investigated territory.

Monitoring stations are located in the middle area of Irpinia in Campania (Italy). Their distribution permit to cover at least 1258 square kilometers. The range time of survey is from November 2016 to April 2017. The measured parameters concerned the carbon monoxide (CO), nitrogen dioxide (NO_2), sulfur dioxide (SO_2), ozone (O_3) and particulate matter (PM_{10} and $PM_{2.5}$). Such pollutants are usually included in the definition of the air quality, as they have short-term effects causing the most serious problems for human health. Therefore, the AQI has been defined in order to evaluate synthetically the air quality level. In agreement with several agencies, this index was calculated on the basis of the daily concentrations of three major pollutants: NO_2, O_3, PM_{10}. The calculation excludes CO and SO_2 that in the last decades have concentrations widely below the legal limits.

The AQI calculation has shown that for most stations the values fall into the first three classes (very good, good and acceptable) to indicate that no pollutant has exceeded the limits imposed. The difference between the AQI classes depends on how much the concentration deviates from the limit value. In this respect it is noted that there are a good number of stations which recorded a very good index throughout the period. This indicates that all pollutants are present in concentration equal to or less than half the limit value. For the rest of the stations there is a slight worsening in March and April of the class, though remaining close to the limits. Only in two stations concentrations of pollutants fall into the mediocre and poor classes, indicating up to two times the limit value. More specifically, the pollutant responsible to this attribution is the O_3 that at ground level in high concentrations can cause harmful effects on the human health. Ozone is a secondary pollutant since it originates in the air from the reaction of primary pollutants favored by particular climatic conditions such as strong solar radiation and high temperature, or presence of high pressure and low ventilation. In this case, having analyzed the "coldest" months, the second hypothesis seems to be more appropriate to explain the recorded values for areas with the worst air quality. The primary source of pollutants is an important highway and a significant industrial concentration.

Lead isotopes in biological matrices to identify potential sources of contamination: the case study of Sulcis-Iglesiente district (SW Sardinia, Italy)

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Keywords: lead isotope ratios, human biomonitoring, mining district, environmental geochemistry.

The Sulcis-Iglesiente district has been, until recently, one of the most important Italian polymetallic mining areas for the extraction of lead. Located close to the town of Iglesias, the San Giorgio area constitutes a dramatic example of an area affected by intense mine pollution.

Epidemiological studies regarding the mining areas of Sardinia have indicated the Sulcis-Iglesiente as a typical example of how dispersion of metal can affect human health.

We have chosen this peculiar area to evaluate whether a supposed prolonged and continuous exposure to high lead concentration can be detected by means of a bio-monitoring procedure that uses the analysis of human scalp hair and the measurement of lead isotope ratios.

Total lead concentrations in 144 human scalp hair samples from adolescents (11–13 years old) belonging to both genders, along with 23 lead isotope analyses in hair samples from Sant'Antioco (10 samples), Iglesias (10 samples) and roadway dust (3 samples) are discussed here.

The hair database consisted of two groups of samples:

1) Iglesias group (IG) consisting of 59 subjects (32 females and 27 males). The town of Iglesias is located near the mining–waste of San Giorgio area. Other potential local pollutants are limited to emissions from vehicular traffic.

2) Sant'Antioco group (SAN) containing 85 cases (52 females and 33 males). The area of Sant'Antioco Island is not affected by intense mine activity and the pyroclastic volcanic rocks, outcropping in this site, are not characterised by metal mineralisation events.

Three road dust samples were collected; two close to the mining area, more precisely one at Monteponi (RD_{MT}), and another one within the urban area of Iglesias (RD_{IG}) and a third sample was collected at Sant'Antioco, an area affected by industrial activities.

Pb concentrations of adolescents living at Iglesias resulted higher than those of adolescents living at Sant'Antioco (median values Pb_{IG}: 1.56 µg/g and Pb_{SAN}: 0.30 µg/g, respectively). The influence of gender did not play any significant role. Hair from children living in Sant'Antioco exhibited lead isotope ratios in the ranges 1.152 – 1.165 for $^{206}Pb/^{207}Pb$ and 2.101 – 2.108 for $^{208}Pb/^{206}Pb$, while hair samples from Iglesias resulted less radiogenic: $^{206}Pb/^{207}Pb \sim 1.147–1.154$ and $^{208}Pb/^{206}Pb \sim 2.106 – 2.118$. These values pointed to a multi-source mixing between the less radiogenic sources, corresponding to the Pb ore deposits, and the more radiogenic sources identified in local background.

These data confirm the real danger of mine wastes in relation to lead exposure of subjects living near the mining sites of Sardinia. We suggest a continuous control of the level of Pb and other metals in the inhabitants of the cities of Iglesiente. Finally, although in the past some doubts have been raised about the use of lead isotopes to identify potential sources of contamination in biological matrices, the data obtained confirm that the lead isotope method remains a powerful technique.

Geochemical mapping and Pb isotopic signatures of geogenic and anthropogenic sources in three localities in SW Spain with different land use and geology

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Keywords: lead isotopic signature, ICP-MS, Iberian Pyrite Belt, geochemical mapping.

The Huelva Province, located in the southwest of Spain, has been submitted to intense anthropic activities, like mining, industry and agriculture. These anthropogenic activities have a potential environmental impact, with the dispersion of chemical elements in the environments and with possible negative effects on the human health. In this study, the concentration of harmful chemical elements in the soil of three case study areas of the Huelva Province have been analyzed and related with the land use and local geology. These study areas correspond to the agricultural Aroche village, El Campillo mining site and urban and industrial town of Huelva. Topsoil samples have been collected and analyzed by ICP-MS. The analytical results have been used to calculate geochemical maps for As, Cd, Co, Cr, Cu, Hg, Ni, Pb and Zn. Also, lead isotopic analysis of selected topsoil samples have been performed, to identify the geogenic and anthropogenic origin of the geochemical anomalies detected in the three study areas. Similarly, human hair samples of donators living in these areas have been analyzed for lead isotopes, to trace the diffusion of selected chemical elements through the trophic chain. The study shows that anomalies of harmful elements are present in the topsoil of the three areas, even in the rural Aroche site, where neither industrial nor mining activities occur. The spatial distribution of these geochemical anomalies is associated to the local geology and land use. Lead isotopic analysis evidenced two clear signatures in the topsoil and human hair samples. The first signature, defined by the topsoils with medium-high concentration of lead, corresponds to the isotopic trend of samples collected where ore deposits and mining activity occur. The second signature, defined by the topsoils with low-medium concentration of lead, corresponds to pesticides and gasoline lead sources.

Arsenic: geochemical distribution and human health risk in Italy

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Keywords: arsenic, human health risk assessment, geochemistry, drinking water, Italy.

Characterization of risks to human health is determinant for risk management and population surveillance. This study represent the first work at national scale for Italy about arsenic occurrence, distribution and human health impact. We analyzed the As geochemical distribution in different environmental matrices on the whole Italian territory, and assessed both carcinogenic and non-carcinogenic risks for different exposure routes and age groups. Geochemical mapping provided a useful tool to distinguish different geochemical distribution patterns and highlight areas hosting As geochemical anomalies. Our results show that many critical areas in Italy are characterized by As levels exceeding the regulatory limits both for soil and water. Its presence is mainly controlled by geological processes and locally reflects the industrial history of the Country. The population of the central Italy, where high content of arsenic in the analyzed samples is due to the presence of alkaline volcanics, are the most exposed to the health risk. Based on the results of our work, it is clear that the consumption of tap water (characterized by As levels up to 27.2 µg/L) for potable use is the most impactful route for As daily exposure and plays an important role in governing both cancer and non-cancer risks for the considered population. It is interesting to observe that more than 80% of the analysed water samples is responsible of an Incremental Lifetime Cancer Risk through water ingestion higher than the benchmark value of 1×10^{-5}. Most of these As concentration levels are lower than the current As standard level for drinking water (10 µg/L). Moreover it is shown that childhood is the most susceptible age stage to As exposure. What could it mean? Should we review the As standard level for drinking water? Meanwhile the debate about low-dose exposure is ongoing, D'Ippoliti et al. (2015) provides new evidence that even arsenic concentrations below the EU limit (10 µg/L) can raise mortality risks. On these basis, our study suggests that further researches should be directed to anchor low-dose arsenic exposure and induced human disease in several areas of Italy. Urgently policy actions are needed and the return on the investment could be substantial.

D'Ippoliti, D., Santelli, E., De Sario, M., Scortichini, M., Davoli, M., Michelozzi, P. (2015): Arsenic in drinking water and mortality for cancer and chronic diseases in Central Italy, 1990-2010. PLoS ONE, 10, e0138182.

Topsoil geochemistry exploration through compositional data analysis and C-A fractal model

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Keywords: soil geochemistry, Campania region, geochemical anomalies, log-ratio transformed data, compositional biplot, C-A fractal model.

Campania region (southern Italy) is characterized by several geochemical anomalies both geogenic and anthropogenic. Parts of these anomalies occur into the World Heritage Territory known as "National Park of the Cilento and Vallo di Diano", where this follow-up study has been carried out. Sometimes the natural relationships that govern the elements distributions are masked by overlapping of different phenomena. Here we propose a methodology based on compositional data analysis (CoDA) and factor score C-A fractal model in order to identify geochemical signatures associated anomalies. Eighty-one topsoil samples were collected over an area of 98 km², and analyzed by ICP-MS after aqua regia digestion. Frequency based method (edaplots, classical and robust compositional biplot) and frequency space-method (factor score maps) were applied to visualize the relationships between variables.The different geochemical patterns were distinguished by a multivariate analysis combined with Concentration-Area (C-A) fractal method. Results show that geochemical data should be transformed under a compositional perspective to avoid artefacts, prior to statistical computations. Indeed, ilr-transformed data show a distinct bimodal distribution for several elements. This type of distribution appears masked considering raw and lognormal data. A "robustification" of the variables dataset permits to found a more clear relationship between variables. Factor analysis based on ilr-transformed variables, has allowed us to distinguish the main phenomena controlling the elements association distribution pattern. A three-factor model accounting for 70.1% of total data variability has been chosen. Factor scores maps based on ilr-transformed variables and C-A plot cut off threshold displayed various geochemical signatures of distinct processes. In our survey area soil alteration phenomena could mask the nature of parental rock. The factor scores maps highlight an antithetic behavior of many elements. Elements characterized by elevated geochemical mobility, such as Ca and Mg, are negatively correlated with Chemical Alteration Index values. Instead, Sn, Th, Be, Al are characterized by elevated geochemical stability; for this reason they are found where high-weathered soils occurs. The elemental association of Co, Cu Fe, Ni, Cr, Zn, K, Mn is mainly controlled by terrigenous flysch deposits and reflects adsorption and co-precipitation by Fe and Mn oxy-hydroxides in oxidizing environment. Arsenic, Pb (exceeding the contamination thresholds established by Italian legislation for soils) and Sb association is related to anthropogenic footprint and is highlighted in correspondence of urban areas and where traffic jams are frequent. According to our results and observations, the proposed method demonstrates to be a useful tool to recognize signatures of different geochemical processes, highlighting additional phenomena which would normally be masked.

Session S25:
Geological carbon cycle

Conveners:

Carlo Cardellini (Univ. di Perugia)
Giovanni Chiodini (INGV, Napoli)
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Carbon fluxes from subducted carbonates revealed by U isotopes at Vesuvius

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Keywords: U isotopes, U-Th disequilibria, subduction, carbon fluxes, Vesuvius volcano.

The fate of carbonate-rich sediments recycled at destructive plate margins is a key issue for constraining the budget of deep CO_2 supplied to the atmosphere by volcanism. Experimental studies have demonstrated that metasomatic fluids/melts can be generated by decarbonation or partial melting of subducted carbonate-pelitic sediments, but signatures of the involvement of such components in erupted magmas are more elusive. We performed new U-Th disequilibria and high precision $\delta^{238}U$ analyses on Vesuvius lavas showing that the measured ^{238}U-excesses require a mantle source affected by the addition of U-rich carbonated melts generated by partial melting of subducted calcareous sediments in the presence of residual epidote. The presence of ^{238}U-excess is anomalous in "sediment-dominated" arc magmas, but it is not unique of Vesuvius volcanoes, with similar characteristic occurring for example in the Lesser Antilles or Sunda arc. Accordingly, we argue that the occurrence of ^{238}U-excesses in 'sediment-dominated' arc magmas represents unique evidence of addition of carbonate sediments via subduction, hence providing constraints on the deep carbon cycling within Earth. In addition, we combined a quantitative mantle enrichment model with published experimental results, in order to provide an estimate of the flux of CO_2 resulting from the subducted carbonates to the mantle source of the Vesuvius and eventually back to the surface, yielding values ranging between 0.2 and 0.8 Mt/y.

A review on CO_2 fluxes from diffuse degassing in Italy

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Keywords: CO_2, Earth, degassing.

Central and southern Italy are affected by an active and intense process of CO_2 Earth degassing from both active volcanoes, and tectonically active areas. Regional scale studies, based on carbon mass balance of groundwater of regional aquifers in not volcanically active areas, highlighted the presence of two large CO_2 degassing structures that, for magnitude and the geochemical-isotopic features, were related to a regional process of mantle degassing. Quantitative estimates provided a CO_2 flux of ~ 9 Mt/y for the region (62,000 km^2). Besides the magnitude of the process, a strong link between the deep CO_2 degassing and the seismicity of the region and a strict correlation between migration of deep CO_2-rich fluids and the heat flux have been highlighted.

Central and southern Italy is also characterised by the presence of many cold gas emissions sites where CO_2-rich gases are released by vents and soil diffuse degassing. Both direct CO_2 expulsion at the surface and C-rich groundwater are different manifestations of the same process, in fact, the deeply produced gas can be dissolved by groundwater or emitted directly to the atmosphere depending on the gas flux rate, and the geological-structural and hydrogeological settings Quantitative estimations of the CO_2 fluxes are available only for a limited number (~ 30) of the about 270 catalogued gas manifestations allowing an estimations of a CO_2 flux of ~1.4 Mt/y suggesting that the contribution from cold gas emission may be significant but far to be reliably defined.

Summing the two estimates the non-volcanic CO_2 flux from the region results globally relevant, being from 2 to 10% of the estimated present-day global CO_2 discharge from subaerial volcanoes. The quantification of diffuse CO_2 degassing, not associated to active volcanoes, in central and southern Italy points out the relevance of non-volcanic CO_2 degassing in tectonically active areas and of soil diffuse degassing from volcanoes, suggesting that the actual underestimation of the CO_2 Earth degassing at global scale, may arise also from the lack of specific and systematic studies of the numerous "degassing areas" of the world, that would contribute to better constrain the global CO_2 budget.

Microbial methane oxidation leading to extreme isotopic fractionation in thermal springs of central Greece

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Keywords: geothermal gases, methanotrophy, stable isotopes.

The Greek territory belongs to the geodynamically active Alpine-Himalayan orogenic belt. As such, it shows intense seismic activity, active volcanic systems and areas of enhanced geothermal fluxes. One of these areas is the Sperchios basin and the northern part of Evia island in central Greece, which present widespread thermal manifestations (D'Alessandro et al., 2014). Five of them with temperatures from 33 to 80°C present bubbling gases whose dominating species are either CO_2 or N_2. All gases contain from 27 to 4000 ppm of CH_4. The isotopic composition of CH_4 in these gases covers a wide range with $\delta^{13}C$ values ranging from -21.7 to +16.9 ‰ and $\delta^{2}H$ values ranging from -124 to +301 ‰.

The hottest manifestation displays the lowest isotopic values within the typical range of volcanic and geothermal systems. All the remaining samples fit a methane oxidation trend reaching very positive values. If we consider the lowest values as the deep hydrothermal marker the obtained $\Delta H/\Delta C$ values range between 5 and 13 which are close to those typical of microbially driven oxidation (Kinnaman et al., 2007).

Although the outlet temperature of the hottest manifestations is at the upper limit for methanotrophic microrganisms (Sharp et al., 2014), we can hypothesize that environmental conditions are not favorable for their survival at this site while they can thrive in the other, strongly consuming methane and producing very positive isotopic values.

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Light hydrocarbons as a proxy to identify the origin of the gas manifestations in Greece

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Keywords: gas geochemistry, stable isotopes, light hydrocarbons.

The geologic emissions of greenhouse gases (CO_2 and CH_4) have an important natural contribution in the global carbon budget. Tectonics, through faults in geothermal and oil producing areas, play a significant role in the release of C-gases in many non-volcanic regions of the Earth. Methane, the most abundant organic compound in Earth's atmosphere, has a potential global warming that is 28 times higher than that of CO_2 on a 100-year time horizon. In this study, $\delta^{13}C$-CH_4, δ^2H-CH_4 and light hydrocarbon (alkane: CH_4, C_2H_6, C_3H_8, C_3H_6, i-C_4H_{10}, n-C_4H_{10}; alkene C_3H_6, i-C_4H_8; and aromatic C_6H_6) gas concentration data of 119 gas samples (103 unpublished data and 16 literature data) from volcanic-hydrothermal, geothermal and cold discharges are used to shed light on the genetic processes that have formed CH_4 in the complex geodynamic setting of Greece. On the basis of the spatial distribution of the gas discharges and their type of emission, the whole dataset was subdivided into 4 main "domains", as follows: 1) Volcanic Arc (VA); 2) External Hellenides (EH); 3) Internal Hellenides (IH); 4) Hellenic Hinterland (HH). Almost each group is characterized, as long as subdivided, in 3 groups based on the type of emission (on-land free or dissolved gases and submarine gases) and a 4th group includes literature data. Concentrations of CH_4 range from < 2 to 925,200 µmol/mol and its isotopic ratios cover a wide range ($\delta^{13}C$ from -79.8 ‰ to +45 ‰; δ^2H from -311 ‰ to +301 ‰) indicating the different primary sources and the secondary post-genetic processes (oxidation) that can significantly affect the origin of this gas compound. Hydrocarbons in the CH_4-dominated gases discharged from the EH are showing a clear biotic origin. In particular, those collected in the Gavrovo-Tripolis zone are showing a dominating biotic origin, whereas it is also noticeable that some gas samples of the Ionian zone are produced by both microbial activity and thermal maturation of sedimentary organic matter. The CO_2-dominated gas discharges from the main geothermal systems of the IH and from the VA most likely predominantly contain abiogenic CH_4 deriving from CO_2 reduction. However, some of the gas discharges of the geothermal and volcanic-hydrothermal systems located in the neritic sedimentary Pelagonian, Gavrovo-Tripolis and Attico-cycladic zones (IH) and in Rhodope massif (HH), seem to exhibit significant contributions from thermogenic sources. The presence of abiotic methane was also recognized in the hyperalkaline aqueous solutions that are issuing from the ophiolites of Othrys and Argolida (Pindos zone (EH)). Most of the geothermal gases of Subpelagonian and Vardar/Axios zones (IH), the cold manifestations of the Rhodope massif (HH) and some of the volcanic-hydrothermal ones of the Attico-cycladic zone (VA) are presenting a microbial oxidation of CH_4.

Chemical weathering and CO_2 consumption at mid latitudes

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Keywords: weathering, carbon, runoff.

Carbon is continuously cycled among oceans, atmosphere, ecosystems and geosphere, and the processes by which C moves through the Earth's reservoirs take place on very different time scales. The short-term C cycle includes processes that transfer C from one reservoir to another in a matter of years, including photosynthesis, biota respiration, and the CO_2 exchange across the air-sea interface. Other processes, such as C transport to the Earth mantle through subduction, and its subsequent release by fluids and melts, occur on a timescale of > 0.1 My and constitute the so called longterm, or geological, C cycle. In the geological C cycle, the C budget of Earth's atmosphere is largely controlled by the relative fluxes of CO_2 consumed by chemical weathering *vs.* CO_2 degassed by metamorphism and magmatism (Berner et al., 1993; Kerrick & Caldeira, 1998). Chemical weathering is a key process for understanding the global carbon cycle, both on long and short-terms, and chemical weathering rates are complex functions of several factors including dissolution kinetics of minerals, mechanical erosion, lithology, tectonics, biota, hydrology and climate. Solutes produced by chemical weathering on the continents are carried to the oceans by rivers. Therefore, the composition of river water is a good indicator of chemical weathering processes (Gaillardet et al., 1999; Donnini et al., 2016), and the flux of solutes is an indirect measure of the transfer of carbon from the atmosphere to the terrestrial rocks. In this work the main factors controlling weathering rates at mid latitudes are studied through the mass balance of solutes dissolved by river waters, both in large regional hydrologic basins and in small mono-lithological basins. Results show that the main factors controlling weathering and consumption of atmospheric CO_2 are runoff and bed rock lithology. In particular, depending both on climatic and geologic variables, runoff acts as a "summing factor" at least in climatically homogeneous regions, and its role in modelling both the long term and the the short-term carbon cycles and climate should be carefully considered.

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Mineralogy of the soils altered by fumarolic activity at Nisyros volcano, Greece

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Keywords: gas geochemistry, stable isotopes, light hydrocarbons.

Nisyros is the easternmost island of the South Aegean Active Volcanic arc in Greece. It is an active stratovolcano known for its intense hydrothermal activity. In this study we present the results of the mineralogical analyses of 20 soil samples collected in the caldera area. Samples were analysed through X-ray diffraction and the results allow us to divide them in two groups: Lakki Plain and Stefanos Crater. In their majority the soils of Lakki Plain have a main mineralogical assemblage that consists of quartz, feldspar and gismondine ($Ca_2Al_4Si_4O_{16}\cdot 9H_2O$). Gismondine as well as stellerite ($CaAl_2Si_7O_{18}\cdot 7H_2O$), which is appearing in some samples, derive from hydrothermal alteration, whilst wollastonite ($CaSiO_3$) is also found as a product of thermally metamorphosed siliceous carbonates. In the Stefanos Crater soils, due to the acid environment and the relatively high temperatures of the fumaroles (about 100°C), the main assemblages mostly comprises hydrothermal alteration minerals like quartz, sulfur, wollastonite, gypsum and gismondine. The lower amount of feldspars with respect to the Lakki Plain soils can be justified by the high percentage of gismondine, their alteration products. Voltaite ($K_2Fe(II)_5Fe(III)_3Al(SO_4)_{12}\cdot 18H_2O$) was also found in some of the samples as a product of hydrothermal alteration of Si deposits. Close to the fumaroles, the occurrence of alunogen ($Al_2(SO_4)_3\cdot 17H_2O$), a sulphide alteration mineral found in fumarolic environments, is also noticeable.

Cold subduction and long-term carbon cycle: insights from geophysical and petrologic data sets from the Alpine region

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Keywords: Alpine subduction, carbon storage.

The long-term carbon budget of planet Earth is largely controlled by the balance between carbon outgassing to the atmosphere and carbon ingassing to the Earth interior during subduction (*e.g.*, Dasgupta & Hirschmann, 2010; Kelemen & Manning, 2015). Carbon ingassing strongly depends on the petrology of subduction (Rohrbach & Schmidt, 2011) and on a range of processes, taking place in the downgoing slab and in the supra-slab mantle, that are only partly understood. Seismic velocity anomalies in the upper mantle may reflect small amounts of melt, and laboratory experiments indicate that melting can be favoured by the presence of carbonate. Although carbonate minerals, graphite, diamonds and carbon-rich fluid inclusions are indeed described in mantle wedge peridotites exhumed at Earth's surface, *in situ* evidence of carbon capture and release is still poorly documented in the upper-mantle depth range. In order to shed light on this issue, we revise here the available geophysical and petrologic constraints from the Alpine subduction zone and the overlying Adriatic upper mantle, within the framework of recent geodynamic reconstructions of the Adria-Europe plate boundary area. We examine the evidence of potential fluid release from the downgoing slab during Alpine subduction, as documented by exhumed slivers of ultra-high pressure rocks, and integrate these observations with predictions of computational thermal models to infer the metamorphic evolution of the Alpine slab at asthenospheric depth, and the potential impact of released fluids on the supra-slab upper mantle. The resulting scenario is compared with the velocity structure unravelled by seismic tomography models, and the potential implications for the long-term carbon cycle on a more global scale are finally discussed.

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The deep carbon cycle in collisional orogens: a petro-chronological approach to understand and quantify metamorphic CO_2 producing processes

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Keywords: calc-silicate rocks, metamorphic CO_2-production, Himalayan orogeny, U-Pb geochronology, deep carbon cycle.

Metamorphic degassing from active collisional orogens supplies a significant fraction of CO_2 to the atmosphere, playing a fundamental role in the long-term (> 1 Ma) global carbon cycle (Gaillardet & Galy, 2008). The petro-chronologic study of the CO_2-source rocks (*e.g*., calc-silicate rocks) in collisional settings is therefore fundamental to understand the nature, timing, duration and magnitude of the orogenic deep carbon cycle. So far, the still incomplete knowledge of these systems hindered a reliable quantitative modelling of metamorphic CO_2 fluxes from collisional orogens.

Phase relations and devolatilization reactions that occurred in high-grade clinopyroxene + scapolite + K-feldspar + plagioclase + biotite + zoisite + titanite ± calcite calc-silicate rocks from central Nepal Himalaya are investigated in the complex NKC(F)MAST-HC system. The equilibria involving plagioclase and scapolite Na-Ca solid solutions, as well as biotite Mg-Ti-(Fe) solid solution are investigated using: (i) $P/T\text{-}X(CO_2)$ pseudosections, (ii) $P/T\text{-}X(CO_2)$ phase diagram sections and (iii) mixed-volatile $P\text{-}T$ phase diagram projections. Detailed petrological modelling allows us to identify and to fully characterize-for the first time-different metamorphic reactions leding to the simultaneous growth of titanite and the production of CO_2. These reactions involve biotite as the Ti-bearing reactant counterpart of titanite. The results of petrological modelling combined with Zr-in-Ttn thermometry and U-Pb geochronology suggest that in the studied sample, most titanite grew during two nearly consecutive episodes of titanite formation: a near-peak event at 730-740°C, 10 kbar, 26 ± 2 Ma and a peak event at 740-765°C, 10.5 kbar, 22 ± 3 Ma.

$T\text{-}t$ data from different titanite generations are correlated to specific CO_2-producing reactions, thus allowing to constrain the timing, duration and $P\text{-}T$ conditions of the main CO_2-producing events, as well as the amounts of CO_2 produced. Such short-lived pulses of CO_2 release could have affected the past climate, possibly accounting for brief warming events.

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Carbonate metasomatism in the lithosphere beneath El Hierro (Canary Islands): ùnew insights on carbon mobilization from deep mantle xenoliths

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Keywords: mantle xenoliths, metasomatism, carbonatite.

Mantle xenoliths from El Hierro (Canary Islands), which comprise spinel lherzolites, harzburgites and dunites, have been investigated to characterize the fluxes of carbon in an intraplate oceanic-island setting. Ultramafic xenoliths were collected from a basaltic lava flow located in the El Julan Cliff Valley. Protogranular to porphyroblastic cpx-poor lherzolites and harzburgites were analyzed by electron microprobe for major elements and by laser-ablation ICP-MS for trace element analyses.

The major metasomatic modification is represented by the appearance of high-Si glass + carbonate ± sulphate micro-veins and patches. Melts show variable SiO_2 contents ranging from 58.9 to 68.6 wt.% and Mg# [= 100*(Mg/Mg+Fe)] comprised between 40.1 and 63.9. Carbonates are Mg-calcites (MgO up to 6.4 wt.%), observed in veins and included in olivine crystals. Multiphase inclusions containing CO_2, Mg-calcite, dolomite, anhydrite, sulphohalite, apatite and Cr-spinel were also identified and characterized through Raman spectroscopy.

These pieces of evidence suggest that peridotites were infiltrated by a carbonate-sulphate-silicate rich melt, in particular, we propose a model whereby carbonatitic melts produced by partial melting of a carbonated eclogite metasomatize the peridotite. As shown by several experimental studies (*e.g.*, Kiseeva et al., 2012), the partial melting of a carbonated eclogite generates a Si-rich melt, which coexists with an immiscible carbonate melt. Our model agrees with evidence from experimental petrology (*e.g.*, Dasgupta et al., 2004) and mineral chemistry analyses (Sobolev et al., 2005), which proposed that melts derived by partial melting of pyroxenite or eclogite layers could migrate and react with the overlying peridotite, leading to the generation of a refertilized lithosphere.Moreover, the HIMU signature in OIB basalts from El Hierro (Day et al., 2009) seems to confirm the presence of a recycled oceanic crust in the lithosphere beneath the island.

Carbonatitic melts generated by eclogite partial melting can therefore contribute in the mobilization of carbon in the lithospheric mantle, suggesting that also in intraplate regions the fluxes of carbon can be significant and should be considered in the global deep carbon budget.

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Is the CO_2 content of subduction-zone fluids higher than previously thought?

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Keywords: COH fluids, subduction zones.

Subduction of the oceanic lithosphere and its sedimentary cover is accompanied by devolatilization processes. CO_2 removal through dissolution of carbonates occurring in altered oceanic lithosphere and its sedimentary cover, along with diapirism of slab rocks and/or melts, provides an efficient way to recycle carbon back to the mantle wedge and, ultimately, to the Earth's surface. However, other forms of carbon, often closely associated with silicates, have been reported in slab rocks and in particular in subduction mélanges. Graphite has been considered to represent a refractory sink of carbon in the subduction slab, owing to its lower solubility in aqueous fluids compared to carbonates. On the other hand, graphite dissolution mechanisms and solute transport in complex COH fluids at high pressure have remained experimentally unconstrained. Moreover, recent thermodynamic models suggest that the presence of graphite is capable of modifying fluid properties and promoting the formation of C-bearing anions, possibly enhancing the complexation of major and trace elements at elevated P and T conditions.

In this study we provide comprehensive experimental constraints on the CO_2 content of high-pressure graphite-saturated COH fluids in increasingly complex model systems at controlled redox conditions (double-capsule technique, using both the nickel-nickel oxide (NNO) and the fayalite-magnetite-quartz buffers (FMQ)), in order to develop a model for the interaction between deep aqueous fluids and silicate-rich subduction mélanges. A carbonate-free compositional range has been explored at $P = 1$ GPa, $T = 800°C$ and $P = 3$ GPa, $T = 800°C$ in order to focus on the role of graphite and silicates in the investigated processes. We synthesized COH fluids in equilibrium with amorphous carbon and crystalline graphite, adding other minerals representative of subduction mélanges, *i.e.*, Mg-silicates (forsterite and enstatite), representative of the mantle component, and quartz, representative of the sedimentary component. Experimental products were analyzed for their COH volatiles by piercing the capsules after quench in a gas-tight vessel and then conveying the emanating gases to a quadrupole mass spectrometer (QMS). Measured data were compared to thermodynamic models. Our results point to the roles of amorphous carbon and of the silica component derived from the dissolution of either magnesium silicates or quartz/coesite alone, even in absence of carbonates, as being able to control the composition of deep COH fluids, in particular enhancing their CO_2 content. This mechanism could be effective especially in subduction mélanges, where silicates and organic matter are thought to be abundant and flushed by aqueous fluids coming from the dehydration of the subducted lithosphere.

Geosphere-biosphere interaction in extreme environments: microbial life's capability of shaping VOCs emissions from the soil in the Solfatara Crater (Campi Flegrei, southern Italy)

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Keywords: VOCs, solfataric fields, soil gases, extremophiles, microbial communities.

Volcanic and hydrothermal areas represent extreme environments, being affected by high-temperature and low-*p*H fluid emissions. Microbial life develops in such a harsh and spatially rapidly changing environment, affecting and being affected by the local geochemical conditions. Whilst efforts have been made to investigate the interaction between biotic and abiotic factors in deep-sea hydrothermal vents, with relevant implications for the origin of life on early Earth, the occurrence and extent of interplay between microbial communities and hydrothermal fluids in continental solfataric fields are still poorly understood.

Solfatara Crater (Campi Flegrei, Italy) represents a perfect natural laboratory to study the relationship between extremophilic microbial communities and CO_2-rich fluids uprising from deep hydrothermal reservoirs. Here, microbial activity was suggested to exert a trivial control on hydrothermal emissions from diffuse degassing. In particular, evidences of shallow production and consumption of volatile organic compounds (VOCs), involving both hydrocarbons and heteroatomic (S-, O- and Cl-bearing) species, were recognized (Tassi et al., 2015), pointing to a crucial role of biochemical processes in shaping the composition of VOCs diffusively emitted from the soil of the crater.

In this study, geochemical and microbiological data of soil and gas samples from two different depths (10 and 30 cm) along 5 vertical profiles and 2 sediment samples from two acidic mud pools (Fangaia Piccola and Fangaia Grande) are presented. Microbial diversity was analyzed by 16S rRNA gene sequencing and *in situ* hybridization in the framework of Census Of Deep Life Sequencing Opportunities 2016-Deep Carbon Observatory. Despite the extreme temperatures (up to 70°C) and *p*H (from 1.3 to 3.6) values, the total prokaryotic abundances ranged from 7.23×10^6 to 439×10^6 cell/g WW. However, remarkable phylogenetic variations in both Archaea and Bacteria communities were observed at changing environmental conditions (*p*H, *T*, soil gas fluxes and interstitial soil gas contents) among the selected sites.

These analytical results provide a detailed picture of biodiversity in a hydrothermal environment and give insights into the complex inter-dependence between the chemical and isotopic features of the fluid constituents involved and the microbially-driven processes. These findings represent an important step forward towards a better comprehension of terrestrial solfataric fields, opening the way to follow-up investigations on the estimation of diffuse VOCs emissions from volcanic/hydrothermal areas and the development of novel bioremediation and biomedical applications.

Tassi, F., Venturi, S., Cabassi, J., Capecchiacci, F., Nisi, B., Vaselli, O. (2015): Volatile Organic Compounds (VOCs) in soil gases from Solfatara crater (Campi Flegrei, southern Italy): Geogenic source(s) vs. biogeochemical processes. Appl. Geochem., 56, 37-49.

Session S26:

Fluid geochemistry in geothermal, volcanic and seismically active areas

Conveners:

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Triponzo: a thermal system in a cold area of the Apennines (Italy)

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Keywords: thermal energy, hydrogeochemistry, Apennines.

Bagni di Triponzo thermal springs, characterised by a Ca-SO_4 composition and temperatures up to 30°C, are located in the eastern sector of Umbria region (Italy) in the Umbria-Marche Apennine. The region is characterised by a low geothermal gradient and low conductive heat flux (Cataldi et al., 1995) and the composition of Triponzo thermal waters significantly differ with respect to the cold waters circulating in the surrounding areas. The origin of the heat transported by the waters of the Triponzo springs is mainly due to a deep component, characterised by high CO_2 and He contents, coming from a deeper reservoir, rising along normal faults and mixing with infiltrating water of meteoric origin. The total amount of thermal water discharged by the system is about 34 $L \cdot s^{-1}$. According to the ternary SO_4^{2-}–F^-–HCO_3^- geoindicator for carbonate-evaporite reservoirs (Chiodini et al., 1995), the fluids at reservoir condition are charcterised by a partial pressure of CO_2 about 0.5 bar and a temperatures between 70-75°C whereas the Silica geothermometers (Truesdell & Fournier, 1977) give a temperature about 62°C. The computed thermal energy transported by advection and discharged at the surface by Triponzo springs is about $3.71 \times 10^{11} \pm 0.56 \times 10^{11}$ J/day.

Cataldi, R., Mongelli, F., Squarci, P., Taffi, L., Zito, G., Calore, C. (1995): Geothermal ranking of italian territory. Geothermics, 24, 115-129.

Chiodini, G., Frondini, F., Ponziani, F. (1995): Deep structures and carbon dioxide degassing in central Italy. Geothermics, 24, 81-94.

Truesdell, A.H. & Fournier, R.O. (1977): Procedure for estimating the temperature of a hot-water component in a mixed water by using a plot of dissolved silica versus enthalpy. J. Res. U.S. Geol. Surv., 5, 49-52.

First geochemical characterization of water and dissolved gases of Coatepeque, Ilopango and Chanmico volcanic lakes (El Salvador, central America)

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Keywords: volcanic lakes, El Salvador, geochemical characterization, water and dissolved gases.

El Salvador is a land characterized by complex fault systems, which are part of a major tectonic lineament in central America where large-volume silicic calderas and craters occur. Among the lakes hosted in these volcanic systems, Lake Coatepeque (on the E slope of the Santa Ana Volcano), Lake Ilopango (inside Ilopango Caldera), and Laguna de Chanmico (associated with the San Salvador Volcano) are of particular interest for the volcanological scientific community, since no detailed geochemical data are available and consequently, dissolved gas accumulation able to trigger limnic eruptions cannot be excluded.

In November 2016, a sampling campaign was carried out in these lakes to collect water and dissolved gas samples aimed at investigating the physicochemical and isotopic features along the vertical water columns in order to provide hints on the biogeochemical mechanisms regulating the behavior of the dissolved gas reservoirs. Water temperature, dissolved O_2, electrical conductivity and *p*H were measured *in situ* by using a multi-parametric probe along the vertical profiles of each lake, whereas the chemical and isotopic composition of waters (δD-H_2O, $\delta^{18}O$-H_2O, and $\delta^{13}C$-TDIC) and dissolved gases ($\delta^{13}C$-CO_2) was determined on samples collected at regular depth intervals from the lake surface to the maximum depth.

Coatepeque, Ilopango and Chanmico lakes show a thermocline at relatively shallow depth (from 30 to 40 m, from 20 to 40 m and from 5 to 15 m depth, respectively), where a sharp conductivity increase and a *p*H decrease were measured. The three lakes are anaerobic below 33, 24 and 4 m depth, respectively. Lake Chanmico shows a Mg^{2+}–HCO_3^- water composition and TDS between 566 and 856 mg/L, whilst Coatepeque and Ilopango lakes display a Na^+–$Cl^-(SO_4^{2-})$ and a Na^+–$Cl^-(HCO_3^-)$ composition and TDS values up to 1226 and 1216 mg/L, respectively. The δD-H_2O and $\delta^{18}O$-H_2O values indicate that (i) the lake waters have a meteoric origin, and (ii) the occurrence of some isotopic fractionation due to surficial evaporation. Deep waters are characterized by the presence of CO_2 and CH_4, albeit in smaller quantities than other lakes hosted in quiescent volcanic systems (*e.g.*, Monticchio, Albano and Averno lakes, Italy). Both the $\delta^{13}C$-TDIC and the $\delta^{13}C$-CO_2 values suggest that CO_2 is mostly hydrothermal in origin, though the carbon cycle is mainly controlled by microbial activity.

Accordingly, further investigation dealing with the speciation and distribution of microbial populations is strongly recommended for an exhaustive description of the processes governing the water and gas composition of the lakes.

Long-term variation of diffuse CO_2 degassing during a volcanic unrests: the case of Campi Flegrei (Italy)

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Keywords: CO_2 degassing, hydrothermal system, volcanic unrest.

Hydrothermal activity at Solfatara of Pozzuoli (Campi Flegrei caldera, Italy) results on a large area of hot soils, diffuse CO_2 degassing and numerous fumaroles, releasing at the surface large amounts of gases and thermal energy. Solfatara is one of the first sites of the world where the techniques for measuring soil CO_2 diffuse degassing were firstly applied and it has become a sort of natural laboratory for testing new techniques to measure CO_2 fluxes from hydrothermal sites. The results of 30 diffuse CO_2 flux surveys performed in the period 1998-2016 are presented and discussed. CO_2 soil fluxes were measured over an area of about 1.4 km^2 including the Solfatara crater and the hydrothermal site of Pisciarelli using the accumulation chamber technique. Each survey consisted in CO_2 flux measurements varying from 372 to 583 resulting in a total of 13158 measurements. This data set is one of the largest dataset ever made in the world on a single degassing volcanic-hydrothermal system. It is particularly relevant in the frame of volcanological sciences because it was acquired during a long period of unrest at Campi Flegrei caldera and because Solfatara release an amount of CO_2 comparable to that released by medium-large volcanic plumes. Statistical and geostatistical elaborations of CO_2 flux data allowed to define the sources of soil diffuse degassing, the extent of the area interested by the release of hydrothermal CO_2 (Solfatara DDS) and the total amount of released CO_2. During the last eighteen years relevant variations affected Solfatara degassing, and in particular the "background" CO_2 emission, the extent of DDS and the total CO_2 output, that may reflect variations in the subterraneous gas plume feeding the Solfatara and Pisciarelli emissions. In fact, the most relevant variations in Solfatara diffuse degassing well correlates with steam condensation and temperature increase affecting the Solfatara system resulting from repeated inputs of magmatic fluids into the hydrothermal systems as suggested by Chiodini et al.(2015, 2016) and show a long-term increase on the amount of released CO_2 that accompanies the ongoing unrest of Campi Flegrei caldera. A general correlation emerges between the increase of CO_2 release and the increase in seismicity and ground uplift. In the period from 2012 to 2016, two main peaks in the CO_2 output coincides with episodes of accelerating ground uplift and of intensification in the seismicity. At the same time, periods of relatively lower CO_2 output corresponds to a period of low seismicity and a pause in the deformation.

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Chiodini, G., Paonita, A., Aiuppa, A., Costa, A., Caliro, S., De Martino, P., Acocella, V., Vandemeulebrouck, J. (2016): Magmas near the critical degassing pressure drive volcanic unrest towards a critical state. Nature Commun., 7, 13712.

Two different approaches to hydrothermal gas equilibria at Solfatara

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Keywords: hydrothermal gas equilibria, gas-geoindicators.

In recent times two different approaches to hydrothermal gas equilibria leading to contrasting results in terms of temperature and pressure estimations were proposed for the fumaroles collected after 1983 at Solfatara. The two interpretations have different implications in terms of hazard and risk assessment at Campi Flegrei because one point to an ongoing process of heating and pressurization of the hydrothermal system (Chiodini et al., 2015; Chiodini et al., 2016), while the other indicates that the observed compositional variations are related to an ongoing phase of depressurization of the system (Moretti et al., 2017). It is worth to note that the two works reach opposite results starting from the same dataset of Solfatara fumarole compositions. The *T-P* estimations refers to an ideal "gas equilibration zone" where the gas species are in thermodynamic equilibrium. The geothermometric and geobarometric relations depend on this general assumption of equilibrium among the gas species in the gas equilibration zone and on further assumptions regarding, what species are in thermodynamic equilibrium, the phase present in the gas equilibration zone (gas or liquid phase), the control (or not) on P_{H2O} of liquid-vapour coexistence, and the occurrence or not of secondary processes changing the relative proportions among the gas species along the ascending path of the fluids from the gas equilibration zone to the fumarolic vents. These aspects will be illustrated together with a comparison of the results of the two different approaches with independent data in order to asses the most reliable geochemical model for Solfatara fumaroles.

Chiodini, G., Vandemeulebrouck, J., Caliro, S., D'Auria, L., De Martino, P., Mangiacapra, A., Petrillo, Z. (2015): Evidence of thermal-driven processes triggering the 2005-2014 unrest at Campi Flegrei caldera. Earth Planet. Sci. Letters, 414, 58-67.

Chiodini, G., Paonita, A., Aiuppa, A., Costa, A., Caliro, S., De Martino, P., Acocella, V., Vandemeulebrouck, J. (2016): Magmas near the critical degassing pressure drive volcanic unrest towards a critical state. Nature Commun., 7, 13712.

Moretti, R., De Natale, G., Troise, C. (2017): A geochemical and geophysical reappraisal to the significance of the recent unrest at Campi Flegrei caldera (Southern Italy). Geochem. Geophys. Geosyst., 18 1244-1269.

Monitoring of hydrothermal gases at the Campi Flegrei caldera (south Italy): geochemical evidences from the pilot hole of CF Drilling Project

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Keywords: real time gas monitoring, Campi Flegrei, deep drilling, geochemistry.

Scientific drilling is the only technique allowing to investigate, in a direct way, processes occurring at depth in active volcanic areas. Data and information obtained by drilling represent the most powerful method for understanding volcano dynamic and then significantly mitigating the volcanic risk. A very important case study is the active Campi Flegrei caldera, one of the highest risk volcanoes worldwide, hosting part of the large city of Naples (southern Italy). The real-time analysis on the gas phase dissolved in the drill mud using a quadrupole mass spectrometer was carried out at the 506 m deep Campi Flegrei pilot hole in the framework of the Campi Flegrei Deep Drilling Project (CFDDP), co-funded by the International Continental Scientific Drilling Program (ICDP). We report the methods used and present the first results of the gas concentrations detected during the entirely process of drilling. Because the main components of drilling mud gas are from the air, in discussing mud gas logging results, we put particular emphasis on He, CH_4 and CO_2 which are the gas components that should originate from the deep fluids. The gas concentration showed a good correlation with the stratigraphic reconstruction along the drill hole. Lithological changes are often correlated with increasing amounts of gas. Our preliminary results provide important information to better understand volcanic and hydrothermal phenomena in the eastern sector of the Campi Flegrei caldera, and allow a joint interpretation of such geochemical data with those collected from the neighbouring Solfatara crater.

Isotope geochemistry of rainfall, thermal and non-thermal waters from the Mt. Amiata area (northern-central Italy): preliminary data (January-August 2017)

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Keywords: central Italy, Mt. Amiata geothermal area, fluid geochemistry, water isotopes.

This ongoing research project is aimed at providing an updated and detailed geochemical-isotopic dataset of rainfall and cold and thermal groundwater systems from the Mt. Amiata silicic volcanic complex and defining a mean vertical isotopic gradient for the meteoric recharge in order to extrapolate a local reference meteoric water line. Accordingly, it is expected to reconstruct the average infiltration altitudes of the largest and youngest volcano in Tuscany (central Italy). Furthermore, an estimate of both water balance of the shallow aquifer(s) and a conceptual model of the fluid are also expected.

Presently, six pluviometric samplers (10 L plastic tanks, equipped with a filter-bearing funnel, containing paraffin oil to prevent fractionation processes) have been placed at different elevations from about 300 m a.s.l. up to the top of Mt. Amiata (1,700 m a.s.l.) on both west and eastern flanks. Rainwater is collected monthly and analyzed for isotopic composition (oxygen and hydrogen) and chloride. This study includes the sampling and analysis of about 150 natural springs emerging at the contact between the Mt. Amiata volcanics and the underlying impermeable flysch units (Ligurian Units l.s.). Discharge rates, temperature, *p*H, electrical conductivity (E.C.) and main, minor and trace (*e.g.*, NH_4, SiO_2, Li, B, Sr) solutes and oxygen and hydrogen isotopes are presently in progress. The preliminary data are in good agreement with those reported by Minissale et al. (1997), highlighting that the spring water discharges are of meteoric origin ($\delta D = \sim -50$ ‰, $\delta^{18}O = \sim -8$ ‰ V-SMOW) with *p*H values from 4.0 to 7.8, *T* from 9.5 to 50°C and E.C. between 0.2 and 3.79 mS/cm (TDS up to 4600 mg/L). The chemical composition of thermal waters can mainly be ascribed to $Ca\text{-}HCO_3(SO_4)$ and $Ca\text{-}SO_4(HCO_3)$ whereas the cold springs generally pertain to the $Ca\text{-}HCO_3$ or $Ca\text{-}SO_4$ facies. Ammonium, SiO_2, Li, B and Sr show a positive correlation with the outlet temperatures being enriched in the thermo-mineral springs. The second step will be that to select the most significant springs for further geochemical and isotopic (*e.g.*, TDIC, As, Hg, HS^-, ^3H) analyses and dissolved- and free-gas composition including $\delta^{13}C\text{-}CO_2$, $\delta D\text{-}CH_4$, $\delta^{13}C\text{-}CH_4$, $\delta^{15}N$, VOCs and noble (He, Ne, Ar) gas isotopes.

Minissale, A., Magro, G., Vaselli, O., Verrucchi, C., Perticone, I. (1997): Geochemistry of water and gas discharges from the Mt. Amiata silicic complex and surrounding areas (central Italy). J. Volcanol. Geotherm. Res., 79, 223-251.

New constraints about CO_2 emission from volcanoes and the time of last activity

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Keywords: deep CO_2 budget, groundwater, carbon isotopes, CO_2 degassing, Mt. Vulture volcano.

We present a detailed study of mantle-derived CO_2 budget from the Mt. Vulture volcano in the southern Apennines, Italy, whose latest eruption occurred 141 ± 11 kyr ago. The relationship between $\delta^{13}C_{CO2}$ and total dissolved carbon indicates that the CO_2 is a mixture of a biogenic and a mantle-derived CO_2 end-members. Our estimate takes into account the CO_2 dissolved in groundwater, the CO_2 emitted from pools and the CO_2 entering the two Monticchio maar lakes. The total mantle-derived CO_2 budget in the study area is 4.85×10^8 mol y^{-1} which is more than double of the previously estimated ones. In addition, such a value is higher than that observed in younger volcanic systems elsewhere, supporting the existence of actively degassing mantle melts below the Mt. Vulture. The spatial distribution of the CO_2 flux suggests a tectonic control driving the gas escape. Regional tectonic discontinuities, which controlled the upwelling of magmas erupted during the last volcano activity, are still the main route for transferring deeply sourced CO_2 toward the surface. Our estimation of CO_2 budget in the Mt. Vulture area, together with literature data on CO_2 budget from historically active and inactive Italian volcanoes, suggests a power-law functional relationship between the age of the most recent volcanic eruption and both total discharged CO_2 ($R^2 = 0.73$) and volcano size-normalized CO_2 flux ($R^2 = 0.66$). This relationship is also valid by using data from worldwide volcanoes highlighting that deep degassing can occur over very long time. In turn, the relationship represent also an important tool to better evaluate the state of activity of a volcano, whose last activity occurred far in time. Finally, our study shows that, unlike the central–northern Apennine where an eastward increase of crustal radiogenic volatile contribution and a decrease in deep CO_2 flux simultaneously occur, in the southern Apennines an active degassing of mantle-derived volatiles (*i.e.*, He, CO_2) occurs from west to east. This difference is probably due to lithospheric tears which control the upwelling of mantle melts, their degassing and the transport of volatiles through the crust.

Geochemical continuous signals processing by multiple statistical techniques: application to the Gallicano thermomineral spring

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Keywords: earthquake geochemical precursors, continuous automatic monitoring station, multiple statistical methods.

Since early 2003 a network of automatic stations (Geochemical Network of Tuscany, GNT) is operating in Tuscany, central Italy, to investigate possible earthquake geochemical precursors in spring waters. The continuous automatic monitoring stations of the GNT have been designed and realized at IGG-CNR-Pisa in keeping with the recommendations of the International Association for Seismology and Physics of Earth's Interior, and are equipped with sensors for the concurrent measurement of different parameters to ensure cross-checking of independent signals.

Here we present data collected over the period 2003-present from the Gallicano thermomineral spring, located in Garfagnana, one of the areas of highest seismic risk in Tuscany. The Garfagnana region belongs to the inner zone of the northern Apennine fold-and-thrust belt consisting of structural units derived from both oceanic and continental domains now represented in the Ligurian, Subligurian and Tuscan Units. The area is tectonically active, and a number of extensional structures (low- and high-angle normal faults) confer a ''semigraben'' type geometry to the local intermountain basins.

The Gallicano spring emerges at an altitude of 209 m a.s.l. and is characterized by an average flow rate of about 1.5 L/s. The discharged water has a medium salinity (up to 4.2 g/L) and a temperature of about 25°C.

The continuous automatic monitoring station installed at Gallicano is equipped with sensors for the simultaneous measurement of temperature, *p*H, electrical conductivity, redox potential, and dissolved content of CO_2 and CH_4. The station operates with flowing water (about 5 L/min), and a frequency acquisition of 1 s for all the parameters. Manual calibration procedures are done on a monthly basis, and/or in conjunction with anomalous variations of the signals. By combining this continuous and discrete monitoring approach, some understanding of the deep circulation paths, and of the geochemical processes governing the chemical evolution of the waters discharged at Gallicano and in the surrounding areas, has been gained, and an integrated hydrogeological and geochemical model of the system has been defined.

Data series have been analysed with multiple statistical methods to highlight possible temporal trends (linear *vs.* sinusoidal, short- *vs.* long-term), and anomalous variations related to seismic activity. The applied methods include: Fourier analysis, multiple regression, factorial analysis, Census I method, Sinclair method, Neural Network Analysis.

A number of CO_2 anomalous concentrations have been recognized in concomitance with three major seismic events occurred in northern Tuscany and Emilia Romagna regions, not far from the Gallicano area. Accurate statistical processing of geochemical continuous signals emerges as a powerful and essential tool to ensure a reliable identification of anomalies, and to possibly increase the confidence in the use of geochemical precursors of earthquakes.

Baseline studies to select the most sound and sensitive sites to install continuous multidisciplinary & seismo-geochemical monitoring networks, stressing the discovering of "sensitive sites" during seismic sequences, *i.e.*, the Amatrice-Norcia one case history

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Keywords: seismogeochemistry, animals behavior with seismicity, fluid geochemistry along active faults.

The paper review methodologically and historically – in the frame of research managing in Italy and abroad- geochemical baseline studies to select the most "sound/sensitive" sites to install continuous monitoring stations, in part described in the parallel abstract of this conference. The paper is highlighting the "site specific" case histories and the possible processes helping in the networks design, occurring before strong-moderate earthquakes, volcanic eruptions, gas-burst or groundwater evolution in geothermal and hydrocarbons fields, mostly in Italy, but also working in European Projects (FP5-6-7) in Greece, Canada, Polonia, India, etc., since 1990 (*i.e.*, Geochemical Seismic Zonation, Automatic Geochemical Monitoring of Volcanoes, 3F- Faults-Fractures-Fluids Corinth-Rift, CO_2-EOR-IEA Weyburn, etc.).

In particular the following criteria are mainly important during the "sensitive sites" selection as described in the paper, after the definition of "geochemically active fault" (EU Project Geochemical Seismic Zonation: Quattrocchi, 1999; Quattrocchi et al., 2003) and the case history of Amatrice-Norcia seismic sequence (2016-2017) addressed to customize a local seismogeochemical network:

- if the network of seismo-geochemical transients is in soil gas is necessary a preliminary study on groundwater to understand the sectors of shallow aquifers more prone to be oversaturated of geogas from below, in the "buffer" body of the aquifers, namely closer to reach the critically state to be degassed at surface in soils (*i.e.*, CO_2, ^{222}Rn, CH_4);
- if the network of seismo-geochemical transients is in soil gas is very important to select areas for future continuous monitoring where the regional faults are crossing each other (Quattrocchi, 1999; Pizzino et al., 2002; 2004);
- if the network of seismo-geochemical transients is in soil gas is very important to select areas for future continuous monitoring where a carrier gas is acting both being CO_2 (Pizzino et al., 2000) or CH_4 (Sciarra et al., 2013);
- if the network of seismo-geochemical transients is in groundwater is very important a preliminary study (at least 50 sites, among wells and springs, in the faulted area, *i.e.*, during seismic sequence, as we discuss in the paper the Amatrice-Norcia one) before and after seismic sequence to realize where the maximum anomalies have been measured and therefore envisaged in the future events too, *i.e.*, Bagni di Triponzo, Campello Al Clitunno, Val Topina, Colle San Tommaso, etc., for the Umbria-Marche border (Quattrocchi et al., 2000), affected by both the Colfiorito 1997-1998 seismic sequence and by the Amatrice-Norcia-Spoleto 2016-2017 one too, I a pore-pressure dominated situation (Frima et al., 2005);
- The Questionary: The Earth is speacking, lissen it is and was very useful in the Amatrice-Norcia seismic sequence to discover around 50 cases of pre-main shocks anomalies, mostly in the animals behavior.

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Geochemical properties of the low-temperature geothermal fluids (thermal springs, paleofluids) from Suio, central Italy

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Keywords: central Italy, geothermal resource, fluid geochemistry, hydrothermal reservoir, water-gas-rock interaction.

Suio (Latina, central Italy), a thermal area known since the Roman imperial times, is located on the northernmost slopes of Mount Aurunci, near the Garigliano river. It is bordered to the east by the Roccamonfina Volcanic Complex, whose last magmatism occurred between 550 and 150 ky ago and to the west by calcareous (Cretaceous) and dolomitic (Jurassic) formations. The Garigliano river divides two distinct zones: (1) a western sector where thermal spas and natural thermal springs occur, and (2) an eastern sector where the fluid emissions consist of dry gas discharges. In this study, we investigate the geochemical features of present and past geothermal fluids in order to assess the origin of the thermal manifestations in this area. Most cold springs (≤ 20°C) have low TDS (≤ 1 g/L), slightly acidic to neutral *p*H, and a Ca(Mg)–HCO_3 composition. Such chemical features are typical of meteoric waters circulating within volcanic and sedimentary rocks. Thermal springs have relatively high TDS values (up to 4 mg/L), temperatures ranging from 21 to 52°C and a SO_4-rich Ca(Mg)–HCO_3 composition. The δ^{34}S-SO_4, ranging from +11.8 to +19.3‰ *vs.* V-CDT, suggests that the sulphate is produced by the dissolution of Triassic evaporites. The chemical composition of the gas phase is dominated by CO_2, H_2S and atmospheric compounds along with relatively high amount of methane and C_{2+} n-alkanes. The hydrocarbons are probably produced by decomposition of organic matter dispersed in the sedimentary rocks. The origin of H_2S is likely related to two processes: (1) thermochemical sulphate reduction (TSR) in the deep reservoir and/or (2) bacterial sulphate reduction (BSR) occurring at relatively shallow depth. Liquid and gas geothermometry suggests a deep fluid source at temperature ranging from 120 to 160°C. These temperatures are confirmed by microthermometric determinations on liquid-vapor acqueous fluid inclusions hosted in two authigenic calcite samples collected from two faults of the study area. Overall, these data show that authigenic calcite of the Suio faults deposited from a low-salinity (0-2.7 wt% $NaCl_{eq}$) geothermal fluid at temperature of 140-220°C. The relatively low R/R_a values (≤ 1) of the present fluids along with the other geochemical evidence indicate that the contribution of deep-originated fluids from the nearby Roccamonfina Volcanic Complex is negligible. Water-rock-heat interaction involving carbonaceous formations is the main source of CO_2, as confirmed by the δ^{13}C-CO_2 values (0±1.5 ‰ *vs.* V-PDB). The meteoric water circulation is driven by the normal faults associated to the local distensive tectonic regime. Under these conditions, decompression affecting the uprising thermal fluids causes the separation of a CO_2-rich gas phase that feeds the dry gas emissions seeping out on the southern limit of the study area. Lastly, this study highlights that the most suitable application for the thermal resource in the Suio area is the spa activity.

Dynamics of magma ascent thought the study of geochemical and geophysical data acquired at the same time

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Keywords: volcanic activity, gas monitoring, micro gas-chromatography.

The rise up of volcanic fluids to the surface produces anomalies that are a function of the structure of the volcano and tectonics in which itself insists.

A chromatography monitoring station (CMS) that have inside a computer, m-GC, sampling system, router, has been developed to allow complete control of the instruments and the automatic transmission of data. The micro gas-chomatography (m-GC) offers a possible alternative to the monitoring of main gases in areas of volcanic and seismic allowing a much higher frequency of analysis. Some specific parts have been realized in order to adapt the characteristic of the m-GC to the automatic collect of gas soils. Some data series have been acquired on gas soils at Zafferana Etnea during 2011 when occurred some episodes of lava fountains emitted from southeast crater. The sequence of data displayed, before a degassing without significative variations of CO_2 concentration, direct evidence that our volcanic system was in equilibrium state, subsequently a degassing impulsive for some days and finally a clear decrease, from 12% to 2% in CO_2 concentrations in few hours. After the concentrations increased and begin to return at similar level showed before the paroxysm.

The state of equilibrium emission of gases from soils is disrupted by the arrival of small batches of magma that disrupt the signal and probably mark the beginning of strombolian activity. When the dynamics of magma are extremely fast, the vesciculation that is produced, does not allow the gas to reach the peripheral sites or this process must occur above the altitude of the monitored site.

The evolution of the volcanic activity during the lava fountain episodes is seismically followed through the continuous monitoring of volcanic tremor. The comparison between volcanic tremor amplitude and CO_2 concentration has revealed a great similarity in their trends and in the sudden variations. Particularly the variation of CO_2 has preceded of some hours the increase of tremor signal due probably to the different altitude of the sites of measure.

Therefore, geochemical and geophysical data together could contributed to define the dynamics related to the rise up of magma on Etna Volcano.

Session S27:

Magma chamber and eruptive dynamics resolved by natural and experimental evidences

Conveners:

Matteo Masotta (Univ. di Pisa)

Alessandro Vona (Univ. di Roma Tre)

Danilo Di Genova (Univ. of Bristol, UK)

Pier Paolo Giacomoni (Univ. di Ferrara)

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High-Mg basalts from Capo Marargiu (Sardinia, Italy): experimental constraints on amphibole stability in a primitive calc-alkaline magma

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Keywords: high-Mg basalt, amphibole crystallization, high pressure experiments, Sardinia calc-alkaline magmatism.

The composition of a high-Mg basalt (HMB) from the Capo Marargiu Volcanic District (CMVD, Sardinia, Italy) was used for a phase relation study at high pressure and hydrous conditions.

The CMVD is a calc-alkaline complex of basaltic to intermediate hypabyssal (dikes and sills) and volcanic rocks (lava dome and flows, pyroclastic deposits) emplaced during the Oligo-Miocene orogenic magmatism of Sardinia. The HMB (10 wt.% MgO) occur as magmatic enclaves hosted in a basaltic-andesitic dome (BA). Minerals within the enclaves are clinopyroxene (Cpx), plagioclase (Plg), amphibole (Amph), olivine (Ol) and oxides (Ox), and those of the BA host are Plg + Cpx + Ox + low-Ca pyroxene.

Thermobarometric estimates indicate that Cpx and Amph from the enclaves crystallized at P = 500-800 MPa and T = 1010-1100°C. In order to investigate the stability of Amph in the HMB magma we conducted preliminary experiments at 800 MPa and in a range of temperatures of 1050-1110°C. $Au_{75}Pd_{25}$ capsules were loaded with ~100 mg of a powdered HMB (sample CM42) and 2 wt.% H_2O (low water experiments, LWE) or 5 wt.% H_2O (high water experiments, HWE). The experiments were run in the piston-cylinder apparatus installed at the *HP-HT* Laboratory of Sapienza University of Rome and held at the target P-T conditions for 3 h.

The stable phases in the LWE are Ol + orthopyroxene (Opx) + Cpx + Plg + Ox and a hydrous basaltic andesite (~ 4 wt.%) as residual glass (Gl). The crystallization degree is higher than 50 vol.%.

Run products of HWE is Gl + Ol + Amph + Cpx + Plg + Ox. The crystallinity is lower than that of the LWE H_2O-saturated basalt (~ 7 wt.% H_2O), as testified by the presence of vesicles.

This preliminary study shows that Opx is stable in a HMB at P = 800 MPa and T = 1050-1110°C and $H_2O \leq 2$ wt.% (*i.e.*, LWE), whereas its crystallization is hindered when magma water content is increased to ~5 wt.%, providing conditions suitable for Amph saturation (*i.e.*, HWE). This modal discrepancy is ultimately reflected in the composition of residual melt, being more evolved in the low-water experiment and more primitive in the hydrous run.

We conclude that (i) the P–T–H_2O conditions of the HWE more realistically represent those of natural enclave crystallization, consistently with thermobarometric estimates, and (ii) at a global scale, the occurrence of amphibole-bearing cumulates in exhumed lower crustal section testify to magmatic differentiation in a water-rich environment nearby the Moho. Importantly, the flux of H_2O from this "wet and hot deep zone" (Perinelli et al., 2017) would play a critical role in the eruptive style of the overlying volcanoes.

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3*D* textural and geochemical investigation to explore magmatic evolution and eruptive dynamic of Pomici di Base plinian eruption (Somma-Vesuvius, Italy)

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Keywords: Somma-Vesuvius, 3*D* textural characterization, magma chamber, conduit processes.

Textural study of volcanic rocks can be of fundamental importance to evaluate the processes and parameters that control eruptive style. In fact, analysis of vesicle and crystal number, size and shape of volcanic rocks can be used to understand the mechanisms and timescale of degassing and crystallization processes during magma ascent in volcanic conduit. Recently this kind of study has been improved by the use of advanced techniques of microanalysis, such as X-ray microtomography, which allow generating 3*D* internal structures of rocks with a resolution in the order of micron or sub-micron.

In this case study we have conducted an X-ray microtomographic and geochemical investigation of volcanic products erupted during the Pomici di Base eruption (about 20 ka). This event represents the first and most intense plinian eruption of Somma-Vesuvius (Bertagnini et al., 1998; Landi et al., 1999), occurred after a period of prevalent effusive activity, and defines the beginning of caldera collapse events.

The obtained results allowed us to reconstruct the evolution of the Somma-Vesuvius magmatic system before and during the eruption as well as to obtain information on the triggering mechanisms and eruptive dynamic. In particular, our geochemical data show the existence of a chemically (from trachytic to latitic composition) and thermally (from 900 to 1050°C) zoned magma chamber, located at a depth of 4-6 km, while the variation the isotopic ratios indicates that a crustal contamination process involved the less differentiated and hotter portion of magmas. A crucial issue that characterizes this eruption is the high mass discharge rate (MDR) that remains stable during the whole plinian eruption phase despite the significant compositional and textural variation of the volcanic products that change upwards from trachytic, highly vesicular, microlite-free pumices to latitic, poorly vesicular, microlite-rich scoriae. Our 3*D* textural results suggest that the assimilation occurred during the late stage of the magma ascent through the carbonatic bedrock. The contamination determined a rapid gas release that contributed to increase the eruptive explosivity and then to maintain constant the MDR. This mechanism seems to be supported by previous experimental evidences (Blythe et al., 2015) and can have critical consequences on volcanic hazard of volcanic systems settled in calcareous rocks.

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A crosschecked model to constrain *P*-*T*-*f*O_2-H_2O of a water-rich K-alkaline system: the unique case of the Predazzo Triassic volcano-plutonic complex

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Keywords: Predazzo volcano-plutonic complex, crosschecked thermobarometry, Triassic magmatism, K-alkaline.

The Triassic Predazzo magmatic complex (southern Alps, Italy) is one of the few worldwide examples of an entirely preserved volcano-plutonic system, where the relationship between the paleo magma chamber, the host rocks, the dyke swarm and the overlying lava flows could be directly observed. Completely preserved from the Alpine tectonics and "frozen" in its original position, this complex is nowadays totally exposed to the surface, resulting in one of the best thermobarometric laboratories of the world. Its multi-pulse intrusive portion is made up of K-alkaline Bt/Amph-bearing gabbros to syenites and syenogranites, whereas the dyke swarm and the volcanic products range in composition from trachybasalts to trachytes. Lavas and dykes paragenesis is instead dominated by Plag and Cpx, with minor Mt and K-Feld.

The present study is focused on the crosschecked determination of the intensive variables of the Predazzo shallow magmatic system, through a comparison between *P*-*T*-*f*O_2-H_2O data from its plutonic, hypabyssal and volcanic portions. The entire fractionation sequence has been investigated, from the deeper Cpx crystallization to the shallow levels where Amph and Bt formed from a K-Na-H_2O-saturated magma. Cpx-melt equilibrium (Putirka, 2008), as well as MELTS software (Gualda et al., 2012) were used to constrain the Cpx equilibrium condition in the less evolved trachybasaltic magmas (1.5-2.5 wt% H_2O, 1150-1180°C, 6-10 kbar). According to Amph and Plag thermobarometers and hygrometers (Anderson, 1996; Lange et al., 2009; Ridolfi et al., 2010), magmas fractionating in the shallow portions of magma chamber were highly hydrated (4-6 wt% H_2O) at 850-700°C and 0.2-1.2 kbar. *f*O_2 (Ishibashi, 2013) was around +1.5/+2 ΔQFM. According to our findings, the Predazzo complex "natural laboratory" could play a key role in the development of a new crosschecked thermobarometric approach, which could be applied to the modern and still active volcanic systems.

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Mt. Etna *vs.* Hyblean Plateau: modelling the mantle source beneath SE Sicily

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Keywords: Mt. Etna mantle, primary magmas, volatile content, K-enrichment, geodynamic of SE Sicily.

The evolved nature of Mt. Etna erupted magmas, their geochemical variations through time and the absence of mantle xenoliths led to a historical and controversial debate about the mantle source beneath the Sicilian volcano. In order to shed light on this topic, the present study is focused on the modelling of the mantle processes responsible for the production of the entire sequence of Mt. Etna magmas, from the 500 ka tholeiites to the nowadays K-rich eruptions, by means of a comparison with the Hyblean magmatism (southern Sicily), its evolution and mantle source(s).

Taking into account the fO_2 of the magmatic system and its effect on mineral-melt Fe partitioning, a backward FC model has been necessary to reconstruct Mt. Etna primitive magma compositions, equilibrated to the segregation conditions (Mg# 68, $Fo_{Ol}88$) from the mantle source. In this, a 2% to 17% addition of dunitic to wehrlitic assemblages (Ol + Cpx in progressive equilibrium) to Mt. Etna less evolved lavas allowed to carry out the primitive compositions for Timpe, AAV, Ellittico, Mongibello and Post-1971 stages, well comparable to the Ol-hosted melt inclusions (MI) compositions and the Hyblean real primary magmas.

Mass balance modelling has been then used to calculate the modal composition of the mantle source, taking into account the composition of the Hyblean xenoliths, that is an Ol + Opx + Cpx + Cr-Sp lherzolite, with addition of small amounts (4.3%) of Amph and Phlog.

A decrease in the source partial melting degrees (from 19% to 13-10%), as well as a change in Amph and Phlog eutectic melting proportion, are sufficient to produce the entire Mt. Etna compositional range, from the tholeiites to the Post-1971 LILE-enriched lavas, leading to the production of primary magmas characterized by a 0.6 to 1.2 wt% H_2O content.

Finally, a comparison between Mt. Etna and Hyblean mantle source processes and the corresponding geodynamic contexts allowed to figure out some points on the magmatic evolution of the articulated and complex area of southeastern Sicily. In this, the different order of magnitude of the effusion rate of the two events (0.01 km^3/ka for Hyblean Plateau *vs.* 0.74-5 km^3/ka for Mt. Etna) could be likely related to two different mantle melting mechanisms, namely a mantle decompression induced by a passive-rifting phase and an asthenospheric upwelling strongly connected to the Ionian slab retreat.

Dynamics of the "El Retiro" subplinian eruption of Turrialba volcano (Costa Rica): evidences from stratigraphic, petrological and textural analyses

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Keywords: magma dynamics, subplinian eruptions, andesite, Turrialba.

Turrialba is an active volcano of the Cordillera Volcánica Central of Costa Rica, which nowadays is experiencing a renewal of the eruptive activity after ~ 150 years of quiescence. Because of its explosive eruptive records in the recent geologic history, and its proximity with the metropolitan area of San José, this volcano poses a serious threat to the population and economy of Costa Rica. In this study, we combined field observations with laboratory analyses to investigate the most explosive eruption occurred at Turrialba volcano in the last 10 ka, named "El Retiro" eruption, that was fed by andesitic magmas. The eruption is constituted by two main pulses, a first more energetic with an eruptive column of ~ 13 km and a mass flow rate (MFR) of ~ 6×10^6 kg s^{-1}, and a second one less intense with a column of ~ 9 km and a MFR of 9.0×10^5 kg s^{-1}. Basing on these data the first pulse can be classified as a sub-Plinian event, while the second one as a small-to-moderate explosive eruption. Chemical and mineral assemblage is constant in all the studied products, suggesting the eruption of a compositionally homogeneous andesitic magma batch. Petrological data suggest that this magma crystallized at pressures between 400 and 0 MPa, and temperatures between 1145 and 1050ºC. Textural analysis on pumice and scoria samples revealed a wide range of porosities (45 – 74%) and bubble number densities (10^5 and 10^8 cm^{-3}), suggesting different magma degassing conditions. In particular, variation in textural features may represent the horizontal zonation of a magma column in which the physical properties of magma changes from the central axis to the walls of the conduit section. This condition could yield to a strong viscosity contrast and thus to a brittle fragmentation of the magma column. In the near future, similar explosive eruptions cannot be excluded at Turrialba volcano. Consequently, further investigations dealing with eruption dynamics at the conduit are important to rigorously assess the volcanic risk.

P-T-fO_2-H_2O modelling of Voragine and New South East Crater magmatic systems during the December 2015 summit activity at Mt. Etna (Italy)

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Keywords: Mt. Etna, plumbing system, thermobarometry, intensive variables.

Since 2011, Mt. Etna activity has been characterized by short lasting (hours/days) eruptions from the summit craters area, with strombolian to lava fountaining explosions, defined as “paroxysmal events”, involving alternatively the New South-East Crater (NSEC), the North-East Crater (NEC) and the Central Craters (Bocca Nuova, BN and Voragine, VOR). December 3rd-8th 2015 activity interested contemporaneously all the summit craters, providing an almost unique opportunity to study the intensive parameters (*P-T-f*O_2-H_2O) affecting the magmatic crystallization in the shallower portion of the conduits. Samples are trachybasalts, namely two scoriaceous lapilli and a bomb from VOR and three lava flows from NSEC. They show a porphirityc texture (P.I. 18-30%) made up of Ol (Fo_{68-83}), augitic Cpx, Plg (An_{60-82}) and Ti-Mt phenocrysts immersed in a glassy to microcrystalline groundmass. The majority of Plg in VOR samples show a oscillatory zoned core (An_{72} to An_{64}) followed by a dusty resorbed rim associated with an increase in An content (An_{78} to An_{82}). Plg in NSEC samples show a H-shaped morphology and an oscillatory zoning core (An_{78-70}) with a peculiar abrupt decrease in An (60-70%) in the outermost rim of the crystal.

SiO_2 varies from 48 to 50 wt% in VOR and from 46 to 48 wt% in NSEC; Mg# ranges from 48 to 51% in VOR and from 46 to 48% in NSEC. (Na_2O + K_2O) varies from 5.7 to 6.6 wt%, with all samples showing a K-affinity. Despite the general intra-plate typical etnean P.M.-normalized trace element patterns, a slight Nb, as well as a marked Zr enrichement characterize VOR with respect to NSEC samples.

Following the thermometer of Putirka (2008) on Ol-liq equilibrium (${}^{ol\text{-}liq}Kd_{Fe\text{-}Mg}=0.3\pm0.03$), *T* is slightly higher in VOR (1120-1130°C) than in NSEC (1100°C). Similarly, *T* and *P* of Cpx crystallization were estimated using the thermobarometers of Putirka (2008) where ${}^{cpx\text{-}liq}Kd_{Fe\text{-}Mg}=0.27\pm0.03$. *P-T* conditions range from 8 to 5 kbar at ~ 1150-1115°C (DT/DP = 11°C/kbar) and from 7 kbar to 5 kbar at ~ 1110-1090°C (DT/DP = 5°C/kbar) for VOR and NSEC respectively. According to the hygrometer of Lange et al. (2009), the H_2O content varies from 1 to 2.4 wt% for VOR and from 1.6 to 2.8 wt% for NSEC. Il-Mt oxybarometer (Ishibashi, 2013) allowed us to estimate the *f*O_2, which resulted 0.1-0.6 ΔFMQ for VOR and 1.8-1.9 ΔFMQ for NSEC.

The collected data suggest that NSEC feeding system tend to be more oxydized and rich in volatiles with respect to VOR. The relatively higher H_2O content could also result in a lowering of the liquidus and viscosity ultimately favouring a faster ascent rate of the magma.

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Vertically zoned plumbing system at Mt. Etna feeding the 2011-2012 paroxysmal eruptions

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Keywords: Mt. Etna, feeding system, crystal-melt equilibrium, intensive variables, magma mixing.

Mt. Etna activity from January 2011 to April 2012 was characterized by 24 short-lasting (few to several hours) eruptions from the New South East summit crater. Despite the violence of the activity, no appreciable geophysical signals were recorded during this period, except for an increase in the seismic tremors just minutes/hours before the occurrence of the paroxysm. This type of activity represents a significant shift from the mainly effusive eruptions of 2004, 2006, 2008/2009 and from the lateral rift-related event of 2001 and 2002/2003.

The 2011-2012 activity thus represent a unique opportunity to investigate the effects of chemical-physical variables (P-T-fO_2) on the crystallization and fractionation processes occurring in the Mt. Etna open conduit feeding system. We investigated the petrographic and geochemical features of lava and scoria clasts from 10 paroxysmal events. Whole rock compositions plot inside the trachy-basalt field with the typical etnean intraplate chondrite-normalized trace element distribution, characterized by positive U, Th and La and negative Rb, K, Nb anomalies.

MELTs and mass balance fractional crystallization modelling suggest that most of the eruptive events were fed by magma differentiating along the conduit and by a deep basic magma recharge during the 4/3/2012 event.

Olivine (Ol), clinopyroxene (Cpx) and plagioclase (Plg) crystal-melt equilibrium conditions were checked before applying thermo-barometric, oxy-fugacity and hygrometer equations by comparing the composition of phenocrysts with those of whole rock, glass and reconstructed composition of the basic magma. Results show that the erupted products are made up of a mixture of phenocrysts in equilibrium with the whole rock or disequilibrated toward more basic or more evolved compositions.

Thermobarometric calculations indicate that Ol is the first phase on the liquidus (~ 1270°C, up to 1200 MPa). Cpx crystallizes from 1200°C, at 700 Mpa in most basic melt (4/3/2012), to 1100°C at 100 Mpa. Plg nucleation is constrained by the dissolved amount of H_2O in the melt and mostly occur above 250 Mpa. Hygrometer determinations indicate that basic magma contains up to 3.7 wt% H_2O.

The overall dataset suggests that the feeding system of 2011-2012 eruptive events was vertically extended without any significant ponding zone. The conduit is periodically filled with a H_2O-rich basic magma at +2 DFMQ average oxidation condition. The H_2O degassing in the shallower portion of the magmatic column ($P < 200$ Mpa) induce a vertical differentiation. In the deeper portion of the magmatic column at $P > 300$ MPa, the femic geochemical signature is preserved due to the low undercooling degree. The intermediate portion (300-200 Mpa) is repeatedly pushed above the H_2O exsolution depth which promotes the plagioclase saturation and nucleation. In the shallower portion (< 200 Mpa) the efficient H_2O exsolution result in a strong undercooling and promote the massive Plg nucleation and differentiation.

Chemical variations of phases grown from a basaltic melt cooled at variable rates

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Keywords: basalt, cooling rate, kinetics, chemical variation, electron microprobe, crystallization.

Tholeiitic basalt is the most abundant volcanic rock on the Earth crust. However, chemical variations of hosted phases induced by variable cooling rates into lavas, occurring at different distances from air and/or seawater contacts, are still poorly constrained. In order to shed new light on kinetic effects, 9 run-products have been experimentally investigated from *superliquidus* condition (1300°C) to 800°C, at P and fO_2 of air, applying cooling rates (CR) of 1, 7, 60, 180, 1800 and 9000°C/h.

The chemical analyses were performed by EPMA-WDS for solid phases with a size of at least 2.5 µm and SEM-EDS for size $\leq$ 2.5 µm. The paragenesis comprise spinel (sp), clinopyroxene (cpx), plagioclase (plg) and glass, with strong variation in their relative abundances (see the companion contribution).

On the whole, SiO_2 content in cpx is poorly variable and similar to the bulk system, whereas the increasing of CR causes a progressive higher introduction of Al_2O_3, coupled to Na_2O; MgO, CaO and FeO display less evident evolutions. In turn, the cpx is enriched in Tschermak and jadeitic molecules as the cooling rate increases. The increasing of kinetics causes the enrichment in Al_2O_3 plus MgO coupled to the depletion in TiO_2 of sp, whereas Fe_2O_3 variation is negligible. In turn, high cooling rates favors magnetite and spinel s.s. components, whereas ulvöspinel one is stabilized by low cooling rates, possibly reflecting the low diffusivity of Ti^{4+}. Plg grows only between 1 and 60/180°C/h and does not show any clear trend. Residual glass is mostly intra-crystalline (distance from crystal rim < 50 µm) and is Al_2O_3- and Na_2O-rich and depleted in FeO, MgO and CaO; the matrix glass (distance from crystal rim > 50 µm) is present only in the experimental runs at CR > 180°C/h, with chemical composition similar to the starting liquid.

These outcomes prove that cooling rate can induce high chemical variability of crystals, even from a completely molten and homogeneous basalt. The broad ranges of T and CR applied allow a) the comparison between chemical and textural features, b) to create a general and robust model on the solidification of MORB lavas, c) compositional changes in plg, cpx and sp are geospeedometers, and d) CR can tune physico-chemical features of glass-ceramic based on very cheap and extremely abundant raw-materials.

Textural evolution of plagioclase, clinopyroxene and spinel from a basaltic melt as a function of cooling rate

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Keywords: basalt, cooling rate, kinetics, texture, image analysis, CSD, crystallization.

Solidification behavior under variable kinetic conditions from a completely molten Iceland MORB has been experimentally modeled between 1300 (2 h at *superliquidus*) and 800°C (quenching in water), at P_{atm} and fO_2 of air, using 6 different cooling rates (CR): 1, 7, 60, 180, 1800 and 9000°C/h. The ranges of cooling rates and temperatures are the largest ever investigated in the Earth Sciences. Experiments performed at 1, 180 and 1800°C were duplicated in order to verify the reproducibility of run-products. The possible "superheating-effect" was investigated for the 180°C/h cooling rate using a higher superheating treatment, *i.e.*, 1400°C and dwell of 40 h.

The textures of run-products have been measured by image analysis technique on 50 SEM micro-photos collected in the BS mode, at magnifications from 90 to 10,000x. Spinel (sp), clinopyroxene (cpx), plagioclase (plg) and glass are the main phases, quantified *via* area%. Each single crystalline phase has been computed by its equal-area ellipse, such to measure: sizes (µm) and ratio of axes, orientation of the major axis (°) and density (#crystals/area). These data have been then used to calculate their crystal size distributions (CSDs).

At 9000°C/h solidification is impeded (crystals < 2 area%), approaching the critical cooling rate (*R*c). Faceted crystals occur at rates ≤ 60°C/h and are dendritic for ≥ 180°C/h. As the cooling rate increases, crystal content monotonically decreases, area% of cpx has an asymmetric Gaussian shape with a long tail on low cooling rates; sp is invariably ≤ 5 area%, whereas plg grows at CR ≤ 60/180°C/h. The orientation of longest axis is random for all phases, except those at 1°C/h displaying a modest 2*D* fabric. The aspect ratio of plg and sp increase as a function of CR, while that of cpx does not show any trend. Also, faster rates cause the increasing of #crystals/area, possibly reflecting an increasing of nucleation density. As the cooling rate increases, CSDs constantly shift upward, became steep and large crystal sizes disappear. The maximum and average crystal growth rates (by CSD) both increase when CR moves from 1 to 1800°C/h.

Therefore, a completely molten and homogeneous MORB as a function of cooling rate is able to change paragenesis and texture and, in parallel, rheological behaviors of portion of degassed basaltic lavas, the most abundant on Earth surface. These outcomes can be used as geospeedometers, constrain the interpretation of crystals in lavas grown under intra- and extra-telluric conditions and allow to realistically model lava flows. These experiments can be also used to design new glass-ceramics.

The effect of oxygen fugacity on the non-isothermal rheology of basalts

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Keywords: viscosity, basalts, rheology, oxygen fugacity.

Accurate prediction of the run-out distance of lava flows, as well as the understanding of magma migration in shallow dyke systems is hampered by an incomplete understanding of the transient, sub-liquidus and disequilibrium rheology of crystallizing melts. This sets significant limits to physical property based modelling of lava flow (especially flow width, length and advancement rate) and magma migration behaviour and the resulting accuracy of magma transport models and volcanic hazard assessment. The importance of the dynamic rheology of a lava/magma on its emplacement style becomes especially apparent in towards later stages of flow and dyke emplacement, where the oxygen fugacity of the system changes. During these intermediate to late stages of migration and emplacement the melt builds increasing resistance to flow, entering rheologic regimes that determine the halting of lava flows and sealing of dykes. Thermal gradients between the interior of a melt body and the contact with air or the substratum govern these rheologic transitions that give origin to flow directing or impeding features like levees, tubes and chilled margins.

Besides the critical importance of non-isothermal and sub-liquidus processes for the understanding of natural systems, accurate rheologic data mimicking natural conditions are scarce and studies capturing the effect of oxygen fugacity on the disequilibrium rheological evolution of lavas are virtually absent.

We describe the rheologic evolution of natural, re-melted lava samples during transient and non-equilibrium crystallization conditions characteristic of lava flows and shallow magmatic systems in nature. The experiments were carried out both in air and at controlled oxygen fugacity in a gas mixing furnace. This allows, for the first time, to assess the influence of a magma oxidation state on its dynamic, sub-liquidus rheologic evolution and its "cut-off temperature", *i.e.*, the point where flow ceases.

Once cooled below the liquidus temperature the apparent viscosity of the liquid-crystal suspension increases drastically from the theoretical temperature-viscosity relationship of a pure liquid.

We find that during the sub-liquidus rheology experiments:

1) Both cooling rate and shear rate have significant and independent effects on the crystallization kinetics and therewith the rheology of natural silicate melts.

2) Dynamic cooling produces different crystallization kinetics/sequences and phase-dynamics than equilibrium or near-equilibrium conditions.

3) Changes in oxygen fugacity may modify the non-isothermal rheologic evolution of crystallizing melts.

The data presented here constitute the first step towards expanding a growing database of sub-liquidus, non-isothermal magma rheology under disequilibrium conditions into the realm of more reduced conditions expected in natural systems.

The origin of the K-feldspar megacrysts hosted in the silica-rich products from Mt. Amiata (southern Tuscany, Italy)

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Keywords: Mt. Amiata, megacrysts, trachydacite.

The Mt. Amiata is a Quaternary (304-230 ka; Laurenzi et al., *2015*) volcanic complex, covering an area of about 90 km^2 and dominated by trachydacitic lava flows and lava domes. Its volcanic activity developed along an ENE-WSW trending structural alignment during two main phases: an older extrusion of extensive lava flows and a younger emplacement of lava domes and coulées in the axial part of the volcano (Conticelli et al., *2015,* and reference therein). All these silicic products contain abundant metasedimentary xenoliths and mafic magmatic enclaves (from latite to trachybasalts) *(*Van Bergen, 1984). The older lavas are generally high porphyritic, medium to coarse grained with a glassy groundmass commonly showing a perlitic texture. The most abundant phenocrysts are complex zoned plagioclase with relict nucleii and broken sanidine plus ortopyroxene, biotite, rare clinopyroxene and resorbed quartz. The rocks forming the younger lava domes and coulées are highly porphyritic and characterized by a peculiar abundance of K-feldspars megacrysts up to 5-6 cm in length coupled with abundant mafic enclaves. The other, smaller, phenocrysts are complex zoned plagioclase with sieve textured relict nucleii (An_{45-86}), ortopyroxene (Mg# 44-52), clinopyroxene (Mg# 61-82), biotite with disequilibrium rims, ilmenite and rarely quartz set in a glassy to microcrystalline groundmass. Here, we focused on the study of textural and core-to-rim chemical zoning of the K-feldspar megacrysts, in order to understand their origin and give insights into the crystallization processes and magma evolution of the Mt. Amiata silica-rich magma. Megacrysts are characterized by large patchy zoned cores with lobate boundary that include a variable quantity of plagioclase and mafic minerals, rhyolitic glass, and abundant fluid inclusions. Relicts of metasedimentary xenoliths (likely restites) were found included in several megacrysts. Large cores are surrounded by a corona characterized by oscillatory zoning and dissolution surfaces. Megacrysts have a nearly constant composition (Ab_{17-22}, Or_{76-81}, An_{1-3}), and variable compatible trace elements (*i.e.*, Ba 1600-8000 ppm), in particular in the external corona. As preliminary results we suggest that the external corona originated by repetitive growth/dissolution events due to magma mixing between silicic and mafic magmas. This hypothesis is also supported by the presence of abundant mafic enclaves. Conversely, we propose that the cores might represent grains of partially melted metasedimentary xenoliths that experienced different extent of reaction and re-equilibration with the host magma and acted as crystallization nucleii.

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Turbulence (non-laminar) and solidification during magma ascent: insights from 2*D* and 3*D* imaging in an Etnean dyke

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Keywords: dyke, bubbles, X-ray micro-tomography, turbulence (non-laminar), solidification.

Bi-dimensional (2*D*) and three-dimensional (3*D*) textures of bubbles and minerals hosted in a 4.3-m-thick dyke at Mount Etna have been investigated to reconstruct fluid dynamic, emplacement and solidification conditions of the ascending magma. Seven samples from dyke rim to core have been collected along this aphyric sub-volcanic body (DK) solidified at depth of 100-300 m below the pristine surface level. These rocks have been analysed in 2*D* by a high-resolution scanner, a transmission optical microscope and a scanning electron microscope with back-scattered electrons signal, and in 3*D* by microfocus X-ray computed tomography.

Observations at field scale and on mesoscopic polished rock surfaces show bubble-rich, -poor and -free patches even into rock portions of a few cm^3; bubbles have variable size and shape, although never attributable to a high degree of strain. The amount of bubbles irregularly changes from dyke rim to core, whereas plagioclase (plg), clinopyroxene (cpx), titanomagnetite (timt) and olivine (ol) show only limited variations. The fabric of bubbles was retrieved by 3*D* orientation of their maximum length (or elongation). Results indicate that bubbles are randomly oriented in space in each DK sample. All these bubble features have been attributed to transitional to turbulent, *i.e.*, non-laminar regimes (Reynolds number > 1000), as envisaged since long time by numerical models, occurred before the crystallization of minerals. Water solubility, volume of bubbles, magma density and viscosity models indicate that at pressure $P > 10$ MPa the DK magma was crystal-free and contained 1 wt.% H_2O, thus close to its *liquidus* temperature, whereas at $P < 10$ MPa it significantly degassed and crystallized. Sudden and marked crystallization was induced by rapid volatile exsolution at very shallow level, triggering a rapid increase of viscosity, decelerating and eventually halting the magmatic suspension. Such a particular solidification path allowed to quench textures and fabrics of bubbles.

Under the effect of cooling rate, low in the inner and high in the outer dyke portions, crystals continued to grow until the complete solidification of the body. Fluid-dynamic computations suggest that the DK trachybasaltic magma ascended with a velocity of a few m/s with a transitional to turbulent regime, before the growth of minerals.

Assimilation of calcite by ultrabasic melts

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Keywords: carbonate assimilation, olivine, ultrabasic melts, CO_2 degassing.

The composition of magmas during their ascent to the surface is variably modified as consequence of several processes such as crystal fractionation, volatile exsolution and crustal assimilation. In particular, the assimilation of sedimentary carbonate rocks at uppermost crustal levels has the strongest effect in changing the chemical composition of magmas.

We performed experiments at 2 kbar and 1100, 1200 and 1300°C using the Quickpress apparatus available at the *HPHT* lab of the INGV (Rome). The starting materials employed in this study were two glasses obtained by melting at 1600°C of a melilite-olivine-nephelinite (~ 38.5 wt% SiO_2) and a vesecite (monticellite-polzenite) from the Bohemian Massif (~ 30.3 wt% SiO_2), mixed with 10, 30 and 50 wt% synthetic pure calcite ($CaCO_3$). The experiments were quenched isobarically after variable time ranging from 1 to 6 hours. The recovered run products show vesicles that testify CO_2 saturation. At 1300°C and 10 wt% calcite, Mg-rich olivine coexists with an ultrabasic glass containing 37 wt% SiO_2; the same phase coexists with 33 wt% SiO_2 glass in runs with 30% added $CaCO_3$. The addition of 50% $CaCO_3$ to the starting material results in the formation of a melt with 29 wt% SiO_2. The CO_2 content of these melts correlates positively with the amount of added calcite, and ranges from ~ 3 wt% (10 wt% calcite added) to ~ 8 wt% (50 wt% calcite added). Similarly, the CaO content of the coexisting olivine increases up to ~ 2 wt% in agreement with thermodynamic calculations derived from the olivine-monticellite solvus. Noteworthy, similar CaO contents have been measured in olivine rims surrounded by monticellite in Polino carbonatite rocks.

These preliminary results extend our knowledge on the effect of magma composition on carbonate assimilation, and provide an alternative explanation on the origin of highly explosive, strongly ultrabasic CaO-rich melts. In addition, our experimental constraints combined with petrographic and mineral chemical evidences, allow to hypothesize a shallow origin of the Umbria-Latium carbonate-rich rocks. A two-stage process, consisting of formation of ultrabasic liquids from carbonated mantle regions, followed by limestone digestion at shallow depths is proposed to explain the composition of Umbria-Latium ultrabasic rocks.

Hydrothermal *vs.* magmatic sources of geochemical anomalies at Campi Flegrei caldera: a review and a joint interpretation of geochemical and geophysical data

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Keywords: volcanic unrest, hydrothermal systems, steam condensation, oxygen isotope fractionation, chemical equilibrium, magmatic degassing, crystallization.

At closed-conduit volcanoes with large hydrothermal systems, an intrinsic ambiguity characterizes the interpretation of unrest phenomena, particularly the recognition of the source (magmatic *vs.* hydrothermal) of detected anomalies.Geochemical data can be effective in reducing ambiguities, but assumptions about redox state and phase coexistence have a large impact on the computation of *P-T* properties, as well as on mass balances of major components. High uncertainty generally remains also in those environments, like Campi Flegrei caldera (CFc), where excellent geochemical databases have been established since decades. We show here this has occurred so far because the thermodynamic treatment of data was biased by "a priori" assumptions about the redox-state and the imposition of liquid-vapour coexistence. In particular at CFc, the "a priori" assumption of steam condensation in fumaroles biases the interpretations towards 1) high pressures of the hydrothermal system, with related high hazard for freato-magmatic eruptions, and 2) huge arrivals of steam injected from a shallow magma. In contrast, we show that CFc represents an excellent example in which the arbitrary assumption of condensation in fumarole emissions is a major source of interpretative bias, because geochemical inference based on steam condensation overcomes major physical-chemical constraints intrinsic in the CO_2-CO-CH_4-H_2-H_2O system. We here demonstrate, by a rigorous thermo-dynamical approach that both geochemical and oxygen-isotope data of fluids discharged at actively degassing CFc fumaroles do not support steam condensation throughout the plume feeding them, which occurs only during the 1982-84 large unrest. To explain the unrest going on at CFc in the last 10-15 years, our interpretation rules out any new magma intrusion at shallow (3-4 km) depth. In fact, both geochemical (including sulfur and inert gas species) and isotopic data are consistent with a continuous infiltration of a deep (7-8 km) CO_2-rich gas which is actively released since around year 2000. Such geochemical inference is further in much better agreement with all geophysical observations, thus allowing, for the first time, to give a very coherent multidisciplinary interpretation to the unrest episodes observed in the last decade. This important result has certainly less critical implications for the short-term hazard in the area, although should not lead to overlook the risk posed, anyway, by long lasting unrests. The adopted rigorous approach to geochemical gas analysis at volcanoes, as applied in this work, allows to overcome drawbacks and misinterpretation which often arise in volcano geochemistry, and should hence represent the 'standard' methodology in all volcanic areas characterised by large geothermal systems.

Degassing *vs.* eruptive styles at Mt. Etna volcano (Sicily, Italy): volatile stocking, gas fluxing, and the shift from low-energy to highly-explosive basaltic eruptions

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Keywords: Etna, degassing, eruption style.

Basaltic magmas can transport and release large amounts of volatiles into the atmosphere, especially in subduction zones, where slab-derived fluids enrich the mantle wedge. Depending on magma volatile content, basaltic volcanoes thus display a wide spectrum of eruptive styles, from common Strombolian-type activity to Plinian events. Mt. Etna in Sicily, is a typical basaltic volcano where the volatile control on such a variable activity can be investigated. Based on a melt inclusion study in products from Strombolian or lava-fountain activity to Plinian eruptions, here we show that for the same initial volatile content, different eruptive styles reflect variable degassing paths throughout the composite Etnean plumbing system. The combined influence of i) crystallization, ii) deep degassing, and iii) CO_2 gas fluxing can explain the evolution of H_2O, CO_2, S and Cl in products from such a spectrum of activity. Deep crystallization produces the CO_2-rich gas fluxing the upward magma portions, which will become buoyant and easily mobilized in small gas-rich batches stored within the plumbing system. When reaching gas dominated conditions (*i.e.*, a gas/melt mass ratio of ~ 0.3 and $CO_{2(gas)}/H_2O_{(gas)}$ molar ratio ~ 5), these will erupt effusively or mildly explosively, whilst in case of the 122 BC Plinian eruption, open-system degassing conditions took place within the plumbing system, such that continuous CO_2-fluxing determined gas accumulation on top of the magmatic system. The emission of such a cap in the early eruptive phase triggered the arrival of deep H_2O-rich whose fast decompression and bubble nucleation lead to the highly explosive character, enhanced by abundant microlite crystallization and consequent increase of magma effective viscosity. This could explain why open system basaltic systems like Etna may experience highly explosive or even Plinian episodes during eruptions that start with effusive to mildly explosive phases. The proposed mechanism also determines a depression of chlorine contents in CO_2-fluxed (and less explosive) magmas with respect to those feeding Plinian events like 122 BC one. The opposite is seen for sulfur: low to mild-explosive fluxed magmas are S-enriched, whereas the 122 BC Plinian products are relatively S-poor, likely because of early sulfide separation accompanying magma crystallization. The proposed mechanism involving CO_2 separation and fluxing may suggest a subordinate role for variable mixing of different sources having different degrees of K-enrichment. However, such a mechanism requires further experimental studies about the effects on S and Cl dissolution and does not exclude self-mixing between degassed and undegassed batches within the Etna plumbing system. Finally, our findings may represent a new interpretative tool for the geochemical and petrological monitoring of plume gas discharges and melt inclusions, and allow tracking the switch from mild-explosive to highly explosive or even Plinian events at Etna.

Clinopyroxene-melt element partitioning during interaction between trachybasaltic magma and siliceous crust: clues from quartzite enclaves at Mt. Etna volcano

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Keywords: Etna, quartzite xenoliths, clinopyroxene-melt element partitioning.

A peculiar characteristic of the paroxysmal sequence that occurred on March 16, 2013 at the New South East Crater of Mt. Etna volcano (eastern Sicily, Italy) was the eruption of siliceous crustal xenoliths representative of the sedimentary basement beneath the volcanic edifice. These xenoliths are quartzites that occurred as subspherical bombs enclosed in a thin trachybasaltic lava envelope. A high-temperature reaction corona developed at the quartzite-magma interface in which alkaline differentiated melts of hybrid origin coexist with newly-formed clinopyroxene crystals different to those found in the host trachybasaltic lava. This characteristic makes it possible to quantify the effect of magma contamination by siliceous crust in terms of clinopyroxene-melt element partitioning. For clinopyroxenes from both lava flow and hybrid melt expected relationships are observed between the partition coefficient, the valence of the element, and the ionic radius. However, for the hybrid melt, there is a decrease in the partition coefficients for transition metals (TE), high-field strength elements (HFSE) and rare earth elements including yttrium (*REE*+Y), and an increase for large ion lithophile elements (LILE) due to coupled substitutions one the *M*1, *M*2 and *T* sites of the type $^{M1}(\mathrm{Al}, \mathrm{Fe}^{3+}) + {}^{T}\mathrm{Al} = {}^{M2}(\mathrm{Mg}, \mathrm{Fe}^{2+}) + {}^{T}\mathrm{Si}$. The different incorporation of trace elements into clinopyroxenes of hybrid origin is controlled by cation substitution reactions reflecting local charge-balance requirements. According to the lattice strain theory, simultaneous cation exchanges across the *M*1, *M*2, and *T* sites have profound effects on *REE*+Y and HFSE partitioning, whereas temperature and melt composition have only a minor effect. As a consequence, partition coefficients for *REE*+Y and HFSE diverge significantly from those derived by magmatic differentiation, causing unexpected elemental overprints on the primary geochemical signature of magma.

Magmatic processes inferred from geochemical and Sr-Nd-isotopic data on the < 5 ka Zaro lava complex, Ischia Island (southern Italy)

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Keywords: Ischia Island, Zaro lava complex, magmatic evolution, mineral chemistry, isotope geochemistry, mingling.

The Zaro lava complex, located on the western sector of the Ischia volcanic island (Gulf of Naples, southern Italy), is the product of one of the few effusive eruptions occurred in the last period of activity (< 5 ka). The complex is made up of a white trachytic main lava flow (Zaro lava *s.s.*), hosting rounded-shaped enclaves of both mafic (shoshonite) and felsic (trachyte) composition. Major and trace elements and isotopic ($^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$) data have been acquired on whole rocks and separated minerals. Mafic enclaves (Mg# = 60-62, CaO = 7.71-8.31 wt%, Cr =117-143 ppm, Ni = 52-61 ppm, Zr =150-164 ppm, Sr = 503-526 ppm, *LREE* enriched compared to *HREE*) have low $^{87}Sr/^{86}Sr$ (0.70495-0.70501) and high $^{143}Nd/^{144}Nd$ (0.51268-0.51269). Trachytic lavas and felsic enclaves (SiO_2 = 60.61-61.71 wt%, K_2O = 6.51-7.43 wt%, Na_2O = 5.00-6.83 wt%, Rb = 243-428 ppm, Sr = 90-158 ppm, Zr = 385-773 ppm) exhibit higher $^{87}Sr/^{86}Sr$ (0.70608-0.70615) and lower $^{143}Nd/^{144}Nd$ (0.51255-0.51256). The strong isotopic difference between mafic enclaves and trachytes rules out a simple crystallization process for the variable facies of the Zaro lava complex. Moreover, in mafic enclaves petrochemical and possibly isotopic disequilibria between phenocrysts and their host rocks suggest occurrence of mingling processes or crystals entrapment from a distinct magmatic phase: indeed, many clinopyroxene and feldspar crystals are in chemical equilibrium with more evolved compositions (trachytic to trachyphonolitic). Trachytic lavas and felsic enclaves are chemically similar and do not display isotopic disequilibria between phenocrysts and host rocks.

The last 5 ka of volcanic activity at Ischia were characterized by emplacement of products resulting from interaction between chemically and isotopically distinct batches of magma (Cava Nocelle, Vateliero and Molara; D'Antonio et al., 2013). Although these products show features comparable to those of the Zaro mafic enclaves, the last have significantly lower Sr and higher Nd isotopic ratios. Therefore, enrichment processes, such as assimilation of continental crust or mantle contamination in different conditions, should be invoked to justify the difference in isotopic features. Additionally, although the two evolved facies of the Zaro lavas have comparable chemical compositions and "uniform" isotopic signature, field analysis shows evidence of mingling between similar magmas with different viscosities. This process could have played a significant role in triggering the eruption.

D'Antonio, M., Tonarini, S., Arienzo, I., Civetta, L., Dallai, L., Moretti, R., Orsi, G., Andria, M., Trecalli, A. (2013): Mantle and crustal processes in the magmatism of the Campania region: inferences from mineralogy, geochemistry, and Sr–Nd–O isotopes of young hybrid volcanics of the Ischia island (South Italy). Contrib. Mineral. Petrol., 165,1173-1194.

Raman spectra of a haplogranitic system: correlation with melt viscosity

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Keywords: Raman spectroscopy, glasses, viscosity, melts.

The structure of silicate melt governs its viscosity, which influences its transport, degassing rate and, ultimately, eruption style of volcanoes. Raman spectroscopy can provide insights into the melt structure and recent studies have shown that correlations between Raman spectra of glasses and melt viscosity can be established. However, so far, these studies focused on simple systems and, therefore, applications to geologically-relevant systems are not possible.

Here, we performed a systematic Raman spectroscopic study on a haplogranitic system with the addition of 5, 10 and 20 wt.% of alkali oxides. The increasing amount of alkali oxides influences significantly Raman spectra of glasses. We observed:

1) A shift of the low-frequency region (250-750 cm^{-1}) toward higher wavenumber and a variation of the Raman features representing the distribution of different silica rings.

2) A dramatic variation of the high-frequency region (850-1200 cm^{-1}) of spectra. This region reflects the relative distribution of Q-species.

We performed deconvolution of Raman spectra in order to study the evolution of the structure polymerization with changing chemical composition. Therefore, a correlation between Q-species distribution and the measured viscosity is presented.

Understanding the relationship between Raman spectra, structure and viscosity represents a crucial aspect for the development of physically-based viscosity models of magma transport.

Experimental observation of extremely rapid clinopyroxene growth in a trachybasaltic melt: clues on phenocryst crystallization kinetics in naturally cooled magmas

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Keywords: clinopyroxene and magnetite growth, crystallization kinetics, Mt. Etna volcano.

We present isothermal/isobaric crystallization experiments performed at P = 400 MPa, T = 1100°C, H_2O = 0-2 wt.%, fO_2 = NNO+2 buffer. The starting composition is a synthetic glass reproducing one of the most primitive trachybasalts (SiO_2 = 47.6 wt.%, MgO = 6.5 wt.%, Na_2O + K_2O = 5.1 wt.%) ever erupted at Mt. Etna volcano (Sicily) and belonging to the Mt. Maletto formation. Reversal experiments were carried out by superheating the starting glass from room temperature up to 1300°C with a rate of 80°C/min. This temperature was kept constant for 30 min and then decreased to the target crystallization temperature with a rate of 80°C/min. The isothermal condition was maintained using variable dwell times of 0.5, 1, 2, 4, 8, and 24 h. Results show that the paragenesis is characterized by the ubiquitous formation of clinopyroxene and titanomagnetite with proportions variable as a function of T and H_2O. Rare plagioclase is observed only in a few experiments under anhydrous condition, while it is systematically absent in hydrous experiments.

Importantly, the time series experiments track the progressive growth of clinopyroxene whose textural maturation proceeds from dendritic (shorter dwell times) to almost euhedral (longer dwell times), likely reflecting a shift in the rate-limiting process for crystal growth. Clinopyroxene and titanomagnetite from hydrous runs show crystal size much greater than that measured from anhydrous runs. However, a crystal growth-dominated regime is documented under both anhydrous and hydrous conditions. In particular, the achievement of larger crystal sizes is hampered only by the impingement either with adjacent crystals or with the capsule walls.

Considering that the *liquidus* temperature of the trachybasaltic melt is 1200°C, it can be concluded that superheating (100°C) and nominal undercooling are thermodynamic driving forces exerting dramatic effects on crystal growth rates. In contrast, no apparent relationships exist between the average sizes of clinopyroxene crystal populations and the fraction of crystallized volume in the experimental products. Therefore, solidification kinetics are extremely fast for mafic alkaline magmas, such as those erupted at Mt. Etna volcano, potentially leading to the formation of millimeter-to-centimeter-sized phenocrysts in just a few hours.

The rheology and the volume of crystal-rich lava flows from Ischia Island (Campania, Italy)

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Keywords: Ischia, lava flows, dome, rheology, textural analysis, volume, risk mitigation.

Ischia Island is a densely inhabited active volcano, hosting a permanent population of about 50,000 people which increases during summer thanks also to the thriving farms, tourist resorts and commercial enterprises. Nonetheless, the risk associated with lava flows in case of renewal of activity is relatively understudied.

We present a textural analysis and a rheological study of natural and partially-crystallized magma from the Arso Lavas (1302 A.D) and Zaro Lava domes and flows (6 ± 2.2 ka). The present work aims at investigating the role of the crystal cargo in the rheological behavior of these lava flows, that are able to flow for a few kilometers, despite their high viscosities.

The eruption duration of Arso Lavas is known because these are the product of the last eruption at Ischia, which occurred in 1302 A.D. With this information it is possible to set constraints to a rheological model that can be extended to estimate duration and behavior of other lava flows in the island, with similar physical properties and chemical composition.

The textural analysis with the crystal and vesicle size distribution is the starting point for the characterization of the Zaro Lava domes and flows and the Arso Lavas and for estimating the rheological properties during the transport and the emplacement.

One of the important results expected from this work in progress is the relationship, in a simplified model, between the velocity of the lava flows and terrain slope. All the data, helpful to apply the Jeffreys equation, relative to the environment and to the area of emplacement, like position, geometry and slope of the channel, have been evaluated by a GIS analysis. The volume of most of lava deposits have been extrapolated by masking a DEM and calculating the volume values above a set of reference plains, taking into account also the shape of lava domes before deflation. Thanks to this metodology it has been possible to estimate also the VEI for each lava deposits which varies in this island between 1 and 3.

Most of these results may be used by the Department of Civil Protection for the risk mitigation in this country.

Exponential decay of concentration variance during magma mixing: robustness of a volcanic chronometer and implications for the homogenization of chemical heterogeneities in magmatic systems

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Keywords: magma mixing, experiments, chemical exchanges.

Magma mixing has been suggested to be a potential volcanic chronometer to estimate the mixing-to-eruption time. Nevertheless, its statistical robustness is not yet established, despite it represents a fundamental prerequisite to apply reliably this conceptual model. Here, a new set of chaotic magma mixing experiments was performed using natural melts in order to evaluate their reliability as potential geo-chronometers. In particular, experiments at different mixing times and at condition relevant for natural magmatic systems were performed. The degree of reproducibility of experimental results was tested repeating one experiment at the same starting conditions and comparing the compositional variability of major elements. We further tested the robustness of the statistical analysis by randomly removing from the analysed dataset a progressively increasing number of samples. Results show that experiments can be reproduced with a high level of consistency, highlighting the robustness of the method to derive empirical relationships linking the efficiency of chemical exchanges and mixing time. In addition, it is shown that the number of analysed samples does not impact significantly on the statistical quality of these empirical relationships. In particular, they remain valid by removing up to 80% of the analytical determinations. Experimental results were applied to constrain the homogenization time of chemical heterogeneities in natural magmatic system during mixing. Results show that, depending on the Reynolds number characterizing the mixing process, chemical heterogeneities can be homogenized in short times, from a few minutes to a few days.

Water content estimation of hydrous natural glasses: a Raman spectroscopy study

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Keywords: Raman spectroscopy, water, silicate glasses.

Water is the most abundant volatile dissolved in silicate melts and strongly affects melt structure, magma transport and eruptive style.

Raman spectroscopy is a non-destructive technique used to investigate the chemistry, oxygen fugacity, and volatile content of silicate glasses. This technique can give insight into the silicate structure and water content of silicate melts and presents several advantages such as: 1) high-spatial resolution, 2) non-destructive character, 3) minor sample preparation, 4) crystals detection, and 5) the possibility to perform *in situ* investigations at high temperature and pressure.

Over the past few decades, several authors adopted different protocols for the quantification of water content of silicate glasses (mostly iron-free) using Raman spectroscopy based on internal and external calibration. Here, we discuss these different approaches using a wide range of chemical composition of glasses, which has never been investigated so far. We used 22 natural samples ranging from basaltic to rhyolitic composition and water content up to 4.5 wt% (independently measured by KFT or TGA). By using two different Raman spectrometers we also explore potential causes for variations in the estimation of water content due to instrumental effects. Based on the results of this study, we show that the difference in instrumental response is the main factor against a unique calibration for the estimation of water content. On the other hand, the choice of the analytical procedure depends significantly on the iron content and its oxidation state. Finally, we suggest a simple correlation between the glass structure as inferred by Raman spectroscopy and the glass transition temperature.

Rheology of H_2O-filled bubble-bearing magmas: experimental determination at low strain rates

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Keywords: bubble, viscosity, magma rheology, strain rate.

As magma ascends to the Earth's surface, bubbles form as a consequence of the evolving saturation state of volatiles dissolved in the melt. Exsolved volatiles strongly control the rheological behaviour of magma and volcanic processes. In this view, the effect of porosity on the bulk viscosity of the magma is a critical element in explaining eruptive styles changing (*e.g.*, explosive *vs.* effusive). Nevertheless, the effects of bubbles on the rheology of magma are not well characterised, especially in silicic magmas. It is known that the presence of bubbles may either increase or decrease the viscosity of the suspension, depending on the deformation environment. A general parameterization is not yet available. Existing models include 1) theoretical models; 2) empirical functions fitted to experiments on analogue materials; 3) empirical functions constrained by few experiments on natural materials.

Here we present a new set of experiments designed to investigate the rheology of bubble-bearing melts at high temperature (750-800°C), low strain rates (10^{-6}-10^{-7} s^{-1}) and variable bubble contents.

Experiments were performed at 1 atm using a Setaram Setsys vertical dilatometer.

The starting materials are 5 × 5 mm cores of natural rhyolitic obsidian from Hrafntinnuhryggur, Krafla, Iceland (bubble and crystal-free) containing 0.11(4) wt% of initial dissolved H_2O.

The experimental procedure is composed by two sequential steps: i) synthesis of bubble-bearing materials by heating and expansion due to foaming; ii) deformation of the foamed samples.

During the first step, the obsidian cores were heated above the glass transition temperature (Tg), at 900-950°C and held for set amounts of time (10-24 h); the volume of the foamed samples increased because H_2O vapor-filled bubbles nucleated and expanded. The change in volume (measured by He-pycnometry) is linked to the change in porosity (ranging between 10-50 vol%). For the second stage, the sample was cooled down to different target T (750-800 °C), and a constant load (150 g) was applied by a silica probe to the core, deformed isothermally for 5-20 hours.

The variation in length (displacement) and volume (porosity) was used to calculate the viscosity of the foamed cores using Gent's equations.

Preliminary results suggest a lower effect of bubbles on the bulk viscosity, compared to recently published experimental data on the same starting materials. The latter were performed at higher strain-rates and the pores were empty (air-filled). Therefore, the observed difference could be ascribed to the lower deformation rates of this study and/or to the presence of H_2O filling the bubbly phase. Additional experiments will investigate the relative contribution of these two factors.

How the modern Etna plumbing system works: messages from the crystal cargo of recently erupted volcanic rocks

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Keywords: Etna, magmatic processes, diffusion modeling, timescales, plagioclase, olivine.

Advancement in the quality of geophysical methods and accessibility of *in situ* analytical techniques during the last twenty years has led to an exponential increase of the knowledge on geometry of volcanic feeding systems and on processes of magma transfer and degassing that drive the eruption onset. Among the multiple techniques of investigation of the plumbing system dynamics, analysis of textures and chemical zoning in minerals has been established as one of the most efficient tools. This study integrates important findings obtained through innovative petrological approaches at Mt. Etna that combine textural, chemical and temporal records of magmatic crystals. Final aim is production of a realistic spatial-temporal reconstruction of magmatic dynamics preceding and accompanying the eruptive activity at Mt. Etna. The post-2011 period has been selected as the best case-study, because it provides the opportunity to evaluate modes and timescales of magma transfer across a very dynamic and articulated plumbing system in a limited timespan. An extensive compositional dataset of plagioclase and olivine crystals from lavas emitted during the paroxysmal eruptions occurred during the 2011-2013 period has been therefore used for these scopes. Plagioclase crystals display various textures at the core and rim indicating complex histories of magma crystallization under variable chemical and physical conditions. The Sr/Ba ratio in oscillatory-zoned plagioclase revealed the coexistence into the plumbing system of low-Sr and high-Sr magma volumes. Fe-Mg zoning *vs.* An in correspondence of plagioclase sieve textures also suggests that gas-flushing had a dominant role in triggering the paroxysmal eruptions. Timescales of crystal residence in the plumbing system from Sr-diffusion modeling are short (17 years on average), suggesting limited magma storage due to efficient transfer dynamics to the surface. Chemical zoning in olivines highlights processes of multi-step magma transfer and residence into various magmatic environments, whose P-T-H_2O-CO_2-fO_2 were constrained by thermodynamic modeling. From a deepest reservoir (~ 600 MPa), the most primitive magma (bearing olivines with Fo_{84} cores) moved along dominant pathways, intercepting other reservoirs at ~ 390 MPa (Fo_{80-82} olivine cores), 250 MPa (Fo_{78} olivine cores), ~ 140 MPa (Fo_{75} olivine cores) and finally at ~ 40 MPa (Fo_{70-73} olivine cores). Fe-Mg diffusion modeling in olivine defines timescales of magma transfer and storage across these magmatic environments, which vary from ~ 1 to 18 months, whereas intrusion and mixing by more basic magma into the shallowest reservoir occurred always within 5 months before eruption. Relevance of this study relies on the thermodynamic constraints and temporal quantification of volcanic processes that may have considerable consequences in development of unusual, high-energy eruptions at basaltic volcanoes generally acknowledged for their weak to mild explosive activity.

The depth of igneous cumulates in the Lesser Antilles island arc

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Keywords: island arc, igneous cumulate, geobarometry, gabbro.

How is the crust made and how do magmas evolve in island arc settings? Geophysical and petrological methods developed in the last decades allowed to acquire new data that can help answering these questions, but the complete picture of these processes is still unclear. One of the reasons is the sampling bias: in active island arcs, access to the plutonic sequences is typically limited to few xenoliths entrapped by the erupting magma and fossil island arc sections are exposed only in very few localities. Another reason is the lack of precise and accurate geobarometers for plutonic rocks that can help constraining their original depth of formation.

In the Lesser Antilles island arc, the volcanic products host a large number of plutonic xenoliths, mostly of cumulate origin, showing a variety of mineralogical compositions. The ubiquity of these xenoliths gives an exceptional opportunity to investigate the evolution of magmatic systems in an island arc setting. The estimated thickness of the crust in the Lesser Antilles varies between 25 and 35 km (*e.g.*, Boynton et al., 1979), suggesting that the cumulates likely equilibrated at pressures < 8 kbar. Therefore, only geobarometric estimates with low associated uncertainties ($1\sigma < 2$ kbar) can provide useful insight into the vertical distribution of lithologies in the crust. We will show that a multiple-reaction approach adopting an internally consistent thermodynamic dataset (*e.g.*, Powell & Holland, 1994) is capable to predict the pressure (*P*) of mafic and ultramafic igneous rocks with uncertainties on the order of 1 kbar. This method has been tested on phase equilibria experiments in basaltic and peridotitic systems and has been then applied to the olivine-bearing cumulate xenoliths from the Lesser Antilles.

Estimated *P*'s along the arc are mostly in range 1.0 – 3.0 kbar, with *P* uncertainties (1σ) for the individual samples varying between 0.7 and 1.8 kbar. No systematic variations are observed between the different islands, even if few samples from Dominica and St Kitts show considerably higher *P* (~ 6.0 kbar). Temperatures, estimated by externally calibrated methods (*e.g.*, Ca-in-olivine thermometry) vary in the range 880 – 1020°C. We will discuss the significance of these estimates for the petrogenetic processes along the arc and how they can be combined with seismic and gravimetric data to produce an integrated model for the crust of the Lesser Antilles arc.

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Session S28:

Basaltic explosive volcanism: magma ascent, degassing and eruptive dynamics

Conveners:

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Insights in the plumbing system of Stromboli volcano (Italy) from seismic tomographic images and ground deformation models

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Keywords: Stromboli, geodetic data, seismic tomography.

In the eastern sector of the Aeolian Archipelago, the NE-SW direction represents the preferential paths for magma ascent from the deep source region into the shallow reservoirs. Beneath Stromboli the deep source of magma is located in the uppermost mantle just above the Moho (9-15 km depth; Martinez-Arevalo et al., 2009). An intriguing open issue is the characteristics of the plumbing system and its relation with the eruptive activity.

Since 1992 the ground deformation monitoring network has revealed important features of the shallow-intermediate plumbing of Stromboli volcano through the modelling of continuous tilt and GPS data recorded during unrest periods and eruptions. Geodetic observation and models from the 1994 (Bonaccorso, 1998) and 1999-2000 (Mattia et al., 2008) intrusions, the 5 April 2003 paroxysm (Mattia et al., 2004), the 2007 eruption (Bonaccorso et al., 2008) and the 2007 paroxysm (Bonaccorso et al., 2012) are here compared to the recent results achieved by seismic tomography.

The seismic images of the inner structure of Stromboli have been obtained by jointly inverting data of seismic local events, recorded in the 2006-2007 period, and offshore air-gun shots, recorded during the 2006 active seismic tomography experiment (Patanè et al., 2017). These new tomographic images highlights: i*)* the position of the Stromboli's shallow magma chamber (between -2.0 and -4.0 km of depth), recognized as a high velocity body (a cooled cumulative magmatic body), that present a roughly NE-SW elongated geometry, and ii*)* the region where magma actually rise and is stored, representing the present shallow volcanic plumbing system feeding the eruptive activity.

In particular, this imaged plumbing system located down to 4 km of depth, where batches of magma are periodically pushed up, coincides with the modeled sources of ground deformations, supporting the most recent petrological and geochemical hypothesis.

We retains that this multidisciplinary comparison represent: 1) an useful tool for a crossed confirm of the respective accuracy of the two independent geophysics datasets; 2) an important achievement for the scientific community investigating the processes of magma dynamics in this volcano and 3) a starting point for the revision and the improvement of the monitoring system of Stromboli.

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Preliminary data on the dispersal area and textural features of products ejected by the 16 March 2017 phreatomagmatic explosions at Etna

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Keywords: Mt. Etna, phreatomagmatic explosions, volcanic hazard.

In the last 20 years, lava fountaining and strong Strombolian activity have often occurred from the South-East Crater (SEC) first and, after 2011, from the New South-East Crater (NSEC) of Mt. Etna. These craters have now coalesced to form a single cone apparatus which resumed activity on 27 February 2017, starting a new eruptive period. A first eruption lasted only 3 days, producing lava effusion and moderate Strombolian activity and building a small cone above the SEC-NSEC rim. On 15 March, the same vent erupted again, while another vent opened in the southern mid-slope of the cone producing low-fed lava flows towards SE. On 16 March, the interaction of an advancing lava lobe with the snow covering the ground produced a fast and unexpected short-sequence of explosions, lasting less than 1 minute. White vapor, brown ash and coarse material rose up quickly, and a group of people (hiking in the dispersal area of the ballistic material) were wounded by the ejected products, with mild to serious injuries.

A few surveys on the phreatomagmatic deposit were carried out in the following days, aimed at evaluating the dispersal area of the products, reaching up to 200 meters away, and collecting representative samples. From the "contact site" between the lava flow and snow, the deposit had an elongated fan shape. In the proximal area, the deposit was poorly sorted and formed by a continuous carpet of coarse ash, lapilli and bombs up to 50 cm of diameter. Both the mass loading per square meter and the grain-size of the deposit gradually, but quite quickly, decreased away from the "contact site", and the distal deposit consisted of a few-cm-sized lapilli located at few meters of distance from each other. We also examined the lithology of the ejected products in order to evaluate if related to "fresh" lava or "old" lithic material. Finally, we analyzed selected thin sections and fine particles under the microscope to find possible textural evidence of the interaction between lava and melted snow. Our preliminary data will be improved for modeling and will provide insight into the eruptive dynamics and the fragmentation process related to this type of phreatomagmatic explosions, which are quite rare at Etna, but represent an important issue for the assessment of volcanic hazard.

Non-standard cooperative processing and interpretation of multi-variate data sets: the example of Solfatara Volcano, Italy

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Keywords: cooperative inversion, seismic reflection, tomography, cluster analysis.

Geophysical techniques are nowadays routinely applied in volcanic environments to image their subsurface structure and understand the dynamics occurring in these complex settings. The use of several geophysical methods allows in theory to obtain redundant and complementary information about the subsurface conditions due to the different sensitivity of the geophysical methods to different parameters such as P- and and S-wave velocities, bulk electrical conductivity, density, etc. However, the geological complexity of volcanoes strongly affects the results and the associated uncertainty of each geophysical technique. On the other hand, a cooperative processing and interpretation of multi-variate geophysical and/or geological datasets can potentially decrease model uncertainty and provide a reliable geophysical imaging, which is fundamental for a better and more accurate characterization of the subsurface.

In this paper, we apply two cooperative processing and interpretation schemes to multivariate data acquired during the MED-SUV RICEN experiment performed at Solfatara from 2014 to 2016. The RICEN experiment goal was to study the changes in the properties of the volcano at small scales through repeated geophysical and geochemical observations over time. We applied two different processing and data integration schemes based on data from reflection seismology, seismic P-wave tomography and electrical resistivity acquired along two orthogonal 2*D* profiles. From these data, we obtain an image-guided electrical resistivity tomography and a post-processing integration of seismic and electric data.

The image-guided electrical resistivity tomography is achieved by regularizing the inversion of the electrical data with structural constraints extracted from a depth converted seismic section using image processing tools. This approach enables to focus the reconstruction of electrical resistivity anomalies along the features visible in the seismic section, and acts as a guide for interpretation in terms of subsurface structures and processes.

To integrate co-recorded P-wave velocity and electrical resistivity values, we apply a data mining tool, the k-means algorithm, to individuate relationships between the two set of variables. This algorithm allows to locate different data clusters with the goal of minimizing the sum of squared Euclidean distances within each cluster and maximize it among different clusters of the multivariate data set. We obtain a partitioning of the multivariate data set in a finite number of well-correlated clusters, representative of the optimum clustering of our geophysical variables. The result is an integrated tomography that shows a finite number of homogeneous geophysical facies, and therefore permits to highlight in a quantitative manner the main geological features of the subsurface.

The paroxysmal activity of the New Southeast Crater, Mt. Etna (Italy), from 2011 to 2013

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Keywords: Etna, New Southeast Crater, paroxysmal activity.

Mt. Etna in eastern Sicily (Italy) is one of the most active volcanoes of the Earth. Its summit craters are Voragine (VOR), Northeast Crater (NEC), Bocca Nuova (BN) and Southeast Crater (SEC), with a new cone formed since 2011 on the eastern flank of SEC and named New Southeast Crater (NSEC). Summit eruptions occurring from these craters produce gas emissions, Strombolian to paroxysmal activity, as well as lava overflows and ash falls that frequently interfere with air traffic. We focus on the powerful episodes of lava fountains produced by NSEC from 2011 to 2013. In particular, the major and trace elements composition of the erupted products, integrated with geophysical and geochemical monitoring data, have allowed to track the pre-eruptive magmatic processes which cause magma evolution, as well as to investigate the factors which may have somehow influenced the eruptive style of the volcano from 2011 to 2013. Finally the comparison of the NSEC eruptive activity from 2011 to 2013 with other paroxysmal episodes of the SEC occurring in 2000 and 2007-08, allowed to individuate a few key-factors, such as the geometry of the conduits, the state of fracturing of the volcano, the dynamics of the melt-gas mixture, whose interplay drives paroxysmal activity at Mt. Etna and influences changes of the volcano's eruptive style.

The 1909 Chinyero eruption on Tenerife (Canary Islands): insights from historical accounts, and tephrostratigraphic and geochemical data

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Keywords: Chinyero, Tenerife, violent strombolian, basaltic explosive eruption, volcanic hazard.

The last eruption on Tenerife (Canary Islands, Spain) started on 18 November 1909 from the El Chinyero vent on the northwestern Santiago rift. This fissural eruption fed by basanitic magma was well documented by scientists and eyewitnesses, but there is a lack of data on the high-energy phase that produced the most significant emissions of ash and lapilli at the onset of the eruption. In this work, we review historical documents (*e.g.*, newspapers, dispatches, telegrams); eyewitness accounts and scientific reports were reviewed from a volcanological perspective and integrated with data from the analysis of deposit features, allowing an accurate reconstruction of the eruption and its dynamics. The 1909 eruption of Chinyero was fed by a compositionally discrete magma batch that ascended rapidly within the crust, producing rather violent pulsating Strombolian explosive activity in the early phases of the eruption. This activity produced a *ca.* 80 m high scoria cone and heavy fallout of lapilli and ash over the entire northern sector of the island of Tenerife. The energy of explosive activity waned after 3 days, giving way to the weak Strombolian explosive activity that contributed to a lesser extent to the buildup of the pyroclastic pile. Eruptions such as those from the Chinyero vent in 1909 are representative of rift activity on Tenerife and constitute a volcanic hazard for present-day inhabitants.

Dynamics of pyroclastic density currents generation and ballistic ejection during shallow hydrothermal blasts: insights from the deposits, physical modelling and numerical simulation of the 13th Century "Breccia di Commenda" eruption (Vulcano island, Italy)

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Keywords: Vulcano Island, Breccia di Commenda eruption, hydrothermal explosions.

Understanding the dynamics and effects of hydrothermal eruptions is crucial in assessing hazard in volcanic and geothermal areas. The active caldera in the northern part of the Island of Vulcano (southern Italy) hosts in its centre the La Fossa cone, that experienced various hydrothermal eruptions, with the most important event which occurred during the 13th Century AD (Breccia di Commenda eruption, BdC). We present a detailed study of the BdC eruption through the integration of stratigraphic reconstruction with sedimentological data. The BdC event occurred in contemporaneous with the eruption of Rocche Rosse (1230 ± 20 AD) from the Island of Lipari. The study of about 170 tephra logs revealed that the eruption occurred in three main phases. The deposit emplaced during the opening, north-westerly dispersal fallout (Phase 1) consists of grey, altered lithic ash bearing accretionary lapilli. The eruption waxed (Phase 2) with several explosions, producing an asymmetric shower of ballistic blocks and the emplacement of narrowly dispersed lithic-rich, stratified pyroclastic density current deposits, followed by a radially distributed, topographically controlled, coarse-grained pyroclastic density current which represent the main body of the breccia deposit. Finally, the eruption waned with the generation of accretionary lapilli-rich ash fall deposits (Phase 3). Tephra units emplaced during pyroclastic density current events range in volume from 2.1×10^4 m^3 to 2.7×10^5 m^3. Sedimentological analyses revealed that the eruption occurred with little or null involvement of fresh magma and that the breccia deposit was mostly composed by lava fragments, suggesting that the crater area prior to eruption was almost filled by lavas, which possibly helped in gas pressure build up. The most intense stages of the eruption (Phase 2) was investigated by numerical simulation. A new three-dimensional numerical model was adopted, describing the eruptive mixture as a Eulerian-Eulerian two-phase non-equilibrium gas-particle fluid plus a one-way coupled Lagrangian ballistic particle phase. At the initial simulation time, a pressurized, high-temperature mixture (initially confined within the shallow vent) can decompress and expand in the atmosphere forming an eruptive cloud, while ballistic particles are rapidly accelerated by the coupling effect of drag and pressure forces. After an initial expansion stage (lasting only 2-3 seconds), the eruptive cloud collapses forming lateral pyroclastic density currents (PDCs). We show that PDC features and ballistic ranges (up to 2.2 km) are consistent with an exploding body having a mass of about 10^9 kg, an initial overpressure above 10 MPa, a maximum temperature of about 250°C and a maximum depth less than 200 m. We finally discuss present findings in the framework of volcanic hazards posed by hydrothermal explosions on active volcanoes like the ones occurred at Ontake (Japan) in 2014 and Tongariro (NZ) in 2012.

The nature of the shallow conduit of Stromboli in the major explosion of 21 January 2010 revealed through textural and geochemical characterization of bombs

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Keywords: Strombolian, conduit plug, textural analyses, melt inclusions.

From May 2009 to March 2010, nine major explosions were recorded at Stromboli volcano. The major explosion of 21 January 2010 from the central crater was the only one characterized by a SSE-SW dispersal direction. This study focus on this bomb-dominated deposit. The quenched rings of twelves bombs was used to perform density/porosity analyses, textural and chemical analyses in order to define the mechanisms operating in the shallow conduit during this major explosion. Although density values of the quenched portions are always lower than the global bombs density values, they confirm their large variations (1.1-2.3 g/cm^3). Textural data highlight a vesicularity between 16 and 60%, with unimodal distributions and a main mode at 1.8 mm. Crystallinity ranges from 30 – 60% and through crystal size distributions (CSDs) measurement microlites (< 100 µm), microphenocrystals (100-350 µm) and phenocrystals (> 350 µm) were distinguished. The presence of a single nucleation event is consistent with a Strombolian burst dominated by a slug characterized by a single bubble nucleation event, growth, coalescence and expansion. Vesicles and crystals content variations are consistent with recent textural studies, which show strong textural variation in the shallow magma. This variability cause important rheological differences but not chemical contrasts. In fact, these samples are characterized by a strong chemical homogeneity. The matrix glasses and the melt inclusions are comparable, with 50-55 wt% SiO_2 and 0.39-0.57% CaO/Al_2O_3. The volatile content is representative of a shallow magma with a maximum of 0.5 wt% H_2O and CO_2 below the detection limit, corresponding to a depth of almost 500 m. For this explosion, all data keep out the participation of the deep magma and only the shallow magma was involved. We suggest that the dense, degassed and crystal-rich magma forms a plug at the top of the conduit, determining the slug accumulation; when the volatile pressure is enough for breaking the plug, the explosion occurs with the same dynamics of the normal activity. The long inactivity of the crater involved (a few days) allow the plug to mature and promote a bigger explosion.

A new hydrothermal moissanite cell apparatus for optical *in situ* observations at high pressure and high temperature, with applications to bubble nucleation in silicate melts

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Keywords: moissanite cell, *in situ* observation, bubble coalescence, degassing, decompression, Ostwald ripening.

Magmatic degassing controls the intensity and the style of volcanic eruptions. Understanding the mechanisms and rates at which volatiles are exsolved and released from the magma is fundamental for the interpretation of the volcanic activity and the definition of the hazard associated to explosive eruptions. Natural samples and products from quench experiments provide only a snapshot of the final state of volatile exsolution, leaving the processes occurring during its early stages unconstrained. In order to fill this gap, we developed a new hydrothermal moissanite cell for *in situ* experiments at pressures up to 1000 bar and temperature to 850°C. The new technique allows the direct observation of various phenomena, such as bubble nucleation, growth and dissolution in silicate melts, at accurately controlled rates of heating, cooling and compression or decompression. Several pilot experiments were performed on a haplogranitic melt at temperature of 750°C and under variable pressure regimes (pressure oscillations between 500 and 1000 bar and decompression from 800 to 200 bar at variable decompression rates). Bubble nucleation occurs in a short single event upon heating of the melt above the glass transformation temperature and upon decompression, but only during the first 100 bar of decompression. New bubbles nucleate only at a distance from existing bubbles larger than the mean diffusive path of water in the melt. Bubbles expand and shrink instantaneously in response to any pressure change. The bubble-bubble contact induced during pressure cycling and decompression does not favor bubble coalescence, which is never observed at contact times shorter than 60 s. However, repeated pressure changes favor the diffusive coarsening of larger bubbles at the expense of the smaller ones (Ostwald ripening). Experiments with the haplogranite show that, under the most favorable conditions of volatile supersaturation (as imposed by the experiment), highly viscous melts are likely to maintain the packing of bubbles for longer time before fragmentation. *In situ* observation with the new hydrothermal moissanite cell allow to carefully assess the conditions of bubble nucleation, eliminating the uncertainty given by the *post mortem* observation of natural and experimental samples run using conventional experimental techniques.

On the eruptive style transition at calc-alkaline volcanoes: the example of the 1913 eruption at Fuego de Colima volcano (Mexico)

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Keywords: Colima, triggering mechanisms, numerical simulations.

The comprehension of triggering mechanisms that lead eruptive style changes (comprising passage from no-eruption to eruption) is one of the most emergent topics in present day volcanology.

An excellent case study for investigating such transitions is the 1913 eruption of Fuego de Colima, Mexico. This volcano is characterised by almost continuous extrusion of lava domes, alternating to lava effusion and Vulcanian explosions. Sporadically, larger explosive events occur, as in 1818 and 1913. The 1913 eruption progressed in 3 phases: opening, vent clearing and sub-Plinian column. The volcanological data were used as inputs and constraints for numerical simulations conducted to reconstruct the pre-eruptive scenario of the volcano (lava dome extrusion) and its following explosive phase (Saucedo et al., 2010). Results show best matches for hybrid geometry (dyke evolving to a shallow cylinder) with a fragmentation level located at depths < 2 km. The volume contained in the feeding system before the explosive phase is less than the whole volume of the eruption (Bonasia et al., 2011), allowing to hypothesise the partial withdrawal of magma from the chamber. The transition from dome extrusion to the unusual sustained explosive phase asks for investigation on what triggered the eruptive style transition. Some hypothesis were analysed: arrival of fresh magma documented in the petrography of products, volcano spreading and/or tectonic earthquakes, which might have reduced local stresses resulting in an increasing driving pressure able to sustain the magma acceleration, fragmentation and its continuous eruption over few hours.

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Helium Isotopes in volcanic gases quantify refill and pressure buildup in magma reservoirs at Mt Etna

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Keywords: noble gas geochemistry, magma degassing, modeling, magma chamber overpressure.

Episodes of magma injection into crustal reservoir are recognized as the main trigger of eruptive activity of volcanoes (Caricchi et al., 2014). The resulting buildup of internal pressure controls the magma amount leaving the chamber, the failure of wall rocks, and dike opening until the eruption (Tait et al., 1989). While gas geochemistry until now has performed pressure (*i.e.*, depth) assessments of gas exsolution (Caracausi et al., 2003; Paonita et al., 2012), recent improvements in the ability to estimate time-dependent pressurization while occurring in the chamber come from inverse modeling of ground deformation data, which however does not consider the internal evolution of the magma reservoir (Gregg et al., 2013; Cannavò et al., 2015). Here we present a pioneering tool that relates changes in $^3He/^4He$ in volcanic gases to the time-dependent outflow of volatiles from a chamber subjected to evolution of its internal pressure due to a magma injection event. Applying this tool to $^3He/^4He$ time series from Mount Etna volcano (Italy) made it possible to estimate key parameters such as the rate of magma input and the volume change in deep chamber preceding eruptions in near-real time, and to compare them with geodetic estimations. This represents an unprecedented use of $^3He/^4He$ to obtain quantitative information on the physics of magmatic systems, in contrast to this parameter only being used as qualitative indicator of volcanic activity (Sano et al., 2013).

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Magma dynamics within a basaltic conduit revealed by textural and compositional features of erupted ash: the December 2015 Mt. Etna paroxysms

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Keywords: Mt. Etna, ash, explosive activity, basalt, volcanic conduit, magma fragmentation.

In December 2015, four violent explosive episodes from Mt. Etna's oldest summit crater, the Voragine, produced eruptive columns extending up to 15 km a.s.l. and significant fallout of tephra up to a hundred km from the vent.

A combined textural and compositional study was carried out on pyroclasts from three of the four tephra deposits sampled on the volcano at 6 to 14 km from the crater. Ash fractions (Φ=1-2) were investigated because these grain sizes preserve the magma properties unmodified by post-emplacement processes. Results were used to identify processes occurring in the conduit during each single paroxysm and to understand how they evolve throughout the eruptive period.

In particular we evidenced that in the studied paroxysms there is always the contemporaneous occurrence within the conduit of a high viscosity portion with a variable content of microlite and a less viscous volume of microlite-free, gas-rich magma.

During each single episode these heterogeneities can develop in few tens of hours. The time scale for the total refilling of the system and the renewal of magma is in the same order of magnitude (*e.g.*, 30 hours between episode 1 and 2).

The composition of these magma batches changes in time and becomes progressively more evolved, as deeper crystallizing storage of magma are tapped. This behaviour, though not unusual in Mt. Etna's shallow plumbing system, is markedly different from those proposed for some recent summit explosive activity on the basis of bulk chemistry.

Our analysis also confirms that the amount and shape of microlites, together with melt composition, have a strong control on rheological properties.

On this basis, we suggest that the transition between weak intracrater Strombolian activity and paroxysmal phases with km-high sustained columns, could be related to relative proportions within the conduit between high (microlite-rich) and low (microlite poor-gas rich) viscosity portions.

As shown in previous explosive eruptions of Mt. Etna, the ratio between these two components control fragmentation style and plume height. The prevalence of a crystalline volume favours brittle fragmentation and higher column heights. Nevertheless, the gas-rich microlite-free magma batches play an essential role because propel the explosive eruptions.

This work confirms that ash studies represent a powerful tool for unravelling the details of eruption dynamics. Combined textural and compositional investigations of ash, whose time of the eruption is well known, are crucial in this respect. Our results also indicate that compositional information from a single ash component can be misleading and that all components should be analysed in order to gain detailed information on magmatic columns and the development of eruptive processes. We also wish to stress that bulk chemistry, traditionally employed for petrological monitoring, may not be very informative in the analysis of such phenomena.

The 1914 Taisho eruption of Sakurajima volcano: stratigraphy and dynamics of the largest eruption in Japan during the 20th Century

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Keywords: Taisho eruption, Sakurajima volcano, Japan.

The AD 1914 Taisho eruption is the most recent large-scale eruption occurred at Sakurajima volcano (Japan). After a 35-year period of quiescence, the volcano suddenly reawakened few days before the eruption with a seismic crisis recorded at Sakurajima island. The eruption developed along two different fissures located on two opposite sides of the volcano, and was characterized by a complex time evolution and changes in the eruptive style. The eruption began with a Plinian explosive phase in which two convective columns sustained for at least two days rose from the two fissures. This resulted in the deposition of a widely dispersed tephra sequence. After this phase, the explosive eruption progressively waned toward an effusive activity that lasted for several months. Lava fronts finally stopped by April 1915. The lava emission was also accompanied for a few weeks by ash emission. The complex sequence of events characterized by contemporaneous explosive and effusive activities is typical of several observed mid-intensity eruptions (as for example in the case of the recent Cordón Caulle 2011 eruption, Chile). The stratigraphic sequence of the tephra deposits comprises alternating coarse-to-fine lapilli and ash beds dispersed toward the ESE and SE. It was subdivided into three lapilli-bearing units (Units T1, T2 and T3, which correspond to the Plinian phase) and one ash-bearing unit (Unit T4, which corresponds to the final ash venting). Grain-size analyses from each unit reveal a marked polymodal distribution generally described by the sum of two or three Gaussian subpopulations. Both the modes and relative amount of the coarse subpopulations vary with distance from the vent, while those of the fine subpopulation remain nearly constant. Volume estimation of the Taisho tephra deposit accumulated during the Plinian phase of the eruption is 0.33 ± 0.11 km^3, obtained averaging the results from different methods. The height of the eruptive column was also assessed by using four different isopleth maps compiled based on different strategies for the characterization of the largest clast. The average maximum height reached by the eruptive column is estimated at 15.0 ± 1.2 km above the vent, resulting in an average mass discharge rate of $1.1 \pm 0.4 \times 10^7$ kg s^{-1}. Finally, three different classification schemes were adopted to classify the eruption, which plots in the Plinian field.

Session S29:

The study of volcanic ash as a tool for eruption mechanisms and tephra correlations

Conveners:

Raffaello Cioni (Univ. di Firenze)

Marco Pistolesi (Univ. di Firenze)

Paola Del Carlo (INGV, Pisa)

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Proximal counterpart of the widespread Y-3 tephra (29 ka): constraints on a large magnitude eruption at Campi Flegrei caldera

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Keywords: Y-3 tephrostratigraphic marker, Campi Flegrei, glass geochemistry, ^{40}Ar/^{39}Ar.

The distal Y-3 tephrostratigraphic marker preserved in sedimentary archives across the central Mediterranean region is evidence of a major volcanic ash dispersal at *ca.* 29 ka. The spatial distribution of this distal tephra horizon and layer thicknesses are consistent with a large magnitude eruption. Glass compositions revealed that this tephra was sourced from Campi Flegrei caldera (CFc), but there is no prominent or widely traceable proximal eruptive unit at the caldera in the right chrono-stratigraphic position. The lack of preserved deposits raises important questions regarding the eruptive mechanisms responsible for such a widespread ash dispersal. Here we present new geochemical data from proximal eruptive units just beyond the eastern sector of CFc. These deposits satisfy the geochemical variability of the heterogeneous phono-trachytic to trachytic Y-3 distal tephra suggesting they are the proximal equivalent. ^{40}Ar/^{39}Ar dating of the eruptive unit in a drill core (S19) yields an age of 28.96 ± 0.8 ka, which precisely matches the currently most precise ^{14}C age (28,680-29,420 cal yrs BP; Albert et al., 2015) of this distal tephra and reinforces the proximal-distal correlation. The proximal deposits are characteristic of phreatomagmatic activity, with efficient magma fragmentation, which would have facilitated the widespread ash dispersal and explains the lack of a coarse, prominent, deposit near the vent.

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Injection of phreatic water into volcanic conduits: insights from numerical modelling

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Keywords: magma-water interaction, pyroclastic deposits, numerical modelling.

The occurrence of magma-water interaction during volcanic eruptions has been widely described in pyroclastic deposits, with significant consequence on the fragmentation dynamics, dispersion of pyroclasts and deposition mechanisms (Sheridan & Wohletz, 1983; Lorenz, 1987). Several external water sources have been proposed (*e.g.*, crater lakes, glacial water, oceans, ground water), but the controlling mechanisms of external water injection are poorly understood, as well as the volumetric magnitude of these processes.

Here we present a modified version of the 1*D* steady-state model presented by de' Michieli Vitturi et al. (2011), which considers the main processes experimented by ascending magmas and the injection of external water into the conduit by Darcy's law. We consider unconfined and confined aquifers, using a set of constitutive equations for describing a representative case of trachytic explosive volcanism.

Our results indicate that unconfined aquifers inhibit the injection of large quantities of external water, whereas thick, confined aquifers are capable of inducing the injection of significant amounts of phreatic water into volcanic conduits driven by pressure gradients (mass fractions up to ~ 20%), particularly when events with low eruption rate are considered. Indeed, from our results emerge that high mass fractions of external water are only possible for limited magma discharge rates (MDR < 10^7 kg/s), which could explain the low eruption rates commonly observed in phreatomagmatic eruptions (*i.e.*, where phreatic water is involved), so suggesting that high-intensity hydromagmatic eruptions are possibly related to superficial water or the inclusion of ground water by extended conduit collapse events (*e.g.*, caldera-forming mechanisms), where the ejection of large volumes of lithic fragments is also expected. Although typical volcanic conduit pressures could produce a pressure gradient able to induce the injection of external water, their fluxes are limited by country rock permeability, injection surface and pressure gradient, and are not large enough for producing a significant effect during high intensity eruptions.

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Hydrothermal alteration of basaltic ash from Etna (Italy), and Implications for Mars

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Keywords: ash, hydrothermal alteration, analcime.

Direct and indirect analyses of Mars have highlighted that rock composition is mainly basaltic and that water-related processes have played a significant role in the modification of the Martian surface during the geologic past. These insights on the Martian hydrothermal environment come from orbital observations and terrestrial analogs. Indeed, there is evidence of the presence of smectite, zeolite, sulphate-rich minerals and phyllosilicate-bearing deposits on Mars from both remote sensing observations and rover missions, indicating extensive aqueous alteration of the basaltic surface, some of which occurred under hydrothermal conditions. In particularly, hydrothermalism is invoked as a likely source for alteration in localized environment, such as serpentine and zeolite (analcime) detections near Nili Fossae (Ehlmann et al., 2011). Interestingly, the composition of basaltic ash deposits from Etna share some remarkable similarities with Martian rocks. In this contest, solid state reactions occurring during hydrothermally altered basaltic ash from Etna (Italy) were studied as a possible analog reactions developed on the Martian soil. Ashes were altered under hydrothermal conditions at constant *p*H and pressure of 5 and 0.1 Mpa respectively, at two different low-temperatures (150 and 200°C) with runs length of 5 and 31 days. Volcanic ash is basaltic in composition and consists, in decreasing order of quantity of plagioclase, olivine, augite and tachylite, sideromelane (amorphous glassy). As a result of several runs, analcime zeolite $NaAlSi_2O_6•(H_2O)$ together with unreacted starting materials has been obtained. XRPD patterns of the products showed that analcime crystallizes at the expense of amorphous material detected in basaltic ash. The yields of the analcime depended greatly on experimental conditions such as temperature, reaction time and quantities of water. Indeed reactions at low T (150°C) at both 5 and 10 days of alterations reactions were inhibited while at 200°C, analcime started forming. With increasing reaction time from 5 to 31 days at 200°C, the yield and crystallinity degree of analcime increase. With addition of water in the reactor-system at 200°C, full reaction occurred and amorphous glassy was totally altered to analcime. This result proves that, in order to achieve total amorphous glassy alteration, large amounts of aqueous solution are as crucial as temperature in the reaction system. Overall, the better conditions for greater amount of analcime well crystallized occurs at 200°C with reaction times of 31 days. These findings are consistent with the hypothesis that analcime detected near Nili Fossae are crystallized under low-temperature in hydrothermal condition.

Ehlmann, B.L., Mustard, J.F., Clark, R.N., Swayze, G.A., Murchie, S.L. (2011): Evidence for low-grade metamorphism, hydrothermal alteration, and diagenesis on Mars from phyllosilicate mineral assemblages. Clays Clay Miner., 59, 359-377.

New inferences on Pele's hair origin by 3*D* X-ray imaging

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Keywords: Pele's hair, Hawaiian volcanism, synchrotron X-ray microtomography.

The term Pele's hair indicates long, thin strands of basaltic volcanic glass formed when small drops of magma are thrown into the air and spun out by the wind. This work provides new insights into the study of morphologic features of Pele's hair related to three typical environments of formation at Hawaiian volcanoes: high fountaining, weak explosive activity and lava ocean entry (magma-water interaction) respectively from Kilauea Iki's Episode 1 event (KI); Halemaumau recent activity (HMM) and Waikupanaha 2009 eruption (LOE). Morphological studies and 2*D* observation revealed that HMM samples are long and thin, with smooth surfaces, while KI are smaller, with stubby shapes and rough surfaces, showing a lot of small furrows. Pele's hair from LOE has slim shapes, with rough surfaces and large furrows. Crystals are present in the samples from KI and rarely in LOE. All the samples are highly vesiculated. In order to get more detailed information on the shape and size of vesicles, their 3*D* inner structure was investigated by phase-contrast synchrotron X-ray computed microtomography (X-ray micro-CT) at the SYRMEP beamline of the Elettra synchrotron laboratory in Basovizza (Trieste, Italy).

3*D* image analysis pointed out that several differences in bubbles number, volume density and shape of vesicles occur among the Pele's hair from the three environments of formation. The most striking difference is in the volume density and number of vesicles, much higher in the KI Pele's hair. Moreover, these fragments display at least two population of bubbles of different size. Elongation (= 1-w/l where w and l are, respectively, width and length of the considered vesicle) is always lower in these samples than in those from HMM and LOE, where few, long bubbles occupy the entire length of the fragments forming empty channels. LOE samples have a higher number of vesicles but a lower vesicles volume density than HMM.

Shape and vesicularity of Pele's hair reflect the explosive style: thin and long fragments with a few long bubbles are formed during passive degassing in the lava lake, where very small droplets of partially degassed magma are spun out and stretched by the wind. During lava ocean entry, a degassed lava flow interacts with cold sea water causing a "secondary" fragmentation and the formation of a small ash column, where droplets of magma are elongated forming vesicle-poor, stretched Pele's hair. The lava fountaining produces coarser drops of poorly degassed magma, which accounts for the formation of stubby, highly vesiculated Pele's hair and for the first population of vesicles. A second population of bubbles probably formed as a consequence of syn/post eruptive volatiles exsolution.

New insight on the palaeogeographic significance of the volcaniclastic level of Amantea basin (Coastal Chain, north-western Calabria)

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Keywords: Amantea basin, tephra, Calabrian basins, paleogeographic reconstruction.

The Amantea basin is a Neogene basin located along the Tyrrhenian margin of Calabria. The onset of the basin started during the Upper Serravallian, in response to the first tectonic subsidence induced by extensional faulting developed in the Tyrrhenian backarc basin. Huge terrigenous sediments infilled the restricted basin area formed by articulated structural highs and N-S elongated depressions. Five main sequences have been discovered, bounded by stratigraphic discontinuities (Muto & Perri, 2002; Mattei et al., 2002). The basal sequence shows a time-transgressive sedimentary evolution for the basin, with facies associations varying from alluvial fan to submarine fan deltas dated by Mattei et al. (2002) to the Serravallian. Tortonian sequences developed upwards in response to the main extensional phase (Muto & Perri, 2002). A volcaniclastic horizon was recognized in nineteen outcrops of the Amantea basin within the first depositional unit of the succession. The horizon varies in thickness from 2 to 6 m and consists of a graded sequence of coarse sand and silt beds with colors ranging from light brownish to dark grey, yellow or deep yellow. It is noteworthy that the coarser layers are massive or bended, while the thinner ones are laminated bended. The sedimentologic characteristics of bedforms suggest a deposition from turbulent flows of syn-eruptive volcanic fragments mixed with sedimentary silico-clastic material in marine environment. Texture and composition of the volcanic fragments suggest an origin from a sub-aerial explosive eruption and primary deposition in a shallow marine environment prior to resedimentation. The rhyolitic composition and calc-alkaline affinity of volcanic glass, as well as the age of the sedimentary succession in which the studied volcaniclastic horizon is interbedded, indicate the late stages of Sardinian magmatic activity as the most probable source area of volcanism. The source volcano had to be located relatively close to the marine basin to allow the supply of pyroclastic fragments and their remobilization by secondary flows. The occurrence of this volcaniclastic deposition in the Serravallian sequence of the Amantea basin is a litostratigraphic marker for the geodynamic evolution of the area. The lack of such horizon in the other coeval peri-tyrrhenian basins allows to consider the Amantea basin as a confined elongated coastal basin area, whose tectono-stratigraphic architecture denotes a structural partitioning of the eastern nascent Tyrrhenian Basin.

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Muto, F. & Perri, E. (2002): Evoluzione tettono-sedimentaria del bacino di Amantea, Calabria Occidentale. Boll. Soc. Geol. It., 121, 391-409.

Experimental leaching of volcanic ashes from Etna and Stromboli

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Keywords: volcanic ash, leaching, experiments of water-rock interaction.

Leaching tests are fundamental tools for the assessment of impact of volcanic ash on the soil-water path. Experiments were carried out on basaltic ash from Etna and Stromboli volcanoes coming respectively from the ordinary activity of Stromboli volcano of April 2016, sampled at Mt Pizzo Sopra La Fossa, and from the explosive activity of Etna volcano (from July 18th to August 7th 2001). Before experiments, ash composition has been determined using X-ray powder diffraction and fluorescence data, optical microscopy observations on thin sections and electron probe micro-analyzer of mineral phases and glass (EPMA).

The experiments were carried out following the procedure described below. A water solution is injected through a peristaltic pump into teflon reactors containing the volcanic ash (Pokrovsky & Schott, 2000a, 2000b). The influence of water *p*H on the release of components from ash was studied using strongly acidic (*p*H = 2), weakly acidic (*p*H = 5) and alkaline (*p*H = 9) solutions, as well as the effect of varying contact times (we performed three experiments lasted about 15 days). The output water solutions have been analyzed through Ion Chromatography and Inductively Coupled Plasma Mass Spectrometer (ICP-MS). The results indicate that elemental concentration of output water tends to decrease with increasing contact time, for all *p*H conditions. Furthermore, it is remarkable that most of dissolution takes place within the first 5000 minutes. After 21,000 minutes, the solution reaches the steady state, suggesting that ash leaching may be related to the sublimates lying on the surface of volcanic ash. The highest concentration of leachates are obtained in acid condition (*p*H = 2), with the exception of Cr for the Stromboli ash, whose maximum abundance occurs during the interaction with neutral solutions, and Se, for Etna ash, whose highest concentration is detected in alkaline solutions. In the last part of the experiments, new peaks of elements (Ca, Mg and SO_4) suggest that dissolution may affect also the glassy fraction. Ashes from Stromboli at *p*H 5 release Al, Fe, Mn e F in concentration exceeding the limit values expected by Italian Law 152/2006. At the same *p*H, leachates obtained from Etna show high concentration of SO_4, Al, Fe and Mg that overtake the threshold limit. As a matter of fact, the interaction between rainwater (*p*H almost around 5) and ash plume from Etna and Stromboli volcano could represent a problem that should not to be underestimated. Future works aim to investigate in details the environmental impact of ash leachate in these two active volcanic areas.

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Chemical composition of ash samples *vs*. eruptive mechanism of 1906 Vesuvius eruption

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Keywords: Vesuvius, 1906 eruption, volcanic ash.

In this study volcanic ash samples collected during the different phases of the 1906 Vesuvius eruption are analyzed in order to obtain information on the eruptive dynamic. Such ash samples belong to the archive of the Museum of the Vesuvius Observatory, that has an exhaustive collection of volcanic ash samples emitted by the Vesuvius volcano during the period of open-conduit activity that has preceded the last eruption of 1944. Of particular interest are the volcanic ash samples erupted immediately before and during the eruption of 1906, collected by R.V. Matteucci (1862-1909) and G. Mercalli (1850-1914), that have occupied the charge of Director between 1903-1909 and 1911-1914 respectively, and have assiduously followed the eruption.

In particular, R.V. Matteucci, who was director at eruption time, systematically sampled ash during the various eruptive stages, whose volcanic activity as well as the assessment of risk for people living around the volcano were detailed described in bulletins that the director sent at the authorities by telegraph every day for mitigation of the effects of the eruption.

The eruption began on the 4th of April with the opening of numerous vents at the base of the Gran Cono and the flowing of conspicuous lava flows towards Boscotrecase and Torre Annunziata. This phase was followed by explosive activity (from the 8th of April) with the development of a volcanic cloud and the fall of pumice and ash on a wide territory causing danger to population, including people working at the Vesuvius Observatory.

Here we are conducting textural and geochemical analyses on the volcanic ash samples erupted during the whole 1906 eruption, preserved in the collection of the Vesuvius Observatory Museum and never analyzed before. The obtained results are compared with the witnesses' description of the volcanic activity at the moment of ash sampling, to identify eventual correlation between geochemical and textural features and eruptive dynamic. Moreover the results of these analyses can be useful, together with those previously obtained for the 1944 eruption (Pappalardo et al., 2014; Cubellis et al., 2016) of similar VEI as well as eruptive dynamic, for the evaluation of triggering mechanisms and spatial-temporal development of this kind of eruption.

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Tephrochronology of a ~ 60,000 years lacustrine sequence from the Fucino basin, central Apennines, Italy

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Keywords: tephra, tephrochronology, Fucino basin, explosive volcanism, peri-Tyrrhenian volcanoes, Late Pleistocene, Holocene.

The study of distal tephra provides significant data and constraints for volcanological reconstructions and represents a chronological tool for Quaternary studies. From a purely volcanological perspective, tephra dispersal and the architecture of pyroclastic sequences, as well as the texture, mineralogy and chemical composition of tephra layers, provide crucial information for determining the age of eruptions, their recurrence, intensity/magnitude and dynamics, as well as the spatial and temporal evolution of volcanic activity. Moreover, tephra layers are isochronous marker horizons that can provide high-resolution time-stratigraphic information if they are geochemically fingerprinted and tied to a known, dated eruption. Tephrochronology studies are particularly important in the Mediterranean region, where most of the numerous volcanoes have been repeatedly active since the Quaternary, even producing very intense explosive eruptions. The Fucino basin has recently received much attention because it possibly represents a new key site for tephrochronology studies. It is located in the central Apennines, Italy, and hosts probably one of the oldest continuous lacustrine successions (*ca*. 900 m) in central Italy. It is also an excellent paleoclimate record of the last 2 Ma and a key continental archive for tephrochronology thanks to its proximity to Quaternary peri-Tyrrhenian volcanic centers. In this contribution we present the results of a multidisciplinary study of three shallow cores collected in the Fucino Basin. The study includes sedimentology, magnetic properties, tephrochronology and ^{14}C dating of sediment sequences. In particular, we report on textural, mineralogical, and major and trace element geochemical data derived from eleven tephra and cryptotephra layers identified in an excellent tephrostratigraphic record covering about the last 60,000 yrs. Findings improve the present tephrochronologic framework for the Fucino Basin and for the central Mediterranean area in general and add some new important items to the list of possible markers for the Holocene. In addition, the age and dispersal of tephra are discussed in term of constructing an age model and the sediment accumulation rate for the Fucino Basin.

Morphologic and dynamic analysis of ash and ash aggregates at Sakurajima volcano (Japan)

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Keywords: ash, ash aggregates, Sakurajima volcano.

Studies on volcanic ash can give important information on the mechanisms of fragmentation, transport and deposition during eruptions of variable style. Morphological and granulometric studies of volcanic ash resulting from vulcanian activity of variable intensity at Sakurajima volcano (Japan) between summer 2013 and October 2014 are here presented. Data were collected on both single ash fragments and ash aggregates directly during fallout. SEM analyses of representative ash grains allowed distinguishing four principal ash types: Blocky Irregular (BI), Blocky Regular (BR), Rough-Vesicular (RV), and Rough (R). These classes were parameterized according to a set of objective shape parameters, in order to define quantitative constraints to the shape of the distinguished classes. The different classes are always present in all the different phases of the observed eruptive activity, without showing distinctive changes in concentration or morphology.

Ash aggregates collected during the same eruptive activity reveal instead important variations. Three main types of ash aggregates are recognized to occur into all the Sakurajima samples; Single Particles, Coated Particles, Cored clusters. Using image analysis techniques, they were characterized in terms of average dimension, grain size of the aggregating ash, and shape features of the aggregated ash, pointing out important differences between the different types. Analysis of high-resolution, High-speed Camera video recordings, allowed finally to collect an important set of measurements of terminal velocity, bulk density, and size of a large number of observed falling aggregates. The resulting data reveal the strong influence of aggregation processes in controlling ash deposition processes at Sakurajima.

Fucino basin: a key site for reconstructing Mediterranean Quaternary tephrostratigraphy

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Keywords: Fucino basin lake, central Mediterranean, tephrochronology, tephra marker, paleoclimate.

During the last decade, tephrostratigraphy has gained growing attention as a powerful tool for dating and synchronizing marine and terrestrial climatic archives. This is particularly true in the Mediterranean region, thanks to the intense explosive volcanic activity during the Quaternary and to the wealth of marine and continental successions in which tephra are found interbedded in sediments (*e.g.*, Petrosino et al., 2016). So far, tephrostratigraphic studies have mainly focussed on Holocene-Late Pleistocene, but the growing number of high-resolution, long-term paleoclimatic inquiries makes it necessary to develop a reference tephrostratigraphic framework, possibly spanning the whole Quaternary.

The Fucino basin (Avezzano, AQ, Abruzzo) hosts a *ca*. 1 km thick, continuous, climatically sensitive lacustrine sedimentary succession, likely covering the last 2 Ma (Giaccio et al., 2015). Recent studies, focussed on the uppermost 82 m of the lacustrine sedimentary succession, have highlighted the presence of several key regional marker tephra layers over the last 190 ka (Giaccio et al., 2017).

Multiple analytical approaches (WDS-EMPA, LA-ICP-MS, TI-MS) and $^{40}Ar/^{39}Ar$ age determinations are used to circumscribe the volcanic sources of distal tephra and to support correlations with individual eruptive units. However, when considering temporally-remote eruptions, additional constraints are required to confidently correlate coeval layers in different archives. We show that the high-resolution paleoclimatic proxy record of Fucino basin allows to precisely define the climatostratigraphic position of tephra layers, enabling us to critically evaluate and refine tephrostratigraphic correlations between climatically sensitive sedimentary successions.

In light of these results, Fucino Basin is an ideal candidate to become a key archive in building up a dense tephrostratigraphic framework for the Mediterranean region.

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A new approach to study the micro-texture of accretionary lapilli: the case of Secche di Lazzaro (Stromboli, Aeolian Islands)

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Keywords: accretionary lapilli, Stromboli, X-ray microtomography, 3*D*.

This study was conducted on samples of accretionary lapilli from Secche di Lazzaro a phreatomagmatic sequence (Stromboli, southern Italy). Here, we combine two analytical techniques, X-ray microtomography and microprobe analysis to study the texture and chemistry of selected accretionary lapilli/pellets. We performed granulometric analysis to describe the spatial arrangement of the accretionary lapilli and their distribution inside the deposit, as well as SEM investigations (BSE images). EMPA analyses of major elements on glasses and minerals were also performed. Although BSE images provide accurate morphological information, they do not allow the real 3*D* microstructure to be accessed. Therefore, non-invasive 3*D* imaging of the lapilli was performed by X-ray micro-tomography (X-mCT). The results of the X-mCT measurements provided a set of 2*D* cross-sectional slices stacked along the vertical axis, with a voxel size varying between 2.7 and 4.1 microns, depending on the size of the sample. This technique helped us to better constrain the crystal and bubbles distribution inside the accretionary lapilli. Chemical analysis on glass and minerals reveals a residual melt composition ranging from 55 to 59 wt% SiO_2 and the presence of olivine, clinopyroxene, feldspar and iron-oxide minerals. This work proposes a new approach for studying small pyroclasts in the field of volcanology. X-ray micro-tomography as a non-destructive technique is by far the only suitable tool for characterizing the internal structure of accretionary lapilli, *e.g.*, by quantifying the grain-size distribution of each component (crystals, melt and bubble) and describing their spatial distribution within the aggregates.

Session S30:

Mapping geological structures and volcanic phenomena for hazard assessment: traditional and innovative approaches

Conveners:

Marina Bisson (INGV, Pisa)

Sonia Calvari (INGV, Catania)

Roberto Isaia (INGV, Napoli)

Augusto Neri (INGV, Pisa)

Claudia Spinetti (INGV, Roma)

Morphological evolution of Somma-Vesuvius caldera during the last century: integration between historical maps and airborne LiDAR survey

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Keywords: Digital Elevation Model, historical maps, LiDAR, morphological evolution, Somma-Vesuvius.

The eruptive history of a volcano can be also investigated through the multi-temporal analysis of its morphological changes. This analysis can be a useful support to improve studies aimed at volcanic hazard assessment for volcanoes which threaten densely populated areas as the Somma-Vesuvius (SV) complex.

The objectives of this work are: a) reconstruction of Digital Elevation Models (DEMs) derived from historical maps of the SV caldera; b) qualitative and quantitative estimation of the most important morphological changes from 1876 to present day.

For the past topographies, three IGM historical maps (1876, 1906 and 1929) have been digitalized and resulting DEMS have been obtained. For the present-day topography, LiDAR data acquired during 2009-2012 years by the Province of Naples have been processed to obtain a very high resolution (1 m) DEM.

The work has been performed by using two specific platforms: ArcGIS (ESRI environment) and Tn-ShArc (Terranova platform). The first allowed to elaborate the acquired data for the DEMs generation and perform spatial analyses to calculate the main morphological parameters. The second was employed to georeference all data in a single reference system (WGS84-UTM-33N).

As main result, this study allowed to quantify the volume and areal variation of some geomorphological landforms individuated within the SV caldera. Then, an overview of the technical procedures employed is also provided along with a comparison between traditional and more innovative techniques.

A large-scale submarine slide offshore Mt. Etna: did the margin collapsed earlier than the volcano?

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Keywords: Etna offshore, gravitational instability, submarine landslide.

Some key structural features have been identified offshore of Mount Etna using multichannel reflection seismics and multibeam bathymetry. A bulge-shaped morphologic high, protruding eastward, charaterizes the offshore area (*e.g.*, Chiocci et al., 2011), with a thrust fault that outlines the boundary of the bulge. The morphologic high is composed by a northern part, where a thick package of sedimentary strata has been thrust and folded, and by a less deformed southern part, which is interpreted as the northern prolongation of the Hyblean Plateau (Argnani et al., 2013). It appears that the onset of thrusting preceded the activity of the Pernicana, that played a relevant role in the last 15 ka, during the main building stage of the present volcanic edifice (Branca et al., 2004, 2011). The onset of Mount Etna magmatism, leading to the intrusion of the large magmatic body, started at about 120 ka (Branca et al., 2004, 2011), and we infer that the intrusion-related deformation could be responsible for the initiation of shortening at the bulge frontal thrust. Folding and thrusting in the northern part of the offshore bulge have a present morphological expression in the Riposto Ridge. This deformation promoted the gravitational instability that originated a large-scale submarine landslide that is some 100 meter thick and covers a surface of over 50 squared km (Etna landslide in Argnani et al., 2013). The extensional faults observed in the Riposto Ridge result from a combination of large-scale folding and downslope gravity sliding. This contribution addresses the geometric features of this large scale slide and speculates on its possible age and causes of instability.

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Three-dimensional modeling of Mount Etna volcano: volume assessment, trend of eruption rates and geodynamic significance

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Keywords: 3*D* modeling, Mt. Etna volcano, emitted volumes, eruption rates, slab breakoff, mantle flow, magmatic source mixing.

First time 3*D* modeling of Mt. Etna, the largest and most active volcano in Europe, enabled us to acquire new information on the volumes of products emitted during the volcanic phases that have formed Mt. Etna and particularly during the last 60 ka, an issue previously not fully addressed. Volumes emitted over time allow obtaining a complete picture about the trend of eruption rates during the volcano's lifetime, also highlighting a drastic increase of emitted products in the last 15 ka. The comparison of Mt. Etna's eruption rates with those of other volcanic systems located in different geodynamic frameworks worldwide revealed that, since 60 ka ago, eruption rates have reached a value near to that of oceanic-arc volcanic systems, although Mt. Etna is considered a continental rift strato-volcano. This finding agrees well with previous studies on a possible transition of Mt. Etna's magmatic source from plume-related to island-arc related. We speculate that anomalously high eruption rates reached by Mt. Etna in the last 60 ka could be the consequence of a significant geodynamic change in the area. As suggested by tomographic studies, trench-parallel breakoff of the Ionian slab has occurred north of Mt. Etna. Slab gateway formation right between the Aeolian magmatic province and the Mt. Etna area probably induced a previously softened and fluid-rich supra-subduction mantle wedge to flow towards the volcano with consequent magmatic source mixing.

Conditional effects of vent location, event scale and time forecasts on pyroclastic density currents hazard maps at Campi Flegrei caldera (Italy)

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Keywords: pyroclastic density currents, hazard maps, Campi Flegrei.

This study presents a new method for producing long-term hazard maps for pyroclastic density currents (PDC) originating at Campi Flegrei (CF) caldera. A doubly stochastic approach combines the uncertainty assessments on the spatial location of the volcanic vent, the size of the flow and the future time of such an event. The results were obtained by using a Monte Carlo approach and adopting a simplified invasion model based on the "box model" integral approximation. Temporal assessments were modelled through a Cox-type process including self-excitement effects, based on the eruptive record of the last 15 ka. Mean and percentile maps of PDC invasion probability have been produced, exploring their sensitivity to the different sources of uncertainty and to the effects of the dependence between PDC scales and the caldera sector. Conditional maps concerning PDC originating inside limited zones of the caldera, or PDC with a limited range of scales were also produced. Finally, the effect of assuming different time windows for the hazard estimates was explored, also including the potential occurrence of a sequence of multiple events. If the volcano entered a new epoch of activity similar to the previous ones, results indicate a mean hazard above 5% in the next 50 years on the entire caldera. Hazard peak is around 25% and it reaches 10% even in some central areas of Naples on the east of the caldera.

Monitoring of the Volcan de Colima activity (Jalisco – Mexico) using COSMO-SkyMed time series: first results

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Keywords: InSAR, volcano, Colima, monitoring, mapping, hazard.

The Colima volcanic complex is the most prominent volcanic center of the western Mexican Volcanic Belt. Located in the State of Jalisco (Mexico), it consists of two southward-younging volcanoes, Nevado de Colima (the 4320 m high point of the complex) on the north and the 3850-m-high historically active Volcan de Colima (VdC) at the south. The VdC has had more than 30 periods of eruptions since 1585, including several significant eruptions in the late 1990s, and the scientific monitoring of the volcano began 20 years ago.

The 26 November 2014, the VdC, began its eruptive activity, which is still in progress. Dense clouds of smoke and ash were released into the atmosphere, as well as significant quantities of gas were emitted from the mouth of the volcano. In the following weeks repeated explosions produced plumes reached an altitude of about 7 km. The surrounding villages and towns were covered by volcanic ash. In particular, the largest city of Guzman, which has about 100,000 inhabitants, located 25 km north east of the volcano, was covered by ash. Any lava flows, pyroclastic flows or lahars can seriously invest in smaller towns (San Marcos, Tonilla and Queseria) located south of the volcanic cone. These towns were already hit by lava during the last intense crisis dating back to 2003-2005.

The COSMO-SkyMed (CSK), is the high-resolution four SAR satellites constellation of the ASI (Italian Space Agency); this mission has a great importance in the fields of prevention, mitigation and monitoring of geophysical risks. CSK is one of the most important SAR mission presently operating able to provide X-band SAR images, with single and double polarization, with different configurations of acquisition. In addition, the CSK constellation makes it possible to overcome what, until its launch, it had been regarded as the most important limit on the use of SAR data for seismic and volcanic emergencies, *i.e.*, the time to revisit.

Principal scientific and technical objectives of our work, are:

i) a systematic analysis of the available radar interferometric data to monitoring topographic changes with a few centimeters accuracy associated with VdC activity within the 2014-2015 period, for pre-, syn- and post- eruptive phases;

ii) mapping lava flows, pyroclastic flows or lahars produced during the present crisis for the improvement study of volcanic hazard in this area;

iii) apply classical- and multitemporal InSAR techniques to CSK high resolution data in extreme condition such as VdC steep topography to perform numerical inversions for the deformation source to determine the evolution of deformation prior (if possible) and during volcanic activity;

iv) verify relations between deformations measured by CSMK and deformations measured in the two previous decades by ESA ENVISAT and ERS 1/2 satellites.

Here we present first results of SAR data analysis. ASI provided SAR dataset (Open Call Project, COSMO-SkyMed ID 167)

Analysis of the volcanic and tectonic structures of Pavonis Mons (Tharsis, Mars) and Nabro (Afar, Eritrea) volcanoes

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Keywords: remote sensing, volcanoes, Mars, Afar.

Remote sensing observations have shown that volcanism is one of the most important processes acting on Mars throughout its history. Pavonis is one of the most important shield volcanoes of Mars, with its 300 km of diameter and 10 km of height, and it is located at the center of a NE-SW trending chain of volcanoes. In this study, we mapped the volcanic and tectonic structures of Pavonis Mons using a mosaic of CTX optical images (Context Camera onboard NASA Mars Reconnaissance Orbiter, with 6 m/pixel resolution). We also used two other types of optical images: HRSC (High Resolution Stereo Camera onboard ESA Mars Express, pixel resolution of 12.5 m), and HiRISE (High Resolution Imaging Space Experiment onboard Mars Reconnaissance Orbiter, ~ 0.25 m/pixel resolution). In addition, the MOLA (Mars Orbiter Laser Altimeter, spatial resolution of 463 m/pixel) DEM (Digital Elevation Model) was used to complement the analysis, together with THEMIS-IR day and night (Mars Odyssey Thermal Emission Imaging System, spatial resolution of 100 m/pixel) global infrared image mosaics. The structures mapped on Pavonis are structural depressions such as grabens and fossae, here interpreted as dike intrusions, together with pit structures and volcanic vents. Furthermore, several effusive features have been identified: among these are lava flows, lava channels, sinuous rilles, and depressions that are interpreted as coalescent collapsed lava tubes. Azimuthal orientations, stratigraphic relationships between different structures and their distribution suggest that magma processes rather than regional tectonics mainly control the development of Pavonis. In particular, the majority of the mapped structures are caused by dynamics of the magma chamber, while a pre-existing fracture system trending NE-SW controls the emplacement of the dikes only in the distal part of the volcano.

Mapping of volcanic and tectonic structures has been also performed on Nabro, an off-rift volcano in the Afar depression in Ethiopia and Eritrea. Nabro erupted on 12 June 2011 (Hamlyn et al., 2014). The off-rift position of Nabro is somewhat analogous to that of Pavonis and the inferred rift system of the nearby Valles Marineris. Hence the comparison between Pavonis and Nabro may provide important clues about rift tectonics and off-rift volcanism. The dataset used to map structures on Nabro was the DEM derived from the SRTM (Shuttle Radar Topography Mission, with a spatial resolution of 30 m/pixel), Landsat and Spot (Satellite Pour l'Observation de la Terre) images. Differently from Pavonis, the structures mapped on Nabro suggest that regional-scale tectonics influenced the formation of this volcano.

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Map of submerged volcanic structures in Italy

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Keywords: volcano, marine geology, EMODnet.

A large part of the post-orogenic volcanism in Italy is preserved in subaqueous domains of the Tyrrhenian Sea and along the Sicily Channel. Over the years, several works, such as the DSDP-ODP Project (Deep Sea Drilling Project, http://deepseadrilling.org/; Ocean Drilling Program, http://www-odp.tamu.edu/) and detailed bathymetric surveys, allowed a significant improvement of the knowledge of these volcanic environments. However, a comprehensive approach to the volcano types classification, based on the available data and on the integration of different datasets, has not been attempted yet. Here, the preliminary results of the EMODnet-Geology Project (http://www.emodnet-geology.eu/emodnet/srv/eng/home) relative to the collection of European submarine data are presented, focusing on the Quaternary subaqueous volcanism in Italy.

This work aimed at homogenizing and validating existing data and allowed a classification of different edifices, based on morphology, chemistry, ages and main structural lineaments. Where possible, the age and style of the most recent eruptions, as well as the presence of active fluid emissions, have been listed in order to support the evaluation of the volcanic hazard.

Significant effort has been dedicated to identify the extent of each volcanic edifice (so far very poorly defined) on the most detailed available bathymetric maps. The new map produced for EMODnet-Geology represents the most updated cartographic representation of the subaqueous volcanic structures in Italy.

Geological mapping methods for hazard assessment in volcanic area-a review

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Keywords: geological maps, volcanic hazard, chronostratigraphy, facies analyses.

Geological maps show the distribution at the Earth's surface of different kinds of Earth materials. But a geological map is much more than that, it is a synthesis of the knowledge on the geology of an area. It is, at the same moment, the first introduction to an area being visited, and the culmination of a geological investigation. Understanding a geological map make you able to predict what occurs at and beneath the surface, and for this reason it his of upmost importance in working on environmental, geography, archaeology, oil reservoirs, coal, aquifers, ore bodies, land subsidence, and much more. Although, geology is undergoing great changes, geological maps remain as fundamental as ever in depicting the geology of a territory. After all, they embody the very matters that set geology apart from other disciplines: dealing with real Earth materials in three dimensions and through time. Today, computer based methods are adding yet further to their power and versatility. Today, new technologies are being employed in the production of maps and in manipulating map information, and geological maps acquired new and upmost importance to promote better environmental understanding and to foster an integrated approach to the planning of future land use. This adds tremendous flexibility to the way we can use maps, but it also makes an understanding of the basic principles behind them more important than ever.

This is particularly true for the geological mapping in volcanic areas. As a matter of fact, if a geological map is the basic tool for understanding the foundations of landscape, a well done geological map of a volcano has a tremendous impact on the provisional plans for the prevision and the mitigation of the effects of future eruptions.This presentation will act as a review inside the old and new methods of mapping volcanoes and their influence on the present-day-used holistic approach to the cartography of volcanoes. We will start from the old (XIX Century) maps, mainly based on lavas distribution; to pass to the petrography-based maps of the first half of the XX Century, that pictured volcanoes as red bodies without a link with the other geological units; going up to the modern maps, based on data derived from chrono-stratigraphy and facies analysis. We will highlights the contribution to volcanic mapping in densely populated areas given by historical sources, archaeological findings, structural analyses, boreholes data, and geomorphology. The utility of grouping mapped units as Eruptive units or Unconformity Bounded Stratigraphic Units, or others, will be discussed in the light of the improvement of the significance of the volcanologic maps, as well as the Geographic Information System contribution in producing thematic maps.

A new isopach map for the Campanian Ignimbrite, Campi Flegrei, Italy

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Keywords: Campi Flegrei, Campanian Ignimbrite, isopachs, large-scale ignimbrite, pyroclastic density current, depositional system.

The Campanian Ignimbrite (CI) eruption (39 ka) occurred at Campi Flegrei, Italy, and has been the most powerful eruption in the Mediterranean area since 200 ka. This study is focused on the revision and update of the distribution and thickness data of the CI, as well as on giving information on the topological aspect ratio of ignimbrite in order to better understand the flow dynamics of the parent pyroclastic density currents that surmounted mountains over 1000 m a.s.l.. We collected more than 200 stratigraphic logs and boreholes, and 30 geological sections and seismic profiles both in proximal and distal areas from 87 published papers. In addition to bibliography work, field work is in progress to evaluate the thickness and the stratigraphy of CI, and the differences between proximal and distal areas. The thickness of flow units (all the PDC units except the basal Plinian fall unit) have been managed into a GIS map file and a database of stratigraphic logs with all the information regarding the stratigraphy, the location and the features of the deposits has been created. Assuming that the paleo-topography was not to different from the present-day topography, isopachs were traced on a map of topographic slope. The largest thickness is 160 m, inside the CI caldera and Campanian plain, and the isopach's spacing is 10 m between 20 and 160 m, 5 m between 5 and 20 m and 1 m between 0 and 5 m. Deposits are channeled inside the valleys bordering the plain, includes the northern area of Roccamonfina, a site of field work. In this study, we defined a slope associated with no deposition, the 0 m isopach. We use the definition of the thickness variations of the ignimbrite to evaluate the relation between transport, sedimentation and topography.

Data uncertainty quantification in volcanic hazard assessment: review and examples

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Keywords: epistemic and aleatoric uncertainty, uncertainty quantification, Somma-Vesuvio, Campi Flegrei.

The availability of new volcanological data employed as input parameters in numerical models have allowed scientist over the past years to produce more accurate hazard maps. However, it is also true that these latter products, which are fundamental for decision-makers when dealing with long-term planning or with the management of emergency situations, might be affected by a certain degree of uncertainty. If a volcanic hazard map might be provided to civil protection authorities and decision-makers with a quantification of the most relevant sources of uncertainty, the resultant emergency planning might be undertaken with a better awareness. The uncertainty depends on many factors, and it is important to quantify the two main sources of uncertainty of a volcanic system: i) the first one related both to the incomplete knowledge of the system under investigation and to errors in data acquisition (epistemic uncertainty); ii) the second one related to the intrinsic physical variability of the system (aleatoric uncertainty). The epistemic uncertainty can affect either data or modeling choices, and in this study we focus on the first case, including an example of the second. This presentation is therefore aimed at briefly reviewing the state of the art of the distinction between different types of uncertainty applied to volcanic hazard assessment: after a theoretical introduction, two examples from two Italian high-risk volcanoes (Vesuvio and Campi Flegrei) will illustrate how data uncertainty has been managed in specific cases related to volcanic hazard assessment.

Heat and mass dissipation during lava flow emplacement: the effect of slope

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Keywords: lava flows, heat dissipation, flow unit morphology, Mt Etna.

During emplacement, lavas modify the pre-existing topography and release a large amount of heat. We consider a channelized 'a'a lava flow unit formed at Mt Etna during the 2001 flank eruption, and we combine a morphological analysis of the pre- and post-emplacement topography with an analysis of the syn-eruptive thermal signature to derive insights about the processes driving mass and heat dissipation. Input data include a LIDAR-derived DEM and an EO-1 satellite image. The obtained results highlight the concurrent effect of three driving factors: (i) the heat released by the open lava channel decreases as the average temperature of lava also decreases with increasing distance from the vent; (ii) a higher slope consistently promotes a higher rate of heat and mass dissipation; and (iii) the advancement of pulses of lava also promotes heat and mass dissipation. The overall counterintuitive implication is that a higher slope tends to promote a shorter final runout.

Session S31:
Geosciences at school 2017

Conveners:

Anna Gioncada (Univ. di Pisa)

Eleonora Paris (Univ. di Camerino)

Fabio Pieraccioni (Univ. di Pisa)

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Valsassina "sopra e sotto": un'esplorazione geologica a due passi da Milano

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Keywords: geoscienze, Piano Lauree Scientifiche, Valsassina (Lecco).

Promuovere la conoscenza delle Geoscienze e la consapevolezza del loro ruolo nella società a livello di insegnamento secondario di secondo grado significa, prima di tutto, fornire una visione organica e interconnessa degli aspetti fondamentali delle discipline. Gli studenti possono sviluppare un vero interesse verso le Geoscienze in prospettiva di studi universitari solo se gli insegnanti sanno fornire loro un ampio panorama delle discipline di base, ma anche delle loro applicazioni, interazioni e relazioni con gli aspetti economici e sociali. In quest'ottica, il gruppo di lavoro UNIMIB del Piano Lauree Scientifiche (Progetto Nazionale Geologia) ha concepito, in collaborazione con gli insegnanti delle scuole superiori coinvolti, un percorso di laboratorio *indoor* e *outdoor* che trae spunto dal contesto geologico della Valsassina (Lecco). Questa valle, rapidamente accessibile da Milano, presenta una grande varietà di contesti strutturali e litostratigrafici (dal basamento metamorfico prealpino alla successione sedimentaria del bacino lombardo) e peculiari caratteristiche geomorfologiche, derivanti dall'interazione tra tettonica ed evoluzione Quaternaria in ambiente glaciale e fluviale. L'area è caratterizzata da un'importante tradizione mineraria attraverso diverse epoche storiche (dall'età romana ad oggi), che ha contribuito a plasmare la moderna geografia umana della valle. Infine, l'area è caratterizzata da vari contesti di rischio idrogeologico, e in particolare da fenomeni di instabilità di versante molti diversi (da crolli in roccia a grandi frane), la cui natura, distribuzione e pericolosità sono strettamente legate ai "paesaggi geologici" in cui si sviluppano. Il percorso didattico si sviluppa a partire da un fase *indoor*, dove gli aspetti teorici e le conoscenze di base sono tracciati attraverso presentazioni e attività di laboratorio (elementi di cartografia, riconoscimento delle rocce a mano e al microscopio), sempre con un approccio interattivo e finalizzato a sviluppare competenza pratica sia negli insegnanti che negli studenti. La successiva fase *outdoor* consente agli studenti di verificare ed applicare sul terreno elementi e competenze acquisite, e di collegare gli aspetti geologici, geomorfologici ed applicativi. Tale scopo viene perseguito attraverso un facile itinerario geologico, la visita a una miniera didattica (Cortabbio di Primaluna) e l'escursione alla grande frana di Bindo Cortenova, che forniscono allo studente un'ampia visione dell'importanza delle Geoscienze nella conoscenza e gestione del paesaggio naturale ed umano.

I colori della Terra. Esempi in ambito ligure-toscano

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Keywords: geoscienze, scuola, minerali, pigmenti, storia dell'arte, Google Earth, alternanza scuola-lavoro.

Il progetto di eccellenza *I colori della Terra* è stato ideato nell'ambito dell'attività di Alternanza Scuola Lavoro per una classe terza del liceo scientifico. Esso si basa su un approccio interdisciplinare e pluriennale, apre alla conoscenza dei pigmenti naturali in rapporto alla conformazione geologica e geomorfologica del territorio ligure-toscano e approfondisce l'utilizzo in campo artistico di terre naturali e rocce. Particolare attenzione è stata riservata alle rocce e alle terre presenti nel territorio. Gli studenti hanno seguito un *iter* didattico-formativo in ambito tecnico-scientifico, con il supporto delle conoscenze derivanti dalle discipline delle scienze esatte (chimica, fisica, scienze, ecc.) e quelle più specifiche del campo artistico sulla teoria dei colori e loro utilizzo. Gli studenti, inoltre, hanno partecipato ad attività di laboratorio presso il Dipartimento di Scienze della Terra dell'Università di Pisa e presso il loro Istituto.

Nel primo laboratorio sulle proprietà dei minerali, gli alunni hanno imparato a riconoscere i vari minerali, ad elaborare schede descrittive basate sulla loro osservazione e a realizzare una mappa dicotomica per classificare e riconoscere un minerale incognito. Inoltre, partendo da alcuni brani tratti dal *Libro dell'Arte* di Cennino Cennini, gli alunni hanno messo in pratica le conoscenze, su pigmenti e leganti, ~~e~~ sulla preparazione dei colori e della pittura su tavola. Hanno quindi preparato delle tempere ad uovo utilizzando pigmenti minerali per una vetrina espositiva allestita presso il Dipartimento di Scienze della Terra (UNIPI) e dei testi per alcuni pannelli esplicativi. Nel secondo laboratorio gli alunni hanno approfondito aspetti teorici e pratici sulla realizzazione dei mosaici. Essi hanno imparato a misurare le principali proprietà fisiche e meccaniche dei materiali lapidei naturali e artificiali, a selezionare quelli più adatti alla realizzazione delle tessere e a creare una piccola opera musiva. Quindi le conoscenze acquisite nei laboratori e in classe sono state condivise mediante cartelle di Google Drive e attraverso la realizzazione di un sito *web* dedicato.

La prima fase di questo progetto triennale è stata caratterizzata da una visita didattica di tre giorni all'Isola d'Elba dove gli studenti, guidati da docenti e ricercatori del Piano Lauree Scientifiche del Dipartimento di Scienze della Terra dell'UNIPI e del loro Istituto, hanno avuto modo di raccogliere, riconoscere e classificare numerosi minerali e rocce. L'Isola d'Elba ha rappresentato per gli studenti il *trait d'union* fra l'osservazione laboratoriale e quella diretta sul campo. Infine, alla chiusura del primo anno di attività, gli alunni hanno geolocalizzato attraverso Google Earth i minerali e le immagini raccolti e creato una sorta di "diario di bordo" digitale sulla loro esperienza.

An innovative and interactive approch for an educational mineralogical museum

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Keywords: museology, cultural heritage, multimedia audio guides, izi.Travel platform, flipped classroom.

During the "Precious Minerals and Rocks" course of the University of Catania Geological Science degree, it was experimented a methodology of teaching based on the flipped classroom with the aim to involve students in an active practice. In particular, the students were engaged to support a pilot project promoted by the Regional Department of Cultural Heritage in Sicily in the izi.Travel platform aimed to improve Sicilian Cultural Heritage. This platform is a free tool for the enhancement of artistic and cultural heritage with the use of new technologies as smartphones and tablets. This combination of art and multimedia, in a global scale, is innovative both for the aspects (participatory and co-creative) and for the wide variety of topics and of stakeholders that could be involved (institutions, associations, Universities and schools). In Sicily, the pilot project on izi.Travel has become a real best practice about co-creation, participation and democratization of cultural heritage, according to the Faro Convention: in about one year-project 130 multimedia audio guides are available.

This approach, shared between professor and students, was utilized with the goal to realize multimedia-interactive audio guides on the Mineralogical Collection of the Department of Biological, Geological and Environmental Sciences of Catania University, following the main rules of museology (clarity, precision and persuasion). The museum offers to different targets of guests rich mineralogical collections made up of thousands of minerals properly catalogued. In particular, the oldest collections of the museum are represented by minerals and rocks offered at the University of Catania by the scientist Giuseppe Gioieni and by the Prince Biscari in 1781. However, the flagship of our museum is represented by the extraordinary collection of minerals belonging to the Sicilian Evaporites series such as sulphur, gypsum, aragonite and celestine. During our work, firstly, we divided the collection of minerals for categories and then we created data sheet (chemical formula, provenance, genesis and uses) and multimedia audio guides with scientific and cultural contents for each ones, in order to promote the department's collection as a real "digital mineralogical guide". Finally, we believe that this project can be a great opportunity to revaluate our Museum and to give the possibility to many students to work for that purpose, considering that this project is a "unicum" in the izi.Travel platform at present.

Teaching geosciences by non-specialists. Geosciences and problem-solving strategies

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Keywords: geosciences, teaching Earth Science, Vajont.

In order to integrate several scales of observation and different techniques on a single geological problem, the example of the Vajont landslide in 1963 offers an excellent framework.

As in many other countries (King, 2008), Geosciences in Italian school represent a small compulsory part of a national science curriculum and are mainly taught by Biology, Chemistry, Physics or Natural Sciences specialists with a little number of Earth Science specialists. How these teachers approach a geological problem ?

The Master di II livello on "Professione Formatore in Didattica delle Scienze" has been a biennial National Project for inservice teacher training realized by the Udine University (A.A. 2013/14-2014/15).

Twenty Science Teachers (Scuola Secondaria di I e II livello) were taught about the causes and effects of Vajont's landslide, then they were asked to examine this event from the point of view of the energy involved. A correct answer has to take into account the mechanical energy of the landslide, the energy absorbed by the lake water, the wave moving toward Longarone, the chemical energy linked to the montmorillonite hydration, the laws of conservation and the transformations associated with the event.

The obtained answers are examined in order to observe the problem solving strategies considered by teachers coming from different scientific disciplines.

Physics and chemistry specialists describe the event as a translation of a rigid-body on the inclined plane but does not remark the constraints revealed by direct observation (internal and external work with respect to the body in translation) thus failing to preserve the mechanical energy. Similarly, they do not realize that Bernoulli's equation can not describe the motion of water, because either of the turbulent flow and the work exerted on the surrounding rocks.

Natural Science and Earth Science specialists have provided further detailed descriptions of the Vajont event, but do not realize that any description (or classification) in Earth Science is always ambiguous because it may be functional to solving a peculiar problem (Ault, 1998).

These data suggest that teaching Earth Science at school needs a better definition of its own methods and goals, other than those of the other sciences.

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Observing the sky, understanding the Earth: an Earth sciences astronomy-related educational package for high school teachers and students

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Keywords: Earth sciences, astronomy, astrophysics, education, dchool, meteorites.

The PhD Research Project "Observing the sky, understanding the Earth" is set in the framework of the UNICAMearth Working Group, with the establishment of an official co-operation between the University of Camerino and the Fondazione Clément Fillietroz-ONLUS, who manages the Astronomical Observatory of the Autonomous Region of the Aosta Valley and the Planetarium of Lignan.

The Project is focused on the link of Earth Sciences with Astronomy and Astrophysics. The study of the celestial bodies far away in space allow us to compare their physical, chemical and geological features to Earth's ones and this helps us to understand better the processes that have shaped and are still shaping our planet and the environment where we live. The great educational potential of this interdisciplinary and multidisciplinary approach has not been capitalized in its fullness yet.

Since 2009, the world astronomical community has been doing greater and greater efforts to connect researchers and educators, with the official support of the International Astronomical Union (IAU). One of the most important result is the astroEDU website, an open-access platform for peer-reviewed science education activities that educators can review, distribute, improve, and remix.

The Project aimed at understanding first the process of identification of 'good' open-access peer-reviewed Astronomy educational activities by the IAU and then how to import, project and adapt this process in the UNICAMearth Working Group framework. The final goal is to suggest a set of 'quality standards' for Earth Sciences educational activities and, following these possible 'golden rules', design an Earth Sciences Astronomy-related Educational Package (in Italian) for high school teachers and students.

The chosen topic for the Educational Package is: "the meteorites as a proxy for the study of the inner composition and structure of the Earth". Even if the topic is already inserted in the Earth Sciences curriculum for the Italian schools and many other countries, little relevance is usually given to meteorites. The Educational Package includes:

- a set of presentations in digital format (pptx and pdf), that the teachers can download and use for 1 to 3 one-hour lessons to depict the topic in an self-consistent way at an introductory level;
- a practical activity about analysis of meteorite samples for a 1 to 2 one-hour lessons, using freely available on line tools (Europlanet Virtual Microscope, Dawn Mission: Find a Meteorite).

In the poster, the authors describe the analysis of the astroEDU experience, how it helped to suggest the set of 'quality standards' for the design of Earth Sciences educational activities, the implementation and exploitation of the Educational Package and the results of a preliminary tests performed in 2016 and 2017 at the Liceo Scientifico e Linguistico «Edouard Bérard» in Aosta, Aosta Valley, Italy, with teachers and students for I and V class.

Earth science knowledges of freshmen: a survey in Italy

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Keywords: Earth science, teaching, learning, alternative conceptions.

Which are real knowledges about Earth science basic concepts of students at the end of high school? Do alternative conceptions live in minds of students? Does a difference in Earth science learning at secondary school exist among students choosing different university degree courses (*e.g.*, biology *vs.* geology)? The answers to these questions and similar others can be useful to the teaching of Earth science both in secondary school and higher courses. Researchers from around the world have already posed these questions for long time (*e.g.*, Dove, 1998). In Italy, Bezzi and Happs (1994) carried out an investigation about the students' ideas on the volcanism in the areas in which they lived and how much their opinions were deeply rooted. We proposed a questionnaire at freshmen of University of Pisa. The students were enrolled at degree courses of geology, biology, biotechnology, natural and environmental science, veterinary medicine, industrial engineering. The twelve questions of the test regarded the geological time, the motion of the Earth around the Sun and its consequences, petrology, tectonics and orogenesis. The test was multiple-choice with four replies. This survey is an open window on the general knowledge of Earth science that a citizen actually has at the end of its schooling. Interviewed mostly gave correct answers in some fields, but showed high uncertainties in several topics. This unsatisfying outcome may stem from different causes, such as alternative conceptions of students about the topics, difficulties of comprehension of issues, non-incisive learning methods. Understanding the reasons of the outcome deserve further in-depth analysis but, in our opinion, this kind of research could give us some interesting hints about the efficacy of the learning and teaching approaches commonly applied in geosciences.

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Museo, scuola dell'infanzia e università in un progetto di educazione scientifica

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Keywords: museo, scuola, didattica, bambini, minerali.

Il Museo di Storia Naturale dell'Università di Pisa da tempo è, oltre che luogo di conservazione di reperti e ricerca scientifica, anche centro di progettazione educativa e studio didattico, in un rapporto attivo e partecipativo con le altre realtà educative del territorio, a partire dalla scuola. In questo quadro, nel Novembre 2016 è stata attivata una convenzione tra il Museo e l'Istituto Comprensivo A. Pacinotti di Pontedera (Pisa), con tavoli di programmazione – progettazione tra insegnanti e esperti museali per la costruzione e lo studio di percorsi didattici scientifici per i bambini della scuola dell'infanzia. Hanno preso parte al progetto le insegnanti delle Scuole dell'Infanzia Diaz e De Gasperi, con un totale di 88 bambini coinvolti. Gli argomenti concordati tra Museo e scuola sono stati ambiente, terra e minerali. Per ogni argomento sono stati individuati i nuclei centrali e identificati i percorsi museali più attinenti, talvolta modificandoli in funzione dell'obiettivo da raggiungere e dell'età dei bambini. Le insegnanti hanno poi definito le unità di apprendimento con tempi, scansioni, attività e collegamenti tra percorsi, in modalità ricerca-azione.

Fra gli argomenti fondamentali della geoscienze c'è il "senso del tempo", tempo che in geologia è molto lungo e di difficile comprensione anche per gli stessi adulti. Crediamo che questo concetto si costruisca nei bambini anche osservando le trasformazioni del mondo attorno a loro e imparando a pensare a "cosa è successo prima" e a "cosa succederà dopo". Il tema dei minerali, da sempre oggetti affascinanti capaci di incantare e far lavorare la fantasia dei bambini, è stato trattato a partire dalla narrazione di una storia, attraverso la quale i bambini hanno incontrato diversi ambienti: la montagna, il ghiacciaio, il torrente, il fiume e la spiaggia, attraverso un personaggio (https://sites.google.com/site/chiccosand/) che compare in tutti questi ambienti, ma si trasforma, diventa sempre più piccolo, più liscio, più arrotondato passando da uno all'altro. Durante e dopo il racconto, i bambini hanno lavorato con i sassi e la sabbia concentrandosi sulle *somiglianze* di oggetti che sembrano molto diversi tra loro e sulle trasformazioni che portano da uno all'altro. Nella seconda parte, sempre seguendo la storia del personaggio, sono stati invitati ad osservare le *differenze* tra quelli che loro chiamano "sassi". Al museo i bambini hanno sperimentato, pesato, graffiato, disegnato i minerali; si sono accorti che ci sono minerali molto pesanti, minerali trasparenti, minerali che luccicano, minerali che si attaccano alle calamite, minerali che scrivono sulla carta, eccetera. In sezione hanno poi verbalizzato le idee e le scoperte fatte, raccontando e raccontandosi, ripercorrendo l'esperienza museale, trasponendo il vissuto graficamente su fogli con i colori. Saranno presentate l'analisi ed elaborazione dei dati raccolti, e la documentazione prodotta da bambini e insegnanti.

The educational and dissemination activities of astronomy and geology held in the Geopaleontological Museum of Rocca di Cave, Roma Tre University

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Keywords: Geopaleontological Museum of Rocca di Cave, astronomy, geology.

The Geopaleontological Museum "Ardito Desio" of Rocca di Cave (RM), proposes several educational activities for schools regarding astronomical and geological sciences. First of all the Planetarium "Skylab" (http://www.planetarioroma3.it/) is a useful and spectacular tool for implementing laboratory and practical activity of astronomy. The planetarium is an inflatable structure that can be easily bring to schools. The activities focus on the movements of the celestial vault, on the description of the main constellations and stories of the seasonal sky and the zodiac. Through interstellar journeys in full-dome to nebulous galaxies and distant galaxies, kids and students have a unique opportunity to learn astronomy and planetary science, being fascinated and amused by the experience. Moreover, the laboratory has always been an important part of scientific education. Some examples of it are the construction of Armillas and Sundials (models and instruments for understanding the apparent motions of the celestial vault and the Sun), and the construction of an Orientated Globe, a perfect model of Earth illuminated by the Sun during different seasons and daytime. A special attention is devoted for allowing to people with disability to participate to the experiences. In particular, blind students are allowed to follow the planetary presentations by means of tactile apparatus which have been specifically designed and realized. The primary educational objectives are: to facilitate the learning process, the diffusion of the knowledge of the sky, and the extension of the cosmic space; to understand the main astronomical phenomena, starting with those responsible for daytime and the alternation of seasons in our planet; to teach respecting nature and environment through illustrations of light pollution issues; to use the history of astronomy and the myths connected to it as an element of intercultural learning to foster processes of mutual knowledge and integration.

An educational approach for a PLS Geological Information Laboratory

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Keywords: educational geological laboratory, geopedology, geology, Scientific Graduates National Project, teaching, Ariano Irpino.

The Geological Survey Laboratory, experimented for no. 25 hours at IISS-CAT Ruggero II in Ariano Irpino (AV), aimed at increasing and improving the theoretical and practical knowledge of fourth and fifth year students on some geological themes and phenomena, typical of the Campania landscape and specifically of the Irpinia–Sannio Apennines. The illustrated case studies refer to environmental hazards typical of the Human-Environment System that require reflection on management organization and territorial planning, the role of anthropization in natural systems alteration, the risk mitigation and geological hazard assessment, the proper management, use and enhancement of local geological heritage.

The topics discussed were also used to properly inform the school about geological studies in view of the future choice of university disciplines and to improve the perception of the importance of the School/University link.

The training course for a.s. 2016/2017 has been structured in seminars, workshops and fronts, co-designed by the teachers of the High School and by researchers at the Department of Science and Technology of the University of Sannio in Benevento.

The themes were as follows:

- the rocks and the sedimentary successions of the territory around Ariano Irpino and their geological representation (reading and interpretation of a geological map-introduction to geological survey);
- from rocks to the soils: a reason for life (an introduction to geopedological survey);
- macro and microscopic observation of rocks typical of the Irpinia region and reordering of the school's collection of rocks and minerals;
- local quarrying of clay and gypsum;
- climate and natural environment changes in Earth's geological history;
- Vesuvius volcano: a danger to be avoided or a resource to be safeguarded?

Laboratory activities and demonstration were also carried out on the field with special daily or half daily tours and with excursions to quarries and local work sites for the extraction and processing of clay and chalky materials.

The produced didactic material (papers, publications, Powerpoint slides, etc.) was left in use at the School for further insights in the classroom.

The learning path carried out also served to increase the professional growth of non-geologist teachers (agronomists, engineers, mathematicians, physicists, letters, etc.) of the High School.

Teaching geoscience from a ship. The case of an Outreach Officer onboard the *JOIDES Resolution*

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Keywords: RET (Research Experiences for Teachers), professional development, inquiry, outreach, science education, expedition.

In the majority of OCSE Countries, the decreasing of graduates in scientific disciplines has been addressed on one hand with a reform of secondary schools curricula and on the other hand by improving the proficiency of Science teachers (NRC, 2012; Wilson, 2013). This last approach takes from the assumption that the way in with Science in taught is responsible for the decline in the interest in science among students. For this reason, the Report Rocard in Science Education (Rocard et al., 2007) considers teachers as "the cornerstone of any renewal in science education".

Studies on science education have found that teachers who lack research experience are less confident in teaching science with an inquiry methodology (Roth et al., 1998), the way that reflects how science really works and is found the most effective regarding students' achievement in science and their confidence in addressing STEM careers.

The International Ocean Discovery Program (IODP) utilizes an educational and outreach program that involves teachers and outreach professionals in the expeditions on board their platforms. This immersive experience gives teachers the opportunity to be part of the research process with the aim to fill the gap that exists between how science is explained in textbooks and the real practice of scientific research.

In this study, we present and discuss the results of the educational project of the Outreach Officer on board the JOIDES Resolution for Expedition 367 South China Sea Rifted Margin.

This research addresses:

1) the effectiveness of an "Education through Expedition" program to disseminate the research in geoscience;
2) the effectiveness of tools like video conferences for building a bridge between scientists and schools;
3) the value of being a teacher at sea as professional development for science teachers.

This exploratory study was carried out with qualitative methodology using questionnaires and surveys.

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PLS in geology: a tool for consolidating the relationship between School and University

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Keywords: PLS, school, university, didactic laboratory.

The Department of Sciences of Rome Tre University has developed through time, specific competences in the field of training of teachers and dissemination of scientific knowledge in the territory of Rome. PLS has allowed these activities to be included in a well-defined project, with a formalized relationship with schools and a long-term exchange with students and teachers. In fact, the PLS project was designed to create a strong connection between School and University in which students, teachers and university professors are all protagonists.The types of activities proposed under the PLS program are of 3 types: seminars on geological themes of general interest, laboratory activities and excursions. Seminars have focused on geological themes representing indispensable contents of the National Guidelines or on highly relevant topics. Examples are: the lithogenetic cycle, plate tectonics, paleomagnetism, evolution of life and environments. The labs were designed for both students (to face the study of the Earth with a critical approach), and teachers who can use them as valuable resources for teaching Geology. A peculiarity of the PLS course was the didactic excursions organized for students and teachers to directly 'touch' the geological history of the Roman area. The didactic excursions that have been designed, proposed and realized in the city are: 1) Excursion to the Caffarella Park, where it is possible to recognize the different forms of the landscape related to the geology of the territory and the action of geomorphic agents that shaped the forms of the Roman area over time; 2) visit to the San Paolo Basilica, where it is possible to observe a unique variety of rocks, coming from different areas of the Mediterranean Basin; 3) excursion through the historic center of Rome to understand how much the geology of the territory, and its resources and associated risks, have influenced the settlement and the subsequent development of the city. An upgrade meeting dedicated to high school teachers was held at Rocca di Cave, where the Geopaleontological Museum "Ardito Desio" of Roma Tre University is placed. Located in the Rocca Colonna, the museum 'tells' the geological history of the central Apennines, with a journey through time that dates back 200 million years ago. This journey helps in interpreting the origins of the landscapes that are visible from the Rocca terrace and the presence, on top of the Prenestini Mountains, of an ancient fossil reef. The Museum hosts an astronomical observatory where teachers are guided through the constellations in celestial exploration. Finally, a note deserves the activities that were successfully devoted to counteracting abandonment of students in Geological Sciences during their first year of attendance. This activity required an active role of University professors in encouraging students to get familiar with geology and passionate them about the knowledge of the territory where they live.

From School to University: the "Strategic Student" initiative of the Italian National Action of Scientific degree for Geoscience

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Keywords: Italian National Action of Scientific degree, geoscience.

The Italian National Action of Scientific degree is an ambitious project designed and promoted by the Italian Ministry of University and Research. Its main purpose consists on stimulating and attracting students towards scientific curricula at a university level. This can be obtained through educational orienteering of students combined with teacher's training.

For most students, the choice of Earth Sciences rises from passion for Nature and for its spectacular as well as fascinating evidences such as earthquakes, volcanic eruptions, minerals, fossils and landscape.

Some years ago, an investigation carried out on students attending the University course in Earth Sciences pointed out that passion for Geosciences was triggered by out-of-school- divulgation activities.

Therefore, a wise choice for university study should start from the need to combine both interest and curiosity for Nature.

Within this frame, the "Geology National Project" comprises actions aimed to orientate students coming from secondary school to Geosciences. These interventions consists of activities also focusing on the role of the geologist in the now-a-day society.

So, the assignments of the Geology courses at the university level must rely on concentrating interests and activities in order to emphasize the student's passion on geology. At the same time, the student must benefit of geological know-how and learn expertise on solution of problems concerning the territory and its resources, by applying the scientific method.

Modelizzazione di minerali con stampante 3*D*

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Keywords: minerali, apprendimento, modelli, stampante 3*D*.

Spesso i ragazzi fanno confusione tra rocce e minerali perché creano nella loro mente "concetti alternativi" (Dove, 1998) di questi elementi naturali facendo riferimento alla loro esperienza quotidiana. Per fare chiarezza su questo argomento, in una classe terza della Scuola Secondaria di Primo Grado Alfieri Bertagnini di Massa, è stato approntato un percorso didattico riguardante le rocce e i minerali. L'attività è stata condotta facendo uso dell'approccio a 5 fasi: osservazione, verbalizzazione individuale, discussione collettiva, concettualizzazione e produzione condivisa (Fiorentini, 2000); questo in accordo con le idee del costruttivismo (es., Driver & Oldham, 1986) e della ricerca-azione (es., Barbier, 2007). Inizialmente, sia per le rocce che per i minerali, è stata proposta un'osservazione libera di alcuni campioni che ha permesso poi di individuarne le caratteristiche comuni importanti per la successiva classificazione. Quindi, per evidenziare l'importanza della forma per il riconoscimento dei minerali, gli alunni sono stati avviati ad una attività di modellizzazione della realtà; questo è stato reso possibile grazie all'impiego di un software per la progettazione e modellazione tridimensionale e di una stampante 3*D* per la costruzione di alcuni modelli di minerale. In questa fase del percorso, i ragazzi hanno misurato angoli, lunghezze di diedri e spigoli di alcuni campioni di pirite, calcite e quarzo; hanno quindi riprodotto su carta e poi su PC l'immagine tridimensionale di quest'ultimi. La fase successiva quindi ha previsto la stampa dei modelli realizzati dai ragazzi per mezzo di una stampante 3*D*. In conclusione, il percorso intrapreso ha consentito agli alunni di partecipare attivamente alle attività proposte e di acquisire le prime basi del metodo di indagine scientifica. Inoltre, il processo di pensiero e di apprendimento, messo in atto durante tutto questo percorso, ha permesso agli alunni di apprendere le prime basi del disegno tridimensionale e di indagare in modo più approfondito sulla natura tridimensionale degli oggetti reali, avvicinandoli ancora meglio ai non banali concetti di diedro, prospettiva e volume già affrontati in ambito matematico e tecnologico.

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From Cosmos to Earth to life to culture. A resilient strategy for natural, physical, and mathematical science outreach activities: the proposal of a "Widespread Museum" for the city of Rome

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Keywords: Rome, scientific walks, widespead museum, outreach, geology.

In recent years, the development of new media, based on information technologies and the diffusion of multimedia tools, has stimulated the diffusion of scientific knowledge, making it accessible to a large audience. At the same time, the rapid increase in the use of these techniques has seen a progressive decline in experiential practice, particularly important for scientific disciplines such as Geology, Astronomy, Mathematics in Architecture and Botany, which find in direct observation the priority medium for the acquisition of scientific knowledge on our planet and on the Universe. The aspect of direct observation is particularly delicate in the context of urban areas where intense anthropization has drastically decreased the possibility of observing "the Earth beneath us and the sky above us" in a context in which the spatial and temporal scales in which the experiences and observations take place have been reduced. These territories are now increasingly "hidden", with the inevitable consequence that global scale phenomena, such as climate change, energy consumption in perpetual growth, natural disasters, are perceived in our society as unexpected, sudden events apparently far from our shared lives.

The present project uses an extraordinary natural laboratory, the territory and history of the city of Rome and its surroundings, to experiment with a new model of the dissemination of scientific culture in the field of Geology, Astronomy, Mathematics in Architecture and Botany. The project is part of the tradition of the Diffused Museum, a model that, moving away from the objective idea of cultural property, extends its look to the cultural and natural heritage. The urban landscape, with its stratifications, its transformations, its "long duration", becomes the object of active observation, through the direct experience of the city and its public spaces. "Scientific walks" become "multipliers of curiosity", offering the opportunity to put some urban resources (museums, parks, documentary memories, squares, streets, libraries) into system so that they represent different but coherent stages of a territorial network. The project includes the Department of Science, Mathematics and Physics and Architecture of the University of Rome Tre. The aim is to define an organizational protocol, based on the collaboration between leaders in the various disciplines, which allows the transmission of scientific knowledge both in the school and in the territorial, capillary, effective and high level. A project to create in the new generations a habit for the holistic perception of cities and the natural context in which they develop.

In the SIMP session "Geosciences at school 2017" special regard will be devoted to the contribution of the geologists to the project and to the direct experience with several classes of High Schools of the Roman territory. Examples of the feedback work will be presented.

Cycling & Science: game together

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Keywords: peer tutoring, experiments, Scientix, Next Lab, STEM, Alliance, Earth resources, bike, game.

This year an important bike competition starts from Alghero, Sardinia and we decided to organize a science outreach activity that put together science and bicycling. The name Cycling with Science is related to the secondary means of transport to get to the several elementary school. In this activity have been involved a mixed group of students from Liceo Scientifico of Alghero, aged from 14 to 16 years old who tried to engage in different science activities primary school children. The high school students proposed to the 7-8 younger 20 density base experiments and 22 light base experiments to the 9-11 years old pupils. These experiments have been chosen from Scientix http://www.scientix.eu/, STEM Alliance http://www.stemalliance.eu/home and Next Lab http://www.golabz.eu/labs Earth Science repositories. In the last day of this project the secondary School students will cycle along the cicle track with an experiment in their basket and involve citizens in their experiments. It will be a festival were sport, Earth science and the community will take part.

Looking for the lithosphere

De Nunzio A.[1], Langella A.[2], Nicoletti M.C.[1], Russo F.*[2], Travaglione S.[1] & the students of Applied Sciences
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Keywords: educational geological laboratory, mineralogy, petrography, volcanology, scientific graduates national project, teaching, Benevento.

"Looking for the Lithosphere" is the title of a small school project, aiming at re-organizing from a systematic point of view an old collection of rocks samples, heritage of the "Galilei-Vetrone" High school of Benevento. This project grew slowly until it became an activity that progressively involved a group of students within the School-Job orientation paths and PLS (National Project of Scientific Graduates), under the supervision of the geologist of the Sannio University.

The training course involved students according to their specific curricular skills hereafter specified:

1. third-year High school students (traditional curriculum and applied science curriculum) followed a mineralogical/petrographical oriented project;
2. fourth-year High school students (traditional curriculum and applied science curriculum) followed a geomorphologic and vulcanological oriented project.

The main purpose of the mineralogical/petrographical oriented project was the restoration along with a new cataloguing of the rocks and minerals of the School.

Experience: a first approach of the investigation was devoted to the identification of the main macroscopical features of these samples (specific weight, color, luster, hardness, cleavage, etc.) followed by simple chemical tests (solubility, acid attack) necessary to provide an easy access to an overall minero-petrographical classification. A more careful characterization was carried out with an infrared photospectometer provided by Sannio University.

The student had also the chance to visit the Regio Museum of Mineralogy of Napoli.

Results: the students produced data sheets of the whole collection of minerals and rocks reporting the scientific name of the mineral or of the rock, the main mineralogical, petrographical and chemical features, the classification, the provenance (whenever possible), the technological applications and industrial uses, and some curiosities.

The main purpose of the geomorphologic and vulcanological oriented project was the study of Somma-Vesuvius and how is important the monitoring of this volcano to foresee any possible activity in one of the most populated area.

Experience: the Somma-Vesuvius volcano has been the object of multidisciplinary scientific studies. The study also considered iconographic-artistic, socio-economic, tourist and anthropological aspects.

Results: a visit to the Ercolano excavations highlighted the risk associated with a Plinian eruption such as the one that interested this area in 79 A.D. This visit has made such a volcanic site perceived as a major georesource to be protected.

Geoscience workshops on Sicilian active volcanoes: implementing the school education through collaboration among different institutions

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Keywords: geoscience, volcanoes, fumaroles, field-work, digital technology, soft skills.

The attention devoted to our valuable geological heritage land has been often lacking in Italy. We have experienced it, as field experimentalist or as science teachers. So, we need to improve the knowledge of Earth-science at any educational level and we think an empiric approach, can be the proper beginning for a successful scientific cognitive path. The geo-tourism essentially attracts foreigners. During our field experiences on active volcanoes, we are still surprised by local visitors who enjoy seasonal activities, like skiing on the flanks of Etna, or doing sea activities on the coastal beaches at Vulcano and Stromboli, but who are not interested in the ongoing volcanic processes. Consequently, we have integrated the social impetus that drives active citizenship with school education in order to relate our scientific knowledge to the professional and existential needs of young students. Two scientific workshops have been carried out in collaboration with the science school teacher, the researcher of a naturalistic association (Geode), and researchers of the INGV. The first (A.Y. 2015/2016) was targeted to the Aeolian isles of Vulcano and Stromboli, the second to M. Etna (2016/2017).

Set goals:

- to increase the sensibility, respect and care for natural environment, as well as the awareness of the natural phenomena characterizing it;
- to overcome the traditional school setting organized in the classroom, using both field and laboratory approach;
- use a more effective (and attractive) teaching style to increase young people cognitive abilities, training also the relational skills, like work ethics, orally speaking, and teamworks;
- to foster the multi-disciplinar approach for solving complex problems;
- to contaminate disciplines with digital technologies highlighting instrumental potentiality and versatility;
- to orient young people into future professional applications.

The didactic pathway provided information on geology, volcanology and on botanic-naturalistic aspects of the Aeolian archipelago, Mount Etna and surrounding areas. We formed groups of students, heterogeneous for class and address, ranging from 28 to 35 items. The didactic experience consisted into theoretical lessons in the classroom and excursions by land and by sea, through the most significant itineraries of Vulcano, Stromboli and Etna (Monti Rossi, Alcantara Gorges). The students were introduced to the volcanologist's task in the field of volcanic surveillance, through an operational approach. Volcanic surveillance is a fast evolving multi-disciplinar research field, aimed to the mitigation of risk. The application of geochemical and of geophysical principles and instrumentations, allow to monitor some changes of energy release occurring in volcanic system.

Field activities have provided: a) learning of the main notions of orienteering (geographic map reading, compass, GPS, Google Earth); b) petrologic recognition in field and by microscope; c) sampling of volcanic fluids emitted from the fumaroles on the rim of the crater; d) simulation of geochemical explorations, using temperature and *p*H sensors on a mesh of acquisition points; e) identification of the main botanical species, typical of the visited areas.

By returning the campaign data, students shared the acquired data and prepared a final presentation with some digital software: virtual padlet, power point presentation, genially presentation. The students' cognitive and soft skills were evaluated as inputs and outputs from the workshops, to qualify the experience, highlighting strengths and weaknesses in the perspective of continuous improvement.

Following the release of L.107 / 2015 "La Buona Scuola", this workshop experience has been recognized as a school-work didactic method ("Alternanza Scuola Lavoro") for high schools (L.107/2015 art.1, 33 – 43). In fact, one of the training objectives set out in Art. 1c.7e;i, is the deepening of the methodological dimension by expansion and innovation of teaching strategies.

Aural Structures: creation of musical models in mineralogy education

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Keywords: mineralogy, crystallography, music, chemistry, STEM education.

Aural Structures is a project aimed to the creation of musical models of crystals and their educational application to mineralogy. The use of music in STEM has been associated to help memorising scientific concepts. However, music (without lyrics) can also be considered in itself as an interesting way to explore and explain the complexity of both natural and artificial structures, and a way to guide learners of any age towards the deep understanding of the difficult concept of molecular order, even for disabled people. For this purpose, we developed a scientifically based model of crystal structures which can give an aural representation of crystals that might be able to improve memorisation and learning through emotional involvement. All sound parameters (pitch, duration, timbre, and dynamics) are based on physical and chemical properties of the atoms involved in the structure. We are currently transposing our approach into a software program that will allow to automatically generate the musical model from the chemical composition and the space group of a given crystal. Once ready, the software might be extended to take additional parameters based on which it will change the sound rendering of the structures, according to the different educational purposes, allowing further development of the approach. Possible applications of this novel educational approach will be illustrated with practical examples about some relevant topics of mineralogy (*e.g.*, solid solutions, polymorphism).

A CLIL tool for teaching geosciences and safety rules in primary school

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Keywords: technology, educative tools, CLIL, primary school.

The aim of this work is to focus on a controversial question concerning the use of computers by children especially in education at the primary school level and the idea to develop more hand's on activities with poor materials in the classroom as cootie catchers (is a form of origami used in children's games) to learn geosciences and safety rules to observe in case of earthquake. On one hand the use of technology in education is absolutely necessary in order to experiment more in pedagogy in the classroom. There are countless resources for enhancing education as apps and e-books to use as amazing educative tools that make learn with more fun and effective. On the other hand parents, teachers, students and policy makers focuses on technology that can be a distraction and can foster more cheating in class and also during tasks. Moreover many of them firmly believe in damages that can be provoked by a continue use of computer that can cause very often a possible disconnect of social interaction and very often for example computer game addiction when youngest refers damages caused by unhealthy excessive amount of time spent playing computer games . The addicted user is very far from the real world while they need more experience with reality, because likely it is not the right age for abstraction. They need to cooperate with other students in social activities as handicraft activities. It is for that Cootie catchers are great tools that can foster students in their Earth science learning. "Give people facts and you feed their minds for an hour; awaken their curiosity and they feed their own minds for a lifetime" Ian Russell (Kassin et al., 2013). When we talk in class about earthquakes we know that content is based on vocabulary that transfer concepts. This tool can help pupils for memorizing scientific concepts and glossary and CLIL methodology. "In consideration of the need for pupils to start using English as a second language (L2) beyond the 2-3 hour a week compulsory "English lesson" in Italian primary schools, the new Italian National Curriculum Guidelines encourage multilingual education. This official stimulus could lead to the achievement of a more bilingual classroom with increased usage of English.., especially through the use of Content and Language Integrated Learning (CLIL) strategies" (Bailey, 2015). "Technology is just a tool. In terms of getting the kids working together and motivating them, the teacher is most important" (Gates, 2014).

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Field-based Earth learning for high-school teachers: training activities from Alps and Apennines

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Keywords: PLS Geologia, Vajont, field training, science high school teachers.

With the purpose to enhance Earth Science competence, PLS Geologia of Bologna, Ferrara and Modena-Reggio Emilia Universities organize an annual geological field training for Science High school teachers. The project (action C of DM 976/2014) is devoted to improve knowledge and skills of teachers but it also addresses issues of how to transfer scientific information to high school students, in order to both broaden student education and enhance competence in Earth Sciences. The courses have been designed to provide an interactive learning environment focused on student needs. The geological field training comprises common lectures, field exercises and activities. Selected case studies in Alps and Apennines offer the opportunity to deal with a variety of landforms and processes and to face with issues such as geological risks, climate change or sustainable resources. Course syllabi are printed and posted on a website that is be housed at each of the participating teachers, it includes also illustrative material, scientific articles, and links to other relevant websites.

The first year field training took place in October 2016 at the Vajont Landslide. The Vajont landslide is one of the best known and most tragic examples of a natural disaster induced by human activity. Many questions have been posed and remain concerning the legal, economic, social and scientific issues associated with the history of the dam and in emergency management of the reservoir slope up to the time of catastrophic failure. In this sense, it lends itself to the development of highly interdisciplinary, not only geological, school projects. Numerous initiatives have been carried out in order to contribute to keeping the memory of the catastrophic disaster alive. Among these the creation of a "multi-centre museum", consisting of historical-natural science paths, permanent exhibitions and other educational and/or popular multimedia material concerning the Vajont catastrophe. The two days field training covered geology, stratigraphy, tectonics and geomorphology of the Vajont Valley, introduced by a scientific seminar and videos. A walk on the crown of the dam gave the teachers the possibility to observe the dam itself and the landslide; a stop at a safe outcrop permitted them to observe the stratigraphy of the area, to learn to use the geological compass; with a visit to the Vajont Museum in Longarone and a stop at the monumental cemetery of the victims of Vajont, the field training ended.

In September 2017 the field training will took place in the Santerno and Senio river valleys (N Apennines), where turbidite deposits of the Marnoso-arenacea Formation (MAF) crop out extensively. The main targets of the field trip will be the MAF stratigraphic and tectonic features, and the landslides that affected this type of rocks.

Additional information on PLS projects are available at: http://plsgeo.unimore.it/; http://fst.unife.it/orientamento/pls; http://www.pls.unibo.it/it/geologia.

Building awareness of their origins from the knowledge of the territory

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Keywords: ambiente costiero, ecosistemi, educazione ambientale.

Brindisi (main town in the Salento peninsula, Puglia, Italy) is an important natural harbor known for centuries as the "Valigia delle Indie". The whole coast that develops in NW and SE deserves great attention to structural characteristics, values, physical-environmental relationships, nature, history, settlement and landscape.

An increased sense of citizenship in young people of 11-13 years of age range is built starting from the knowledge of the territory understood as a set of experiences and climbing habits from individual perception to the collective. The 3 years of junior high school is proposed to the students with a general overview of the landscape of the province: the study of the coastal environment as a result of geological processes and ecosystem relationships is a key part of the curriculum.

This specific comprehensive teaching programs in the 2nd and 3rd year include the study of ecosystems and a general overview of the geology of the planet Earth.

The extracurricular part of the program consists of projects aimed at the knowledge of the area by hiking the sites and use of various technologies, both physical-chemical (environmental analysis) and computer (for the geographical classification). In particular in the coming months they will be examining the lagoon environment analysis of the biotope Torre Guaceto, a wetland safeguarded according to the Ramsar Convention 1972. For the computer part every year a literacy course is organized which includes the knowledge of the use of GIS and image processing.

During these winter months also some classes will prepare for participating in a race at the national level based on knowledge of ecosystems.

The Scientix project: an opportunity to share best practices in Earth science teaching

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Keywords: Earth science, STEM, teacher professional development.

Scientix is a project funded by the Horizon 2020 programme of the European Union for research and innovation, that promotes and supports an Europe-wide collaboration among STEM (Science, Technology, Engineering and Maths) teachers, education researchers, policy makers and other STEM education professionals. Scientix is coordinated by European Schoolnet, a Brussels-based consortium of thirty ministries of education, which is a driving factor for innovation in teaching and learning and fosters pan-European collaboration between schools and teachers. Scientix is represented in Italy by a National Contact Point (Indire) and by 39 ambassadors, STEM teachers from middle and high school interested in promoting STEM topic and teaching activity. The Scientix project supports teachers in their professional development with face to face workshops, moodle courses and webinars, and provides a repository of teaching materials, developed by different European project on STEM topics.

The Scientix projects include also teaching resources and tools focusing on Earth science, available for teachers with no geological background that would like to improve their knowledge in this field. In addition, we would present teaching materials included in Scientix repository focused on geological topics as useful tools to engage students in Earth science. Moreover we would share our experience as Scientix ambassadors in order to invite new teachers, policy makers and stakeholders involved in Earth science education to participate in Scientix community and share best practices and experiences.

Speleology as an opportunity to realize didactic laboratory on the territory

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Keywords: education, lesson plans, karst landscape.

The study of Science in Secondary schools is based on the observation of environment, so it is very useful to introduce a link to the territory in which the students live into the didactic activity. This arrangement helps to learn the genetic processes of landscape forms. This paper proposes a teaching program that includes the use of the karst landscape as a natural laboratory, allowing to introduce other disciplines too, such as hydrology, hydrogeology and biology, and environmental protection. The activity includes several learning objectives based on the age of the students: observation and application of basic concepts for middle school students, analysis of karst for the high school students. The participation of students from different levels of education allows to carry out the activity through the peer-tutoring enabling the development of multi-disciplinary skills.

An experience on prepare not geologist for teaching geosciences at school

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Keywords: Geoscience education, teachers training, geography teachers.

Geoscience contents are usually presents in school curricula worldwide, although with remarkable differences. As well is quite difference the profile of academic study of the teachers in charge to teach this contents, the common point it's in general a lack of preparation in geoscience during his/her own degree. As in Italy most of the teachers that teach Earth Science content are biologist in Brazil are biologist or geographer.

As geography is considered a human science usually geography students have not great motivation in study science disciplines and that difficult even their understanding of the contents. We do not enter in the discussion if geographer are the most adapt professional profile for teaching geoscience in secondary school, by the way, as they are involved in this activities for law in a pragmatic way we will analyse the experience of a new discipline introduced at Unicamp (Brazil) that focus prepare geography teachers to teach geosciences content at school.

The curricula of geography course change a lot from university to university, at Unicamp this degree is inside the Geoscience Institute as the geology degree, probably for this reason there is a good balance between human and physical geography in Unicamp geography curricula, so future geography teachers received a good training in geoscience as well.

Since march 2017 were introduced a new discipline focus in improve the ability to teach geoscience at school. In this discipline theoretical and practical aspect are equally worked with great emphasis on methodology based on constructivist, inquired based science education and field trip. Several experts, including PhD students and schools' teachers that are doing project in geoscience education were invited to give seminars in order to show practical examples realizes in real schools.

The group analysed in this study is composed by the 28 students of the discipline. All the students are of the second year of the geography degree devoted to prepare school geography teachers. The discipline provides weekly six hours of activities, two of them are presencial in university classroom. The students were divided in two group, the first group, that is the day course, include 15 students, the second group, that is the night course, involve 13 students.

During the lectures of the discipline and during the field we observe and take note of behaviour, attitude, questions and answer and interactions in the work-group. The qualitative analyses of this data show a progressive increase in self-confidence of the students for teaching geoscience. Further study will be necessary to verify if this attitude will be maintained and confirmed when the students start to give lecture as professor in secondary school.

Il tempo della natura e il tempo dell'uomo: una lunga storia di cambiamenti climatici

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Keywords: cambiamenti climatici, storia della Terra e della vita, fattori antropici e naturali.

Nelle ultime decadi le variazioni climatiche hanno avuto ripercussioni sui sistemi naturali e antropici in tutti i continenti e gli oceani. In molti casi, le variazioni nelle precipitazioni e la fusione dei ghiacci hanno alterato il ciclo idrologico modificando la risorsa idrica da un punto di vista qualitativo e quantitativo.

Le attività antropiche, le città, le fabbriche, hanno contribuito al cambiamento climatico? Cosa sono i cambiamenti climatici e quanto influiscono sull'ambiente, la sua vegetazione, la sua fauna? Molte specie terrestri e acquatiche in risposta ai cambiamenti climatici stanno modificando o hanno già modificato la loro presenza e il loro comportamento nei vari ambienti. Come l'ambiente risponde ai cambiamenti nei tempi geologici e nei tempi storici? Quanto il sistema antropico ha modificato l'ambiente ed è stato modificato dai cambiamenti in corso?

Queste sono alcune delle domande che ci siamo posti nelle nostre classi terze e abbiamo deciso, insieme ai nostri alunni, di cercare le risposte osservando ciò che ci circonda ma con uno sguardo che indaga nel passato. Lo studio delle scienze della Terra, e della paleontologia in particolare, ci offre gli strumenti per comprendere che la storia della Terra e della vita su di essa non è stata altro che una lunga serie di cambiamenti. In particolare ci fornisce prove evidenti di antichi e ciclici periodi in cui sono avvenute variazioni climatiche, anche in un passato recente.

Gli obiettivi essenziali di apprendimento di questo percorso didattico, sviluppato nelle classi terze della Secondaria I grado, possono essere così sintetizzati: comprendere come cambiamenti climatici avvenuti in passato abbiano portato a cambiamenti di esseri viventi che popolavano la Terra; conoscere i processi che hanno agito nel corso del tempo geologico per comprendere come e perché l'ambiente cambia e per prevedere ed affrontare i futuri rapporti tra uomo e ambiente; comprendere come non debbano essere i cambiamenti di per sé a dover far riflettere, ma i tempi con cui essi si manifestano.

Hiring students as citizen scientists: a learning unit based on open data from an Antarctic drill-core

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Keywords: geoscience education, citizen science, IBSE (Inquiry-based Science Education), Antarctica, open data.

Students feel particularly engaged in science whenever they can experience the real work of scientists, gathering, representing and interpreting data to gain evidence about natural phenomena. At the same time, students feel proud if they can help scientists to get new evidence from data sets already existent in open access repositories acting as citizen scientists (Silvertown, 2009). The present work aims to promote a learning unit, developed during the doctorial period of one of the authors at the University of Camerino (Italy) and targeted at upper secondary school students (Macario, 2014). The unit is evidence-based driven and approached using the "5 Es learning cycle" (Bybee et al., 2006). After a preliminary brainstorming as Engage phase, working groups of students are invited to examine some basic features of the clasts included in a drill-core section (ANDRILL AND-1b), whose high definition pictures are fully accessible online (http://coreref.org/projects/and1- 1b/viewer/). These data are considered relevant in understanding how the Antarctic glacial system has worked in the past, during advance and retreat stages linked to periodic climate changing (McKay et al., 2009). In the following Explore phase students use simplified schemes and are guided by questions and templates in describing number, shape, size, roundness and lithology of each clast that is adequately detectable in a given portion of core. At a later stage, all data are reported as tables or plotted as diagrams. In the Explain phase, students are invited to interpret trends and patterns they can evidence. Then, the overview of the full core section is cooperatively built up, in order to infer the behaviour of the glacial cover over the drill site. Finally, in the Elaborate phase, all these evidence are discussed in a plenary session under the supervision of the teacher who will help students to understand the meaning of their results, which are compared with palaeoclimatic models previously described for the region considered. Therefore, they are invited to propose a model for the dynamics of the glacial system under exam in the time period examined. The activity is concluded by a self-assessing session in which students evaluate all the contributions given by peers. All the materials used to perform the activity are available on demand.

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Inquiry Learning Space: an innovative tool to teach Earth science in secondary school

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Keywords: Earth science, STEM, teacher professional development.

The Go-Lab Project (Global Online Science Labs for Inquiry Learning at School) (http://www.go-lab-project.eu/) opens up online science laboratories (remote and virtual labs) for the large-scale use in school education. The overall aim of the project is to encourage young people aged from 10 to 18 to engage in science topics, acquire scientific inquiry skills, and experience the culture of doing science by undertaking active guided experimentation.

To achieve this aim, the Go-Lab project creates the Go-Lab Portal (http://www.golabz.eu/labs) allowing science teachers finding online labs and inquiry learning applications appropriate for their class, combining these in Inquiry Learning Spaces (ILSs) supporting particular lesson scenarios, and sharing the ILSs with their students.

Here we will show the steps for designing an ILS using the Earth sciences laboratories (https://goo.gl/PpIziy) "Historic Climate Trends" and "Orfeus Earthquake Data Center" from the Go-Lab project. ILSs are online learning spaces that can be used by mobile devices so that make virtual laboratories accessible real-time wherever students are located and at any time of the day. The results show that if teacher uses ILSs in classroom, these can increase in students love to geoscience experiments, the growth of their critical thinking skills, the willingness to give and receive help, the learn from their own mistakes, the openness to different ideas and the ability to argue in group.

Learning on Gaming improves integrated development of basic science skills and fosters curiosity towards the Earth sciences

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Keywords: Learning on Gaming, Earth sciences, innovative teaching, Game Based Learning.

According to the European Commission (Eurydice 2016), it is necessary to improve student learning levels and their acquired skills, and at the same time to train, motivate and renew the teaching staff.

The aim of this work is to use the latest Information and Communication Technologies (ICT) to create innovative educational products for students and new materials for teachers, to effectively respond to the European Union instances.

Learning on Gaming (LoG) is a project based on a new didactic methodology: a Computer Class Role Playing Game (CCRPG), GeoQuest. Unlike virtual games, which digitally reproduce reality, GeoQuest world is created with drawings and pictures, music, sound effects and videos, realizing an ambience for a full and complete immersion into the game. Adventures include laboratory activities that can be made in the classroom or in a lab during the game, or can be viewed on specific recorded videos (Maraffi et al., 2016). The GeoQuest game includes interdisciplinary adventure paths based on topics of Geology, Volcanology, Mineralogy, Environmental sciences and has been created for 11-14 and 15-18 students year old.

The first data collected during the experimentation were processed according to the methodologies indicated in the literature (Martìnez Godìnez, 2013). A result is the students' response to CCRPG (51%), which is significantly higher than that of PowerPoint-supported lessons (34%) and traditional (frontal) lessons (15%). Moreover, the evaluation of the effectiveness of the activities was carried out by considering the following parameters: participation, comprehension of the themes, ability to convey complex interdisciplinary topics, ability to interact in a foreign language.

The results obtained until now confirm that Learning on Gaming, proposed through the CCRPG GeoQuest, can improve an integrated development of basic skills and European key competences and foster Earth sciences disciplines.

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From field and lab experiences to school desks: a "Piano lauree scientifiche" project at Pisa University

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Keywords: Piano Lauree Scientifiche project, hands-on activity, field work.

Piano Lauree Scientifiche Project (PLS) is a MIUR funded project to increase high school students' interest in basic sciences and to improve teachers training.

During the first years of the project field work and hands-on activities, based on the direct observations of geological processes, have been used as strategy for integrated learning, at different students' levels, in the area of Geosciences.

Fieldwork and lab activities have a big potential, for both students and teachers, to develop competencies promoting interdisciplinary learning. They enhance interdisciplinary approaches and that is why we used them as teaching strategies to consolidate theoretical concepts and to develop specific competences.

Approaching to field geological examples and to hands-on activities theoretical and difficult concepts could become easier to understand thanks to the direct observations of the different processes.

The PLS comprises four main themes and for all of them we privileged "pratical" experiences.

The main activities we organized, according to the main four themes included in the project, are:

1) several lab activities, at Earth Science Department of Pisa University, to teach and learn sciences addressed to secondary school students;

2) fieldwork activities to let secondary school students to be aware of their interest in Earth science disciplines;

3) field based summer schools for teachers to directly observe the main effects of plate tectonics;

4) field trip across the northern Apennines for first year bachelor students.

Plate tectonics: discovering ocean and continent on the Apuan Alps

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Keywords: Alpi Apuane, plate tectonics, summer school.

A Summer School for teachers, focused on understanding plate tectonics by the direct observation of its effects in the field and with the aid of hands-on activities, has been proposed in the frame of "Piano Lauree Scientifiche" project. Rather than being a theory to be known only from school books, plate tectonics can be, in fact, discovered in our landscapes and rock outcrops.

The Summer School has been organized, im collaboration with the "Parco delle Apuane" as a three days field trip across the Alpi Apuane massif in northern Tuscany, during which different tectonic units have been observed, deriving from both oceanic paleoenvironment (*i.e.*, Ligurian Units) and continental crust (Apuane Unit and Tuscan Nappe)

During field observations special attention has been posed to the study of brittle and ductile deformation of different lithologies that have been deformed at different structural levels , *i.e.*, in different pressure and temperature ranges, developed during plate collisions and subsequent exhumation of the rocks towards the surface. Interactive observations have been addressed to recognize different rock types and to define how they are oriented in the space to understand their relative geometric relationships fundamental to reconstruct the architecture of the belt.

Outcrop scale structures have been related also to mountain scale ones (*i.e.*, pluridecametric folds) leading to the construction of the chain.

During the first day we focused also on the development of natural cave and karstification processes. In this view we visited the "Antro del Corchia" cave that represents one of the best examples in the northern Apennines belt. Not far from the Antro del Corchia cave we had the opportunity to visit the old mine of Levigliani were we discussed about related mineralizations that till not far ago represented a very strong commercial activity for the region.

During the last day, various interactive lab activities have been proposed regarding mainly classification problems of rocks and minerals, determination of rock ages and interpretation of topographic and geological maps.

Lettura del paesaggio in chiave interdisciplinare. Scienze, geografia ed educazione tecnica in sinergia per un apprendimento multiplo

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Keywords: didattica interdisciplinare, lettura del paesaggio.

Il paesaggio rappresenta un elemento chiave del benessere individuale e sociale (Convenzione Europea del Paesaggio, Preambolo, capoverso n. 9), i suoi caratteri derivano dalla natura, dalla storia umana, dalle reciproche interrelazioni (Codice Urbani, art. 131).

Tanto le *Indicazioni Nazionali per il curriculo della scuola dell'infanzia e del primo ciclo di istruzione* (Decreto Profumo del 2012) quanto la *Raccomandazione del Parlamento Europeo e del Consiglio del 18 dicembre 2016* (2006/962/CE) fanno della lettura del paesaggio un obiettivo fondamentale. Di qui la scelta delle scriventi, di presentare un contributo relativo ad attività didattiche rivolte a studenti della scuola di base, di età compresa tra gli 11 e i 14 anni.

Evitando confini convenzionali tra discipline che non hanno riscontro con l'unitarietà tipica dei processi di apprendimento (ogni persona infatti impara attingendo liberamente dalle sue esperienze e rielabora), si intende allenare i ragazzi a cogliere nell'insieme dei caratteri che concorrono a formare la fisionomia di una scena paesistica, la concatenazione che li lega ed in questa concatenazione, un'espressione delle leggi generali dell'organismo terrestre (Paul Vidal de Lablache). A partire dall'osservazione con tutti i nostri sensi, abbiamo indicato il metodo per scoprire, descrivere, interpretare i rapporti di causa-effetto che esistono fra le componenti fisiche ed antropiche di un territorio: dalle strutture geologiche al rilievo, dal rilievo al clima, dal clima all'idrografia, alla vegetazione, all'uomo potente agente di modellamento del paesaggio, al pari di quelli atmosferici. Applicando al paesaggio il metodo cartesiano di costruzione della conoscenza, gli alunni sono stati avviati a leggere nel caso specifico, la Valle del Potenza (Marche), come una radiografia superando l'iniziale approccio estetico ed emotivo, per ricostruirne i processi genetici.

La raccolta, la catalogazione ed il confronto dei dati è stata elaborata attraverso la produzione di plastici, disegni e schede di classificazione del paesaggio in esame, usati poi per la valutazione degli alunni. Attraverso l'uso della cartografia ufficiale, della bussola, di schede di rilevazione e immagini da telerilevamento è affiorato in maniera naturale il concetto di regione nella sua accezione polisemica.

L'insegnante di scienze ha mostrato come esaminare campioni di vegetazione ripariale e di suolo tipici del territorio collinare marchigiano per imparare a "vedere" analogie tra le foglie e la diversità nei colori dei suoli.

In una logica ricorsiva, si è partiti dal mondo reale per ritornare su di esso passando per le fasi di conoscenza teorica ed esperienza pratica.

Earth science learning research: metaphysics or science?

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Keywords: teaching, research, scientific societies, Earth science.

The teaching of science associates both the scientific method, introduced by Galileo, and learning methods. Students have to observe a phenomenon, experiment and do their deductions. This learning approach has its roots in the constructivism, where pupils replace prior ideas with new knowledges (Driver & Oldham, 1986). Learning sequences, planned with these objectives, cannot be improvised but theoretically studied and practically experimented. So, learning theories have to associate with science to form science teaching. Earth science teaching is peculiar within other scientific disciplines. Earth transformations occur at very different pressures, temperatures and times from daily experience. So, Earth science need models for teaching. Earth science teaching has to be supported by learning theories associated at disciplinary contents for avoiding the rise of "alternative conceptions" (Dove, 1998). The question is: who has to do the research of Earth science teaching? This researcher must have scientific expertise and deep knowledges of learning features. This figure must be filled by Earth scientists, such as for mathematics, physics and chemistry. Earth science researchers interested about teaching are very few. Until recently, in Italy, by an academic point of view, didactics for school and Earth science were two separated and faraway worlds. Now more researchers have approached didactics for school through the Piano Lauree Scientifiche. The first difficulty that researchers face is to find a space where to publish their researches about didactics. Earth science academic compart seems to consider teaching research like a no-science or metaphysics, papers are considered not scientific and so not worth publishing. Instead, didactic research has got a scientific status. The data collection may be different compared to Earth science research, but results are scientific. Initially, research methodology is qualitative but then becomes quantitative (Libarkin & Kurdziel, 2002) to confirm data. Findings of teaching research must find place in a scientific context to not remain a metaphysic reasoning. It should be allowed to Earth science teaching researchers to access at an editorial space on scientific journals and didactic commissions in scientific societies and associations. If it is important to do Earth science research, it is important to do didactic Earth science research for improving skills of students that could be future researchers in Earth science.

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An approach path to Earth science

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Keywords: Earth science, teaching, Apuan Alps, scientific degree course plane (PLS).

The guidelines actions of DM 976/2014 consider "to put at system the practice of the lab" for the teaching of basic sciences, in particular for the training orientation of students of the last three years of secondary school". The DM 976/2014 regards the Scientific Degree Course Plane (PLS) to impassion to Science and to increase the number of university students. Earth Science Department proposed at I.I.S. "A. Meucci" of Massa an approach path to Earth science for third classes students of Scientific High School and Quantity Surveyors. The sequence envisages a first knowledge about Earth science and then labs to deepen some aspects of geology for the two further years. First year was organized in three segments: a meeting in class to know better the Earth science, a field trip on Apuan Alps for a day and a lab with the georadar. The activity began in classroom with a brief funny test about some aspects about geologists' employment. This was the icebreaker for talking about branches of Earth science together with students and discover opportunities of job. The appointment was to the successive Saturday with only interested students at geology. Seven students (six males and one female) got at the meeting. Students were led at Campocecina in Apuan Alps for an excursion. The field trip consisted of a backwards travel in the geological time: from the current anthropization of landform for marble quarries to the deposition of Jurassic carbonatic platform. Last segment was the use of Georadar in the garden of the school looking for something buried. The students participated to the experiment using the Georadar with the help of the teachers and after that the teachers introduced them to the processing of the collected data using the Georadar software in the classroom. The experience was positive for Department of Earth Science and for I.I.S. "A. Meucci" because it showed that put together synergies leads at an active participation of students in an important propose regarding their future lives.

Analysis of Earth sciences teaching methods and contents in high school curricula after the Gelmini reform

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Keywords: Gelmini Reform, curricula, final reports, topics.

This work analyzes the contents and the way of teaching "Earth sciences" in the various high schools of provinces of Cremona, Lodi and Mantova (Lombardy region, Italy) after the Gelmini Reform (2010). The main purposes are to analyze a) how the curricula have been changed according to the reform, the annual programming and the final report, b) check the degree of adjustments to the National Guidelines (first biennium, second biennium and fifth year), c) in case of divergence from the pre-reform teaching methods, investigate the reasons. (Realdon et al., 2014). Seventy-five high school science teachers were interviewed using a questionnaire and the contents of the work plans (containing preventive programming) and the final reports were analyzed, both referring to the school year 2015/2016, obtaining a total of 663 documents. A comparison was also made between the various high schools: scientific (science disciplines with the option of applied sciences) classic, linguistic. In the first biennium topics that are not currently included in the National Guidelines are proposed.

The comparison between the topics actually carried out in school and the original work plans shows that the programming was never fully respected (156 documents out of 299 totals). The questionnaires allowed us to highlight which topics were dealt with most and which least. In the first biennium of all the high school types, "Climate of the Earth" and "Geomorphologic Study of Earth Surface Structure and Processes" were treated the most and the least, respectively (93.6% and 66.7%). In the second biennium, the most popular contents are: "Mineralogy and Petrology" (55.4%), "Earthquakes" (50%), "Volcanism" (36%). Finally, in the fifth year, the topics covered are "Plate tectonics" (73.8%) and "Meteorology" (59.5%).

Regarding the non-covered topics in relation to the original programs, in all high schools only those in agreement with the National Guidelines for content and period were considered. Among these only 45.7% of the total content of the "Earth Sciences" programs were carried out in school.

This analysis shows a vision of Earth sciences not integrated with other disciplines and not as a complex discipline functional to obtain a comprehensive view of the Earth system. Instead, the idea of skipping entire topics not only do hinder comprehension but also the interest of the students, who see Earth sciences as separate chapters of a book, with gaps in-between and without links one to the other.

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Evaluation of theatre as a way to promote Earth sciences skills debating

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Keywords: theatrical arts, creative writing, skills debating, changing climatic conditions.

This research aims to investigate the efficiency of theatrical arts to improve scientific debating and to transfer specific knowledge.

After an analysis of previous experiences of theatrical arts for scientific outreach and education useful to identify weaknesses and the strengths of the educational strategy (Chemi & Kastberg, 2015), the project was planned.

It started as a laboratory of creative writing prompted from personal studies on the Earth sciences topic and related arguments carried out by the students, with the aim to produce a script where they are authors/actors.

The script has a central idea: the complex relationship between glacier and man, the first one inserted in a geological context (the Alps with their origin, structure, rocks and minerals) and the second one interacting with the glacial environment under different factors (natural, historical, artistic and cultural). A constant dialogue between man changing following his history and glacier changing under changing climatic conditions allow for the involvement of more topics and disciplines thus increasing knowledge, awareness and sensitivity to geoconservation. Under such educational approaches, geology (orogenesis, tectonics plates, petrography and mineralogy, glaciers, climate changes) have been discussed as well as art, physics, history and literature. The building phase was tested by teachers attending Summer School at the University of Camerino in terms of contents and didactic suitability; then the reviewed script was tested through a dramatization useful to promote discussion and reasoning (Simon & Richardson, 2009). An evaluation phase considered the script, the rehearsals and the last performance (dramatization) focusing on the students' debating skills and on the transfer of specific knowledge. The first goal is analysed by: i) design criteria useful to assess students' debating; ii) comparison of students' levels before, during and after the theatrical activities; iii) comparison of a control class (all students 17 years old).

Specific criteria (number of sentences, specific words related to the topic, complexity, formal correctness, justification, statistic data, bibliographic references, opinion, scientific data, ability to argue both for and against, ability to argue schematically using bulleted lists, tables, lists,) were evaluated. Results are encouraging both in terms of acquired knowledge, specific abilities and transversal skills achieved were learn to learn, working in group, communicate, entrepreneurship. To estimate the transfer of specific knowledge to the general public a questionnaire was distributed to the public and the results seem really positive.

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Simon, S. & Richardson, K. (2009): Argumentation in school science: breaking the tradition of authoritative exposition through a pedagogy that promotes discussion and reasoning. Argumentation, 23, 469-493.

System approach to Earth sciences by means of a vertically articulated curriculum on marine micro-plastics

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Keywords: micro-plastics, micro-beads, system approach.

Differently from ocean garbage patches, known since many years, marine micro-plastics only recently have become popular in the media and are still new as an educational topic.

Apart their growing relevance as a global environmental problem, they appear a suitable topic to be exploited in the teaching of Earth sciences according to a system approach (King, 2008) addressing the interactions between the different “spheres” making up the planet and between humans and these components of Earth system through bio-geochemical cycles. Microplastics, in fact, relate to multiple topics included in science curricula: marine environments, food-chains, weathering, water cycle and river runoff, oil geology and petroleum chemistry.

Inspired by this issue, we developed a series of practical activities for students of different age with the use of different communication styles and teaching techniques.

For younger students (age 3-7) we address the topic of micro-plastics bioaccumulation in marine food chains by means of visible models (giant “micro-plastics” built with plastic bottles) and dramatization. We use a performance in which pupils act as fish of different size and trophic level: the biggest one – a tuna – ends up as a “meal” shared by pupils group. Teachers guide the performance, play other characters and stimulate observations and remarks about the origin of micro-plastics and the correct management of plastic objects. The performance has been documented in a video and presented in a national teacher workshop (3 Giorni per la Scuola, Napoli 2015).

For students aged 8-13 the approach is more traditional. The activity begins with observation and manipulation of common household plastic objects, followed by physical/chemical testing of different polymers, aimed at understanding the characteristics that make these materials valuable and troublesome at the same time. The fate of plastic objects is then addressed through the observation of beach litter and of beach sand containing natural components and man-made fragments, including micro-plastics. In this way pupils can directly experience the fate of dumped plastic, discussing more sustainable management of plastic objects.

For older (14-16) students we introduce primary micro-plastics by means of personal care products containing micro-beads: students learn to recognize the presence of micro-beads by reading the product’s composition, touch and observe them, then measure micro-beads content of one of these products and calculate a possible annual dispersion of micro-beads from their town to the sea. The activity is followed by discussion about possible solutions to micro-beads water pollution.

Lesson plans containing these activities are freely available (Realdon, 2015; Realdon, 2016) Micro-plastics activities have been evaluated through satisfaction questionnaire given to class teachers with positive results. Students’ learning has been informally assessed by questioning them at the end of each activity.

King, C. (2008): Geoscience education: an overview, Stud. Sci. Educ., 44,187-222.
Realdon, G. (2015): Microplastics: small but deadly. Sci. School, 34, 32-35.
Realdon, G. (2016): Scheda didattica – Un’immensa zuppa di plastica. Sci. Magaz., 15, 7-8.

How does the geologist work? The educational approach of a PLS Laboratory

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Keywords: PLS, natural risks, geology, global change, Irpinia.

The lab experience consisting in a 25 hours course based on Earth sciences "information", developed at Liceo Scientifico *Aeclanum* in Mirabella Eclano. Such experience was aimed to improve either the theoretical or practical knowledge of a group of students attending the fourth and the fifth classes about some specific themes and phenomenon characterizing Campania's landscape and namely the Irpino-Sannita one. Cases study have been referred to those risky situations that involve the relationship between man and the environment. This consideration requires a reflection on a specific management and planning of the territory in the presence of human activities, if a change is to be expected

The formative planning for 2016/17 school year has been structured with seminaries front lessons and lab activities done in cooperation between school teachers and researchers of the Sciences and Technologies Department of University of Sannio. Discussed topics were also used to properly inform all students about geological studies in view of the future choice of university and to improve the perception of the importance of the school/university linkage. The specific topics were as follows:

1. human impacts;
2. Vesuvius, a real dangerous presence or a resource to safeguard?
3. climatic changes;
4. the soil resource;
5. seismicity and risk;
6. tectonic and volcanism of Phlegrean Fields;
7. enviromental geochemical analysis and the potentially toxic elements in the water.

To complete the programme, demonstrations and lab activities have been performed in open air excursions, as at the water springs of Serino (AV).

All the materials produced during the didactic action (maps, publications, power point slides, etc.) are now at disposal of the school for any further usage in classroom activities. Moreover these procedure has contributed to enhance the professional capabilities of all non-geologist teachers who work in this school. They have also been involved in interesting interdisciplinary researches on a great relevance aspect of Geosciences. In particular, within a project called "SOS Climate", a daily pollutant survey was conducted by processing the data from monitoring units available on web. The results of this survey combined with welfare data allowed the environmental quality for the middle area of Irpinia.

Geosciences laboratorial experiences in the Middle-school

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Keywords: mineral, rock, fossil, laboratory.

A third-year Middle School Class of the town of Vezzano (Reggio Emilia) took part in a specific project dedicated to Earth sciences. The activities concerned experimental laboratories on the recognition of minerals, rocks, fossils and the observation of various landscapes. To deepen the study was organised in different phases. During the first step, the fundamental of chemical knowledge were acquired, followed by mineralogical principles and rock classification related to their genesis. The second step considered the typical landscapes modified by weathering. Finally, the main old biological taxonomic groups were explained: indeed, several living beings originated fossils because of their mineralized parts.

From time to time, laboratory experiences were performed by pairs of students freely aggregated, provided that the couples were flexible in the four laboratories.

During "Mineral-laboratory" every pair was provided with a short block-note, the essential features of about twenty minerals and an experimental kit. This kit was composed of a precision scale and a graduated cylinder, and several objects to determine the hardness of the minerals. On the desk the pairs of kids could test other mineral properties such as cleavage, fluorescence, magnetic properties, acid reaction and streak colour.

During "Rock-laboratory" every pair was provided with a short block-note and the description of about ten common rocks of the three genetic groupings, some of which were of generic class while some others more specific. Every pair had a magnifying glass and could test the reaction through hydrochloric acid, as well as rock flotation and softening by water immersion. Each pair had to examine a tens of rock samples.

During "Fossil-laboratory" every pair was provided with a short block-note, essential features of the main fossil groupings and five samples belonging to several taxonomic groupings, in order to make comparative observations and the following recognition of the fossils.

The "Landscape-laboratory" started with a slide-show of about forty images of landscapes modified by weathering. The students in pairs had to describe what weathering agent had acted on every specific landscape. In the end, every pair delivered its observations to the teacher.

At the end of all three laboratories on minerals, rocks and fossils, the students had to elaborate own observations and hypothesis about the classification and the identification of the samples contained in the various boxes, each of them containing the name of the sample.

Environmental education through geosciences: chocoland, an edible experiment

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Keywords: environmental education, geomaterials, IBSE, sustainable development.

Students are usually not aware of the relationship between their lifestyle and its impact on the environment. This is true regarding the use of non-renewable resources, like geomaterials, usually considered infinitely available. The teaching of Environmental Education in the Italian schools (11-13-years old students) allows approaching, for example, the concepts of georesources and ecosustainable development. Geosciences become therefore tools to study complex topics, connecting different skills and competences also from other disciplines. The proposed activity, based on the IBSE approach, was organized to make pupils identify variables, find relationships and confront each other, to respond to the IBSE question: "Which are the economic advantages and environmental consequences of mining"? They carried out their investigation in groups, by simulating mineral extraction making use of chocolate-chip cookies: each group bought the mine (biscuit), tried to pull out minerals (chocolate chips), bought staples and toothpicks (mining tools) and filled up a form where gains and losses were recorded. Groups earned when a chocolate chip was pulled out but they also needed to payback environmental damages it caused (*e.g.*, lost soil surface, ecosystem impairment etc). In the last phase the groups fulfilled an identical form, but they did not extract new minerals anymore but they used those they already extracted (re-use and recycle). The hands-on asset and the use of chocolate cookies made pupils protagonists of their own learning, since they were involved through several perceptual channels (Head, Hearth and Hands). Besides, the topic used interdisciplinary connections (*e.g.*, History, Technology, Math etc) which allowed to describe the use of metals in the antiquity, link the mineral resources to actual objects of everyday life, make graphs and calculations. Moreover, a practical application of recycling was carried out in collaboration with the Technology teacher: pupils realized simple objects made from recycled or recovered materials, as an example of environmental liability and conscious consumption. So far the project has been carried out only halfway. However, it is possible to highlight some observed points of interest. 1) The students demonstrated a high level of concentration, but also an emotional involvement, which reflected positively on the acquisition of competences. 2) Experiments allowed pupils to observe, measure, collect and interpret data, starting from a practical situation. 3) The IBSE approach influenced positively the students' ability to identify relationships. 4) Pupils retrieved manual skills through realization of handcrafted articles made with recovered materials. 5) The use of geoscience topic allowed following all the process of production of an object, with many interdisciplinar connections, introducing the students also to the concept of circular economy.

Design and experimentation of educational activities in geosciences for secondary school

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Keywords: school, experimentation, geosciences, education.

This work reports the results of a Master Degree Thesis in Earth sciences focused on the design and experimentation of educational activities in geosciences and developed under the PLS geology national program promulgated by the Italian Ministry of Education, University and Research (MIUR). The main goal was to test a training course, closely related to the Ministerial program for third-class high school students, consisting of lectures, laboratory activities and field works. For this training course we chose two third-classes from scientific and classic high school Martin Luther King (Genoa, Italy).

The educational activities were subdivided into five modules (minerals, igneous rocks, sedimentary rocks, metamorphic rocks, and geology of Liguria) and were developed from October, 2016 to February, 2017 for a total of 13 hours for each class.

For each module we provided a preliminary test ("test in"), to determine numerically the basic knowledge, and an assessment test ("test out") to evaluate knowledge and skills aquired during the development of the project. Finally, rating tests were proposed to evaluate the effectiveness of the project and to highlight any issues and criticalities.

The results obtained, evidenced a significant improvement of skills acquired by students, a progressive better response to the presented issues, a generally better attitude towards learning geology and a greater awareness of the relevance of the role the Earth sciences play in our daily lives. Students evidenced good autonomy in the application of acquired knowledge or basic skill (how to classify, to compare, to describe, and to find the reasons) and even higher level skills, *i.e.*, problem-posing ability (analysis of the problem) to the problem-solving capacity (solve the problem). Finally, it is worth to note that all results indicated that laboratory activities were perceived by a majority of students as an effective means of learning science.

The most important issues emerged from the analysis of assessment- and rating-test results were i) the timeframe in which the project was developed and ii) the fragmentation of the Earth science in the scientific and classic high school programs which is scheduled over three years (first, third and fifth years, respectively). Althoug the first problem can be resolved by reducing the number of modules in this type of experimentations, it stresses the insufficient number of hours devoted to Earth sciences by ministerial programs. The second problem is even worse; the fragmentation of the Earth sciences over three non-consecutive years and the new organization of the different topics pose particularly significant issues since it interrupts the learning continuity of a particularly complex and widespread subject.

In conclusion, this experience of collaboration among high school and university is certainly to be repeated in the future also in other types of schools to compare the data obtained in different cultural contexts.

Right about to explode. Outreach activities for Earth sciences

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Keywords: outreach, uncertainty, experiments, party popper, volcanology, Earth science, dissemination.

In this presentation we will present a few examples of outreach activities carried out to talk about volcanoes and other geological processes. Through the years, we tested different approaches, ranging from traditional lessons to more informal, interactive activities where participants are directly involved in the discovery process. Engaging activities are usually more effective in keeping the attention alive, but we find that too much emphasis on the entertainment may prevail over the actual transfer of scientific information, depending on conditions and age. While kids usually enjoy these kinds of programs, making sense of the game in relation to the actual natural phenomenon may be difficult. We will discuss some of the activities we propose, trying to hightlight both strengths and weaknesses.

First, we describe a promising storytelling approach. Then, we focus on a game that explores the complexity of decision making under uncertainty. The game is based on party poppers whose explosion is triggered by pulling a string: participants are asked to guess the load required to explode the poppers. Participant's guesses and the visualisation of results are realised via web pages, using Free Software components. This approach makes the experiments easily recordable and allow to involve wide audiences in the activity. The distribution of guesses and the actual outcome of each experiment are discussed with the participants to gain information on the behaviour of the party poppers. While repeated experiments may help to constrain the amount of pull required to trigger the explosion, each popper is different and each explosion hits rather unexpectedly. We will discuss the outcome of these activities and share related outreach materials (video and booklets, in Italian, English and Spanish), all available through our institutional websites.

Primary and secondary school students explore geosciences in extreme environment: attitude and knowledge acquisition

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Keywords: experiential education, learning in natural environment, greenhouse gas emission, extreme environment, plant adaptations.

Most pupils are curious about the natural world showing a great love for it, and learning in natural environment has a great impact on their behaviour, attitude toward science learning and learning achievements (OFSTED, 2008; Natural England, 2012). Hopefully this enthusiasm will influence their future choices as well. We propose an outdoor science experience in a kind of terrestrial extreme environment, *Bossoleto mofette* (Mofeta del Bossoleto, Rapolano Terme, Siena), where pupils can approach different disciplines. Many school teachers of the villages nearby the site, have been wishing to show this special and inaccessible location to students, because of its singular value and because it allows an interdisciplinary experience. This site is a doline formed by collapse of the parent rock underneath, namely fractured travertine. The area is characterized by natural emissions of CO_2 from soil and caves and water resurgences. A CO_2 lake (Kies et al., 2015) forms every night with CO_2concentration close to 85% at one meter from the ground. This high concentration of CO_2 and the typical geomorphology of the area cause also an extreme greenhouse effect during the daytime, which drives adaptation responses in the biological communities here living.

Students from primary and secondary schools, guided by researchers in an experiential field trip, learn about many scientific aspects of this unusual place, making a multidisciplinary experience about geology (geological aspects like formation and weathering of travertine), botany (species, physiological adaptations), biocenosis (living communities), gas and climatology (gas concentrations and properties, greenhouse effect). The visit includes explanations but also direct observations and measurements.

This study reports about the results of a pre-post survey on a sample of primary school students about (i) their attitude toward science, (ii) expectations about the experience and, after the field trip about satisfaction (iii) and achievements (iv) in terms of knowledge transfer, raise of curiosity and interest. Finally, an example of authentic assessment for upper secondary school is here presented, proposed after the outdoor activity, which could be useful to test competence and skill in geoscience learning at the end of the first biennium level.

Kies, A., Hengesch, O., Tosheva, Z., Raschi, A., Pfanz, H. (2015): Diurnal CO_2-cycles and temperature regimes in a natural CO2 gas lake. Int. J. Greenh. Gas Control, 37, 142-145.

Natural England (2012): Learning in the Natural Environment: Review of social and economic benefits and barriers. Natural England Commissioned Report NECR092. www.naturalengland.org.uk. ISSN 2040-5545.

OFSTED (2008): Learning outside the classroom: how far should you go? Crown, London, UK.

Session S32:

Open Poster Session

Hydrogeochemical contribution to the knowledge of the multilayered aquifer of the Pisa alluvial plain

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Keywords: hydrogeochemistry, stable isotopes, Pisa plain, low-temperature geothermal energy.

Hydrogeochemical surveys are useful for characterization of groundwaters and for the construction of hydrogeological conceptual models of water circulation in the subsoil.

This study is focused on the Pisa plain, covering the area delimited by the Serchio river to the north and the Colline Pisane-Livornesi to the south and by the Tyrrhenian coast to the west and Pontedera to the east. The plain hosts a confined multilayered aquifer (Baldacci et al., 1994; Sarti et al., 2015), which is characterized by an interlayering of sands and gravels, locally separated by low-permeable clay layers. In particular, this study is focused on the shallow sediments (up to 200 m) of the plain, which are characterized by two main permeable levels.

In this work a chemical and isotopic study has been performed on a set of well samples associated to a specific permeable level. In order to investigate the possible feeding areas of these aquifers, also Monte Pisano springs have been sampled.

The chemical analyses allowed to identify the main hydrogeochemical patterns and the main processes involved. The upper permeable level of the multilayered aquifer is characterized by four different facies: Ca-HCO_3 (67% of the samples), Na-Cl (15%), Na-HCO_3 (10%) and Ca-SO_4(Cl) (8%). In the lower level there are three facies: Ca-HCO_3 (43% of the samples), Na-HCO_3 (33%) and Ca-SO_4(Cl) (24%).

Water stable isotopes have been used in order to investigate the water origin and the principal recharge areas of the confined multilayered aquifer. The δ^2H and $\delta^{18}O$ values are within the local average values relative to central Italy (Longinelli & Selmo, 2003) and range from -32,8 ‰ to -40,9 ‰ (δ^2H) and from -5,5 ‰ to -6,9 ‰ ($\delta^{18}O$). This method allowed to compute the average altitude of waters infiltration, highlighting the feeding coming from the Monte Pisano alluvial fan to the central sector of the plain. This hypothesis is supported also by the good match between the chemical composition of the spring waters, which represent the resurgences of the meteoric waters infiltrating in the Monte Pisano debris cover, and the one of the well waters that circulate near the main Monte Pisano alluvial body.

The research contributed to the knowledge of Pisa subsoil for the implementation of low-temperature geothermal plants for heating and cooling.

Baldacci, F., Bellini, L., Raggi, G. (1994): Risorse idriche della pianura Pisana. Atti Soc. Tosc. Sci. Nat., Mem., Ser. A, 101, 241-322.

Longinelli, A. & Selmo, E. (2003): Isotopic composition of precipitation on Italy: a first overall map. J. Hydrol., 270, 75-88.

Sarti, G., Rossi, V., Giacomelli, S. (2015): The Upper Pleistocene "Isola di Coltano Sands" (Arno coastal plain, Tuscany Italy): review of stratigraphic data and tectonic implications for the southern margin of the Viareggio basin. Atti Soc. Tosc. Sci. Nat., Mem., Ser. A, 122, 75-83.

Shallow aquifer characterization through an integrated geophysical approach: the case of Laterina, Italy

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Keywords: shallow aquifer, geophysics, integration, tomographic methods, clusters analysis.

The need to obtain a detailed characterization of the subsurface and its interpretation, often requires to apply several and complementary geophysical methods. Due to the different sensitivity for geophysical methods, as ERT, Seismic refraction/reflection, gravimetric, one can obtain many information useful to describe the subsoil variations. The goal of the approach in this paper is a unique final model showing information due to the characteristics highlighted by several geophysical methods.

The studied area, into the municipality of Laterina (Arezzo, Italy), is a shallow basin filled by lacustrine and alluvial deposits (Pleistocene and Olocene epochs, Quaternary period), with alternated silt, sand with variable content of gravel and clay where the bottom is represented by arenaceous-pelitic rocks (Mt. Cervarola Unit, Tuscan Domain, Miocene epoch).

We performed electrical resistivity and P wave refraction tomographies over the same line with the aim to obtain two different, independent and integrable data sets. For the seismic data has been processed also the reflected events, remarkable contribution to draw the geologic setting.

The input data for the integration method proposed is based on the tomographic results obtained by separated processing; moreover, this approach does not need "a priori" constraints between the different geophysical parameters, often a heavy hypothesis in not well-known shallow terrain and rocks.

Through the k-means algorithm, we perform a cluster analysis for the bivariate data set to individuate relationships between the two sets of variables. This algorithm allows to individuate clusters in variable number, with the aim of minimizing the dissimilarity within each cluster and maximize it among different clusters of the bivariate data set. We obtain a partitioning of the data set in a finite number of well-correlated clusters, representative of the optimum clustering of our geophysical variables. The optimal number of clusters "K", corresponding to the individuated geophysical facies, depends to the multivariate data set distribution and in this paper is estimated with the Silhouettes (Rousseeuw, 1987).

The result is an integrated tomography that shows a finite number of homogeneous geophysical facies, which therefore permits to distinguish and interpret the aquifer in a quantitative and objective way.

Rousseeuw, P.J. (1987): Silhouettes: a graphical aid to the interpretation and validation of cluster analysis. J. Comput. Appl. Mathem., 20, 53-65.

Co-seismic displacement on October 26 and 30, 2016 (M_w 5.9 and 6.5) earthquakes in central Italy from the analysis of discrete GNSS network

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Keywords: co-seismic deformation, GNSS measurement, earthquakes in central Italy.

On October 26th 2016, immediately north of the epicentral area affected by the M_w 6.0, August 24th earthquake, a strong earthquake (M_w = 5.9), with a focal mechanism showing W-dipping normal faulting, occurred at the boundary between Marche and Umbria regions (central Apennines, Italy). Four days later (on October 30th), the main-shock (M_w = 6.5) of the whole seismic sequence occurred in the same area. The central Apennines are characterized by northeast-verging thrust-propagation folds, involving Mesozoic-Tertiary sedimentary successions. During the 2016 sequence, coseismic deformation has been recorded at the rear of the Sibillini Thrust which separates the main mountain chain from the Marche-Abruzzi foothills. This contractional structure has been partly dissected and/or inverted by NNW-SSE trending Quaternary normal and oblique-slip faults. The major event (October 30) induced extensive geological effects at the surface and structural damages in the broader epicentral area up to a distance of 30 km. According to the report of the Istituto Nazionale di Geofisica e Vulcanologia (Summary report on the 30 October, 2016 earthquake in Central Italy M_w 6.5; Gruppo di Lavoro INGV sul Terremoto in Centro Italia, 2016), the hypocenter of major event was located at 42.8322°N, 13.1107°E at a depth of 9.2 km. Following the August seismic events, we installed five new geodetic points located on both sides of the principal fracture zone and carried out two campaigns of GNSS measurements, the first one at the end of September (30-09/02-10, 2016), the second one early November (11/13-11, 2016) that covered the period of the October events.

In this brief abstract, we provide the results of our geodetic campaigns that registered the co-seismic displacement occurred in the period between doy (day of year) 2016/274 and doy 2016/318, therefore documenting the two latter major shocks. We also compare our results with the available surface deformation field of the broader area obtained on the basis of the DInSAR technique and particularly the elaboration realized by CNR-IREA of Sentinel-1 radar imaging of Copernicus European Program of 26/10-1/11 (http://www.irea.cnr.it/index.php?option=com_k2&view=item&id=761:nuovi-risultati-sul-terremoto-del-30-ottobre-2016-ottenuti-dai-radar-dei-satelliti-sentinel-1). The comparison shows an overall good fit.

It is worth to note that these earthquakes occurred in a sector of the central Apennines characterized by high geodetic strain-rates (*e.g.*, D'Agostino 2014), where several continuous GNSS stations are operating.

D'Agostino, N., (2014): Complete seismic release of tectonic strain and earthquake recurrence in the Apennines (Italy). Geophys. Res. Letters, 41, 1155-1162.

Gruppo di Lavoro INGV sul Terremoto in Centro Italia (2016): Summary report on the October 30, 2016 earthquake in central Italy Mw 6.5. DOI: 10.5281/zenodo.166238.

Short-term soil microbial biomass response to different zeolitite amendments

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Keywords: zeolitites, microbial biomass, soil amendments, ergosterol, enriched zeolitites.

Within the many environmental applications, natural zeolitites (rocks containing more than 50% of zeolite minerals) are known to be a suitable material for agricultural purposes by improving soil physicochemical properties, nitrogen use efficiency (NUE) and consequently crop yield (Galli & Passaglia, 2011; Reháková et al., 2004). However, the short-term effects of the application of this inorganic amendment to soil microbial biomass activity and population are largely unexplored.

To this purpose, a silty-clay agricultural soil was amended in three different ways by the addition of chabazite zeolitites both at natural state (NZ, at 5 and 15 wt%) and pre-enriched with NH_4^+ ions after treatment with pig-slurry (CZ, at 10 wt%). Soil *p*H, dissolved organic carbon (C), total dissolved N, mineral N (NH_4^+, NO_3^-, NO_2^-), microbial biomass C and N immobilization and ergosterol were periodically measured over a time course of 16 days in a laboratory incubation experiment where the zeolitite amended treatments were compared to an unamended soil. We took advance of the very high ^{15}N natural abundance of the pig-slurry employed in the enrichment process of CZ for tracing eventual incorporation of the N added into soil microbial biomass by the mean of Extraction-Fumigation-Extraction method followed by EA-IRMS analysis.

Results show that ergosterol content and microbial C/N ratio of the soil amended with 5 wt% of NZ increased starting from day 9 of incubation, suggesting that fungal biomass was probably favored, although the same behavior was not found in the soil amended with 15 wt% of the same material.

Concerning the soil amended with CZ, strong interactions with soil microbial biomass were observed. Since the begin of the incubation, microbial biomass N, NO_3^- and NH_4^+ were strongly related, suggesting immobilization of high NH_4^+ levels among the incubation but also nitrification processes especially starting from day 7. Moreover, isotopic measurements confirm the microbial immobilization of the N introduced with CZ since day 2 of incubation. The high dissolved organic C and microbial biomass N suggested an increase of mineralization and immobilization processes.

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An integrated GIS to protect the cultural heritage against natural hazards (heritageGIS)

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Keywords: heritage, geohazards, GIS, protection.

The recent seismic crisis in the Marche region and the extensive damages reported by the cultural heritage has prompted the necessity to a better knowledge and awareness of the geological hazards which put at risk the national cultural heritage. The availability of a precise documentation of all the historical and artistic data regarding each monument has been proved to be important, but missing of the relevant information regarding the nature of the territory and the potential risk produced by natural hazards. The "heritage GIS" project consists of an attempt to concentrate all the information regarding each single monument of a city through a spatial planning performed using GIS softwares, collecting all the information, from the original historical documents to the maps and sequence of restoring activities, complete of photographical evidences. The data, reported in a GIS, are added of all the cartographical and geological information regarding the area where the monument is located and of the hazards evaluation.

San Lorenzo in Doliolo, an Abbey Church in the city of San Severino Marche, central Italy, has been chosen for the preliminary study. It was built in VIII or IX Century, on a temple dedicated to godness Feronia, and reused in XI-XII Century by the Benedictine monks, the actual complex being the result of rearrangement of the structure and restorations during its long history. The inside presents a rectangular floor plan, which spread out onto three levels: the well preserved Crypt with medieval columns, frescoed by the Salimbeni; the impressive Basilica, with three naves and the Apse, with the raised floor. The church was chosen because it represents an unicum which requires protection and preservation.

Starting from the CTR (Technical Regional Chart), it has been created a map of the area where the building is located and a DEM (Digital Elevation Model) (Kweon & Kanade, 1994) to produce the slope map. The geological map, the geomorphology of the area, the hydrology data, have been added in a suitable scale. The flooding hazard (authorities of the Marche Region) was then overlapped. Taking into account the precipitations in the last 30 years, with the data of the neighboring rain gauges, it has been calculated in the whole territory of San Severino Marche municipality, an interpolation performed through a simple cokriging based on altitude as independent variable (Nynierola et al., 2000). In addition it was calculated the 95th percentile of monthly precipitation in order to know the possible occurrence of water bombs that could trigger the hydraulic-hydrogeological hazard. In order to complete the database of natural hazards it has been considered the seismic hazard as the municipality of San Severino Marche is located in seismic zone of degree 2. This rate identifies a zone where strong earthquakes can occur, with an acceleration between 0,15-0,25 g and a probability of exceeding equal to 10% in 50 years.

After the creation of all the separate layers, the analysis focused in the calculation of a map of the risks (Canuti et al., 2000) joining all critical issues in this location, with a scale based on 3 levels high, medium, low. San Lorenzo in Doliolo is in an area at medium risk, mainly due to landslide hazard of grade 2 (in a scale 1-4) and seismic hazard.

The earthquake events happening just after the completion of this study, proved the importance of storing all the information about historical monuments in an integrated GIS, available to the Authorities and the researchers but also to the Civil Protection, for documentation, risk prevention and conservation for the future.

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Noble gases and rock geochemistry of intraplate volcanics from the SE Turkey

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Keywords: Amik Basin, Toprakkale volcanic district, noble gases, trace elements, Turkey.

We present the results of a combined noble gases (He-Ar) and petro/geochemical study carried out on volcanic rocks from SE Turkey, with the aim to better constrain the parent mantle for both volatiles and solid products and its role in the geodynamic framework of the area. The studied area is the northern prolongation of the strike-slip Dead Sea Fault (DSF) and extends from the southern branch of the Karasu Fault up to its junction with the East Anatolian Fault (EAF). This eastern Mediterranean region is characterized by the convergence of three plates: Africa, Arabia and Anatolia. The studied volcanic rocks have been erupted during different magmatic pulses, through fissure-type eruptions and exhibit sodic alkaline affinity and are mafic in composition (basanites and basalts). The major and trace elements composition indicate that the involved mafic melts could be the result of 0.8-2% partial melting of a predominantly spinel and garnet + spinel mantle, which has typical features of intra-plate OIB magmatism. The $^3He/^4He$ ratio of fluid inclusions in olivine crystals ranges from 7.29 to 8.03 Ra (being Ra the atmospheric $^3He/^4He$ ratio of 1.39×10^{-6}), which implies a rather homogenous He isotopic signature of the mantle source. Such values are commonly recorded in MORB-like reservoirs (namely 8 ± 1 Ra), confirming that lavas erupted in SE Turkey did not suffer important processes of crustal contamination. Combining the main evidences from the geochemical data of both rocks and noble gases of fluids inclusions, we propose that small volumes of alkaline magmas over the Amik Basin and Toprakkale-Erzin areas, have been produced by variable degrees of partial melting of an originally depleted mantle source probably metasomatized by amphibole-rich veins (Niu, 2008; Pilet et al., 2011) or recycled oceanic crust during the ascent through lithosphere. Further combined studies, including lithophile elements isotopes, are needed to gain a better insight on the mantle metasomatism processes across the three convergent plate tectonics.

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Experimental study of monazite solubility in granitic melts

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Keywords: rare earth elements, monazite, solubility, granitic melts, ore deposits.

Monazite is one of the most important rare earth elements (*REE*) minerals and occurs in granitic/rhyolitic rocks with compositions ranging from peraluminous to peralkaline. It can also be a significant host for geochemically useful elements such as U and Th, and it can serve as an indicator of magmatic temperatures and petrogenetic relationships in silicic magmas. The stability of monazite can affect the behaviour of *REE* and plays the dominant role in controlling *REE* abundances in felsic magma suites. The behaviour of rare earths in felsic systems has considerable economic importance, as some of the most important rare earth deposits are related to granites (Chakhmouradian & Zaitsev, 2012).

In the frame of more general work aimed at studying geochemical behaviour of *REE* in different granitic magmas, we have determined monazite saturation and solubility in a series of synthetic silicate glasses of granitic composition.

The solubility of synthetic La-monazite ($LaPO_4$) and Ce-monazite ($CePO_4$) in hydrous haplogranite-based peraluminous to peralkaline melts was determined at experimental conditions from 750°C to 850°C, 1 kbar to 2kbar, water saturated conditions. Three sets of high temperature 1 atmospheric experiments were done for each composition ($HPG8_{0.9}$, $HPG8_{1.5}$, and $HPG8_2$, where subscripts indicate molar alkali/alumina ratio) at 1400°C. Major and minor elements analyses were determined by electron microprobe.

Monazite solubility strongly increases with the peralkalinity of the melt, similar to previous observations concerning apatite and zircon solubility. Microprobe analyses show that the solubility of both Ce and La monazite depends strongly on temperature and melt composition and is especially low for peraluminous compositions, and highest in peralkaline compositions.

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PS-InSAR time series analysis of pre- to co-seismic deformation: the 2009 L'Aquila earthquake (central Italy) case study

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Keywords: L'Aquila earthquake, pre-seismic, co-seismic, PS-InSAR.

The co-seismic ground displacements due to the M_w 6.3 6th April 2009 L'Aquila earthquake (Chiarabba et al., 2009) has been analyzed using the Differential SAR Interferometry technique on satellite images (Atzori et al., 2009) where it is shown the hard co-seismic subsidence in the hanging wall of Paganica Fault (PF) and a light uplift in the footwall.

In this study we have applied the PSInSAR technique (Ferretti et al., 2001).

Seismological data (Chiaraluce et al., 2011) indicate that the 2009 L'Aquila seismic sequence started in the mid part of January 2009.

The PSInSAR data cover a 20 years long time span, which encompasses both the pre-seismic and co-seismic phases.

They consist, moreover, of time series datasets (TS) of ERS (1992-2000) and ENVISAT missions (2002-2010), both ascending and descending orbits, that have been obtained by the Piano Straordinario di Telerilevamento Office (Ministero dell'Ambiente).

Before the 2009 L'Aquila earthquake, either in the PF hanging wall and footwall, the TS signal in ascending LoS, do not show any significant ground deformation. Conversely the TS signal in descending LoS, point to a positive displacement, only in the PF hanging wall; in the PF footwall TS signal in descending LoS, is lightly subsident.

The geometric composition of ground motion gives, for the PF hanging wall, an overall deformation pattern that, starting from year 2000, is oriented towards the east and upward, pointing to uplift oriented about 23° with respect to the horizontal. Few months before the 2009 earthquake, *i.e.*, starting between July to November 2008, a reversal of the displacement is observed. The deformation signal in the descending LoS turns to negative while, in the ascending LoS the displacement remains roughly horizontal, with a total deformation pattern, just before the 2009 earthquake, oriented towards the west and downward (pre-seismic subsidence). In the mid part of January 2009, *i.e.*, roughly coeval to the beginning of the seismic sequence, the ascending displacement make a narrow peak (about + 5/10 mm) before coseismic subsidence start.

By the first satellite data, in ascending and descending LoS, following the April 6 main shock, a sudden and strong coseismic subsidence of the PF hanging wall is identified. Coseismic subsidence characterize the PF foot wall too, through about ten kilometers radius area in the eastern sectors of the PF.

The PSInSAR data deformation scenario, on a decadal time scale, indicate that, in the study region, the preseismic phase has been characterised by a complex pattern. In particular, they highlight the occurrence of a uplift in the PF hanging wall, predating the earthquake occurrence by about 10 years; a reversal of motion (pre-seismic subsidence), occurred less than a year before the main shock, both in the PF hanging wall and footwall.

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The Republic of Moldova underground waters: good amount *vs.* bad quality

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Keywords: Republic of Moldova, water geochemistry, isotopic tracers, dissolved gases, trace elements.

Groundwater in the Republic of Moldova (33,840 km^2) has a long history of usage as drinking and has enough reserve potential (about 3.0 km^3/year of fresh water). Republic of Moldova has large spectrum of underground mineral waters (16 reservoirs), most of which affected by contaminants originated by natural sources and anthropogenic activities. The deep aquifers with mineral waters of different ages are situated at 200–1000 m depth: Vendian crystalline basement rocks (V), Silurian crystalline limestone (S_1), Cretaceous limestone (K), Baden-Sarmatian limestone and clay-sand deposits (N_1b-s_1), middle Sarmatian limestone and clay-sand deposits (N_1s_2). Other younger aquifers are not studied. The aim of this investigation was to determine the geochemical and isotopic features of the most important thermo- and mineral waters from the Republic of Moldova in order to trace their flow pathways and evaluate their source(s). Inorganic natural tracers and stable isotopes are useful tools to fingerprint the water source and solutes, respectively.

In the present study, the main results obtained in the study areas of Moldova carried out in the deep aquifers with mineral waters located along the Prut and Nistru rivers are presented and discussed. In this framework, 54 samples from the most important underground reservoirs were collected and analyzed for major and trace species and dissolved gases. Furthermore, an inventory of isotopic ($^{18}O/^{16}O$ and $^2H/^1H$ ratios in water and $^{13}C/^{12}C$ in dissolved CO_2) features, including tritium units in selected samples (clustering around 0) was also provided. By a geochemical point of view, the Moldavian waters showed neutral to alkaline *p*H, Total Dissolved Solids (TDS) between 515 and 75,846 mg/L and mostly negative *E*h values. They displayed a relatively high variability in terms of composition, being classified as $Ca(Mg)$-$HCO_3(SO_4)$, Na-Cl and Na-HCO_3. In the mineralized waters (between 1 and 120 g L^{-1}) from the Baden-Sarmatian aquifer, trace element distribution revealed significant anomalies for F^-, I^- and Br^- (up to 13.2, 23.7 and 140.5 mg L^{-1}, respectively). Moreover, high values of As and Ni are found in the Dubasari waters (up to 13.8 µg L^{-1} and 43 µg L^{-1}, respectively). The dissolved gases were mainly dominated by N_2 (from 0.16 to 0.78 mmol/L), while CO_2 and CH_4 were between 0.02 and 0.66 mmol/L and 0.00005 and 0.44 mmol/L, respectively. Carbon isotopes in dissolved CO_2 were very variable ($^{13}\delta$-CO_2 from -25.2 to +2.8 ‰), the most positive values being associated with the waters collected from the oil field in the southernmost part of the country. Oxygen and hydrogen isotopic ratios were ranging from -15.8 to -0.9 ‰ (V-SMOW) and from -104.5 to -32.8 ‰ (V-SMOW), respectively, suggesting a meteoric source slightly modified by prolonged water-rock interactions.

μ-LIBS in mineralogical and petrographic applications for cultural heritage

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Keywords: μ-LIBS, mineralogical application, petrographic application, cultural heritage, 3*D*-Elemental Mapping.

The LIBS technique is a widely used spectroscopic technique for elemental characterization of materials(Hahn & Omenetto, 2012). Unlike other similar techniques, it can also detect the presence of light elements such as sodium and magnesium by the analysis of plasma plume generated by laser ablation. Each single point of measurement is the result of the ablation of a small portion of the sample that generate a small crater on it and whose diameter varies depending on the power, wavelength and type of the laser as well as the type of material being analysed.

In recent years, we have focused on the development of mini-destructive equipment, with very small spots (around 7-10 μm through coupling with dedicated microscope) and able to quickly map sample areas (Pagnotta et al., 2017). The use of a dedicated microscope through which to focus the laser beam and collect plasma light has paved the way for all those applications that target the mineralogical and petrographic study in cultural heritage.

It goes from the simple analysis of patinas, on both metals and rocks, with depth profiling, passing through the fast clustering of archaeological pottery to the compositional mapping of surfaces of artificial materials such as ceramics, and, finally, to the 3*D* reconstruction and three-dimensional mapping of ablated volumes highlighting the greater or lesser presence of certain elements.

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Geology of Piemonte region (NW Italy, Alps–Apennines interference zone)

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Keywords: geological mapping, geodatabase, Alps, Apennines, Piemonte.

The geological map of Piemonte (GeoPiemonte Map), realized by CNR IGG Torino and ARPA Piemonte is a representation of the geology of the region, available as a graphical issue at the 1:250,000 scale (Piana et al., 2017) and a WebMapService at 1:70,000 scale hosted on the ARPA Piemonte geoportal (http://arpapiemonte.maps.arcgis.com/apps/webappviewer/index.html?id= fff173266afa4f6fa206be53a77f6321).

The GeoPiemonte Map is supported by a large database, (several thousands data) semantically based on controlled vocabularies: IUGS GeoSciML vocabulary (http://www.geosciml.org), and INSPIRE EU Directive (Data Specification on Geology v.2). A dedicated ontology (Lombardo et al., 2016) has been also created to semantically constrain the Map: it is available as "wiki pages" at http://www.di.unito.it/~vincenzo/ontologies/OntoGeonous.htm.

The GeoPiemonte Map was built firstly using lithostratigraphic criteria, *i.e.*, subdividing rocks into Geological Units (GU, formal and/or informal formations or members) on the basis of their compositional and textural features. The GeoSciML "Geologic Unit" Taxonomy was chosen as reference conceptual scheme to establish the hierarchy of the regional-to-local scale geological subdivisions, while the GeoSciML "Earth Material" and "Rock Material" Taxonomy was used for the lithological description of the Mapped Features. The discontinuities (of both primary and secondary origin) were classified following the GeoSciML "Geological Contact" and "Geologic Structure" Taxonomy.

The reconstruction of the geological evolution, upon which the subdivisions of the Map Legend were grounded, was displayed by the definition of a number of main "Geologic Event" (remarkable modification of a given geological context induced by tectonic, sedimentary or petrogenetic processes). Many of these Geologic Events are represented by regional-scale discontinuities preserved in the geological stratigraphic record and correlatable across different geological domains.

The GU of the GeoPiemonte Map were thought as parts of a single first-order domain: the Alps-Apennines orogenic system. The GU were then ascribed to their original paleotectonic context, namely the palaeoEuropean or palaeoAdriatic continental margins, the ocean-continent transition zone, the Liguria-Piemonte and Vallesan oceanic domains, the syn-orogenic magmatic bodies and sedimentary basins, as well as some main large scale "tectonic slice zones".

The non-metamorphic sedimentary successions of the main syn-orogenic basins (Tertiary Piemonte Basin and Alpine Foreland Basin) were subdivided into Unconformity Bounded Stratigraphic Units -UBSU- or Synthems, each ones resulting from major tectono-sedimentary events. Similarly, the meta-sedimentary succession resting on the main tectono-metamorphic units of western and Ligurian Alps were correlated across these units and subdivided into informally defined "para-synthems", separated using the same chronostratigraphic subdivisions used for the non-metamorphic synthems.

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Seismic reflection profiles and deep geological sections across the area interested by the 2016-2017 earthquake sequence

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Keywords: 2016-2017 earthquake, seismic profiles, seismogenic fault, subsurface geology, Apennines.

Starting from August 24, 2016, a long seismic sequence struck a wide area of the central and northern Apennines of Italy, including nine $M_w > 5.0$ earthquakes, located at depths between 6 and 12 km. Geological, geodetic and seismological data acquired during the seismic sequence univocally envisage a complex system of NNW-SSE trending, seismogenic normal faults. These active tectonic structures are well known at the surface, and consistent with previous seismotectonic studies.

This work provides a new reconstruction of the subsurface geology of the area generated by the integration of surface geological and subsurface data, as a contribution to improve 3*D* geological and seismotectonic models. A large dataset of 85 seismic reflection profiles has been kindly provided by the Italian oil company (ENI) for this study. Thanks to these data, a detailed tectonic interpretation of the active faults was performed along three geological sections crossing the main seismogenic faults and interpreted to a depth of about 12 km.

The interpreted seismic profiles shed light on:

- the stratigraphy of the seismogenic layer, and in particular the lithology of the rocks hosting the mainshocks of the sequence;
- the complex 3*D* geometry of the seismogenic faults, which need to reconcile the high-angle (dip > 65°) normal fault exposed at the surface, with their angle (dip < 50°) at hypocentral depths as indicated by focal mechanism solutions.

Answering these questions is fundamental for better understanding the rheological properties of the seismogenic rock volume, as well as the co-seismic deformations of the topographic surface, observed by geodetic techniques.

Motta S. Anastasia eruptive center: a true neck?

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Keywords: Sicily, Etna, Motta S.Anastasia, neck, transpression.

In the area located between the southern edge of the Mt. Etna volcanic edifice and the Catania plain, in eastern Sicily, a small sub-alkaline volcanic body crops out upon which lies the town of Motta Santa Anastasia. This insulated outcrop is surrounded by the Mid-Late Pleistocene sedimentary basement of Etna and is commonly related to the earliest subaerial activity of Etna magmatic district which major evidence is the subaerial tabular lava flows outcropping along the left bank of the Simeto river, between Adrano and Paternò towns on the SW slopes of Etna.

Although its age and significance in the framework of the magmatic evolution of the Etnean area is pretty clear, the complex volcanic and structural attitude of the Motta S. Anastasia volcanic outcrop is not entirely understood.

The volcanic body, 400 m elongated inside a N-S oriented eruptive fissure, 200 m wide and about 60 m high, shows in eastern face well-developed columnar jointing and is commonly recognized as volcanic neck.

Lavas are tholeiitic in composition and around the sub-volcanic body also proximal pyroclastic deposits are locally observable also; in fact, scoriae lapilli and bombs with a breadcrust are found in the volcanoclastic preserved and stacked at the base of eastern flank of body wall, that occasionally includes sedimentary lithic fragments made up of alluvial cobbles, the latter one most common in the northern and southern part of the volcano.

Bombs and spatters are also present on top of the volcanic body, at base of the overlain Norman Castle, and according to the huge dimension of a such volcanic pipe, Motta S. Anastasia neck is today depicted as the remnant of large volcanic cone.

Nevertheless, a recent preliminary survey performed in Motta S. Anastasia neck area within a large private project, showed that the volcanic body exhibits a roughly "U" shape synform with major axe WNW-ESE oriented and locally are evident typical tectonic features like fault mirrors and compressive deformations and joints possibly related to two recognized major strike-slip faults, trending WNW-ESE and NNE-SSW respectively.

Although some similar compressive features in intrusive and sub-volcanic bodies are common and could be also related to emplacement mechanisms of the magmatic body itself, fault mirrors found and some minor shear features are almost certainly related to post-emplacement tectonic activity.

The pattern of recognized faults affecting the volcanic body is analogous to surficial fault pattern already known in scientific literature, especially for what concerns WNW-ESE trending right lateral faults; instead, huge unknown NNE-SSW trending faults are today well observable in several active quarries in Misterbianco-Motta S. Anastasia area and exhibit left lateral strike fault movements.

Furthermore, similar faults have been imaged at depth by seismic surveys performed in Motta S. Anastasia area by Oil Companies which depicted the Motta S. Anastasia eruptive center at tip of two major faults trending WNW-ESE and NNE-SSW respectively.

In this framework, observed faults and compressive features affecting the volcanic body, the huge erosive rate requested by a neck model and no finding until now of lithic fragments of Motta S. Anastasia eruptive center in alluvial terraced deposits downstream the neck area, the age of the tholeiitic lavas which radiometric age (320.0 ± 48.4 ka) differs from the age derived from paleomagnetic surveys (200 ka), and, finally, the stratigraphic position of eruptive event and preservation of bombs, spatters and finer volcanoclastic on top of the volcanic body which exhibit also same deformations of the other parts of the eruptive center, could be related to a very small short-lived volcano which lavas might have emplaced in subaereal condition in a narrow active river valley carved in the S. Giorgio Sands and suddenly involved in a coeval strong transpressive tectonics affecting the area located between the southern edge of the Mt. Etna volcanic edifice and the Catania plain and still active in this sector of eastern Sicily.

Further more detailed surveys of the volcanic body focused on this specific topic could later answer to the exposed question.

Mineralogical and geochemical study on beach placers of the Calabrian coast as potential source of *L-REE*

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Keywords: heavy minerals, sand, *REE* source, SEM-EDX, XRF, Calabrian coast.

With this contribution we hope to increase the interest in the field of the *REE* potential resources, proposing a new mining site, located along the Calabrian coastline.

The Calabrian Arc, is represented by Sila, Serre, Poro and Aspromonte Massifs, and also includes the southern portion of the Coastal Chain (Calcaterra & Parise, 2010). It consists of a series of Palaeozoic plutonic–metamorphic nappes, locally overlain by a Mesozoic–Cenozoic sedimentary cover. The metamorphic chain, was dismantled by the erosional and gravity-related processes induced by the high uplift rates occurred in the Quaternary time. In response to the strong uplift, land areas were affected by very high denudation rates, due to the action of seasonal streams characterized by high transport capacity. This favored very high sedimentation rates on the continental shelf and originated the S. Eufemia Gulf sandy sediments. They result from dismantling of mainly kinzigitic gneisses (Serre Massif) and are characterized by accumulation of valuable minerals, known as beach placers, formed by gravity separation.

to the proposed results highlight the potential use of the identified beach placers as L-REE source. To reach the goal we carried out a mineralogical and geochemical characterization of the heavy mineral component through a multidisciplinary approach including Scanning Electron Microscopy (SEM-EDX), X-Ray Powder Diffraction (XRPD) and X-Ray Fluorescence (XRF) analyses. SEM-EDX and XRPD analyses evidenced the presence of the heavy mineral phases as magnetite, ilmenite, garnet, rutile and monazite.The XRF bulk chemistry data put in evidence very high amount of Ce (2283 – 2850 ppm), La (1043 – 1330 ppm), Nd (1400 – 1700 ppm) and Th (409 – 464 ppm).

We put in evidence that the identified “beach placers” might represent a topic of interest related to the proposals of the “Horizon 2020” project, for sustainable primary and secondary raw materials productions.

Calcaterra, D. & Parise M. (2010): Weathering in the crystalline rocks of Calabria, Italy, and relationships to landslides. Geol. Soc. Eng. Geol. Spec. Publ., 23, 105-130.

Mantle xenoliths from Sardinia

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Keywords: Sardinia, mantle xenoliths, metasomatism.

A selection of mantle xenoliths from different localities of Sardinia (Pozzomaggiore, Giara di Gesturi, Dorgali) has been investigated for petrographic study. The work has been conducted using a polarizing microscope and a Scanning Electron Microscope in the laboratories of the Department of Earth Science of Sapienza University of Rome.

The first stages of Cenozoic volcanism in Sardinia started around 38 Ma and continued until ~ 15 Ma essentially with volcanic products (mostly in pyroclastic facies) plus very minor plutonic bodies in the southern sectors of the Island (Sarroch area). The chemical compositions of these products resemble those emplaced in subduction-related tectonic settings, mostly with arc-tholeiitic to calcalkaline affinities. After a ~ 3 Ma *hiatus*, the igneous activity continued from ~ 12 Ma to ~ 0.1 Ma in several districts throughout the entire island with the emplacement of mainly effusive tholeiitic basic-to-acid lavas and mildly alkaline sodic basic-to-intermediate lavas. The least differentiated alkaline magma are often characterized by the abundant presence of mantle xenoliths.

All but one sample are characterized by lherzolitic compositions, the only exception being represented by one dunitic sample. These xenoliths show the typical anhydrous paragenesis of olivine, clinopyroxene, orthopyroxene and spinel. The presence of spinel limit the maximum depth of provenance to less than 80-90 km. The textures range from protogranular (coarse) to porphyroclastic to granuloblastic (equigranular). In the last case I have noticed a reduction of the crystal dimension with increase of deformation.

Olivine always occurs as large crystals with irregular boundaries in porphyroclastic textures and more straight edges in coarse and granuloblastic textures. Its composition is close to forsterite (Fo_{90-92}) with only minor increase of the fayalitic component towards the rims. Orthopyroxene, with enstatite-rich composition, is more abundant in harzburgitic compositions and rarely shows exsolution lamellae of clinopyroxene. When in contact with the host silica-undersaturated lava, enstatite shows reaction rims and is strongly resorbed, forming tiny assemblages of olivine. Clinopyroxene is close to pure diopside in composition, and occurs in smaller crystals compared with forsterite and enstatite. It is often characterized by spongy texture, interpreted as the effect of incipient melting. Brown interstitial or vermicular Cr-spinel was found between minerals in minor amount and small feldspars were found within the glassy pockets of the spongy clinopyroxenes, probably as consequence also of some host melt infiltration. Hydrous phases were not observed.

On the basis of petrography and qualitative mineral chemistry, the investigated mantle xenoliths reflect the derivation from a lithospheric mantle variably affected by partial melting processes.

The importance of laser scanning in the analysis of "exhumed" crime scenes: a new method for recording and documenting clandestine graves

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Keywords: clandestine graves, laser scanner, forensic geology, forensic archaeology, forensic engineer, forensic sciences, criminal investigation.

A multidisciplinary forensic investigation has been undertaken by a team of scientists belonging both to Messina University and the Messina Scientific Investigation Department of the *Carabinieri* Army. The study has been conducted on a test site where two clandestine single graves, containing human remains simulated by dummy parts, have been surveyed by two 3*D* laser scanners, in order to freeze the "exhumed" crime scenes by recording and documenting all the features of the walls and floor of the graves. Dug in a sandy soil overlying a bedrock of Pleistocene sandy gravels, the graves were recovered by means of careful stratigraphic excavation. This archaeological methodology is strongly recommended and should be applied whenever possible. Indeed, it preserves the original cut of the grave, as dug by the offender(s), as well as possible biological/physical/chemical evidence contained in the filling and/or preserved on the cut and nearby on the outside. By contrast, arbitrary excavations destroy the grave cut and related evidence.

The graves cuts have been identified by a "time of flight" laser scanner. This technique is non-destructive, repeatable, and does not alter the state of the site. A motorized head moves the scanner light with two angular degrees of freedom, declination and right ascension, in order to sweep the detection area. The scanner has been coupled with a high-resolution photo camera positioned on the top of the instrument to allow a full and real post-scanning image reconstruction of the state of the site.

To fully detect the target, from different observation points, the instruments have been positioned in two different stations. The two stations have been matched by using 3 markers for the accurate alignment of the points. Overall, 1,990,769 and 163,753,755 points have been detected for the two graves.

In the post-processing phase, to maintain the certified precision, no point-manipulation operation has been executed. For this reason, only the geometrical and topological properties of the excavations have been measured, and the sections have been reconstructed using special software.

Even better than a photographic survey, the 3*D* scanning allows all the geometries detected to be frozen in time and space. This enables the time analysis of features that are fundamental for precise and accurate forensic investigations, such as:

i) the pattern of the grave cut;

ii) the geopedological profile and layering to discriminate the related crosscutting relationships with the grave cut from possible anthropogenic marks (tool marks, etc.);

iii) position of both items (bullets, etc.) and traces (tool marks, footprints, body impressions, etc.).

Particularly the grave cut pattern could provide vital clues to investigators concerning the *modus operandi* and behaviour of the offender(s), especially in the case of serial killers.

A new GIS-based approach for the search of simulated clandestine graves

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Keywords: forensic geology, ground search for clandestine graves, missing people, police investigation.

One of the applications of Forensic Geology (or Forensic Geosciences) is related to the construction of the RAG (Red-Amber-Green) color-coded maps of the prioritisation system (known as the traffic light system). This system provides search scenarios that may be used in forensic sciences for delineating and prioritizing the ground search for crime-related buried cadavers or items (weapons, explosives, etc.).

Three different ground search scenarios (RAG maps) were reconstructed in a test site using a GIS-based RAG color-coded prioritisation system for the search of three clandestine graves dug in the country side of Messina (southern Italy). The considered factors (diggability, slope, vegetation, anthropogenic structures, geomorphological instabilities, visibility) were examined and stored as geographic entities in different layers of a GeoDataBase, developed in ArcGIS. For each of these entities, the Red, Amber, and Green color-coded classes were assigned (as attributes) to the areas provided of high, medium, and low susceptibility to host the burial. The geographic entities were linked both to the Digital Surface Model (DSM) and the Digital Terrain Model (DTM). The RAG map was obtained overlaying and crossing, according to certain criteria (established in the related conceptual and logical model), all the different entities with the related RAG. The resulting search scenarios were elaborated using the DTM or the DSM and considering or not the visibility factor. Each scenario resulted to be composed of areas assigned to the Red, Amber, and Green color-coded classes corresponding to the high, medium, and low priority search, respectively.

The RAG map considering the DSM-based visibility factor was realized hypothesizing that the concealment was made during the light hours and that the coverage effect was played by landscape, as well as by vegetation and anthropogenic structures. This defined a search scenario with RAG color-coded areas covering the 2.2%, 30.9%, and 66.9% of the entire search area, respectively.

The RAG map considering the DTM-based visibility factor was realized hypothesizing that the concealment was made during the light hours and that the coverage effect was played only by the landscape. This defined a search scenario with RAG color-coded areas covering the 0%, 17.6% and 82.4% of the entire search area, respectively.

The RAG map without considering the visibility factor was realized hypothesizing that the concealment was made during the night hours (without the possibility for the offender to be seen). This defined a search scenario with RAG color-coded areas covering the 3.5%, 61.7% and 34.8% of the entire search area, respectively.

The highest extent of the high-medium priority areas (65.2%) obtained in the GIS-based RAG map of the search scenario realized not considering the visibility factor suggested that this one was the most heedful search scenario to be adopted by the searchers.

Estimation of the rock volumes involved in a graviquake: the M_w 6.5 Norcia earthquake case-study

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Keywords: Norcia earthquake, volumes computation.

In this work, we analyse the seismic sequence that affect the Umbria-Marche Apennine (central Italy) since August 2016, focusing on the M_w 6.5 Norcia earthquake, nucleated along the Mt. Vettore extensional fault on October 30th 2016.

We investigate the ground deformation pattern and the source geometry responsible of the 2016 central Italy seismic sequence by joint exploiting the multisensors and multiorbits satellite measurements (*i.e.*, Sentinel-1 and ALOS 2) and their integration with the available geological/structural and seismological data.

In this context, benefiting from satellite and *in situ* information, we investigate the most suitable geological scenario that governed the spatial evolution of the Norcia seismic sequence. Starting from DInSAR (*i.e.*, Sentinel-1 and ALOS 2) and seismological data (*i.e.*, hypocentral distribution and available focal mechanisms), we compute the rock volumes involved in the earthquake nucleation process. In fact, earthquakes hypocentral distributions suggest that the rock volume is delimited by the Mt. Vettore fault and by an antithetic fault. We compute both the collapsed rock volume, included between the two faults, and the consecutive uplifted rock volume. Specifically, according to Doglioni et al. (2015), we consider as accomodation volume the difference between the subsidence and the uplift phenomena recorded during the mainshock event and mapped via DInSAR technique. Therefore, the Norcia extensional earthquake was caused by the collpase of the hangingwall volume confined by the main normal fault and the antithetic fractured dilated zone and it was characterized by the dissipation of gravitational energy, stored during the interseismic phase. When the stress related to this gravitational energy exceeds the strength of the dilated zone and of the main normal fault, the rock volume collapses slipping along the main fault, generating the earthquake, while the downward hangingwall block movement happens in favour of gravity.

Doglioni, C., Carminati, E., Petricca, P., Riguzzi, F. (2015): Normal fault earthquakes or graviquakes. Sci. Rep., 5, 12110.

Aftershocks in seismic sequences: a comparison between extensional and contractional tectonic settings

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Keywords: aftershocks, normal faulting, thrust faulting.

Aftershocks decay through time, depending on several parameters peculiar of each seismogenic regions, such as the mainshock magnitude, crustal rheology, stress changes along the fault, etc (Shaw, 1993). However, the exact role of these parameters in controlling the aftershocks sequence is still unknown (Utsu & Ogata, 1995). Using two different methods to compare aftershock sequences with similar rheological parameters, we show that the tectonic setting primarily controls aftershocks duration. In fact, for a given magnitude, the aftershock sequences within extensional settings are longer, on average, and the number of earthquakes is larger than those within contractional ones. We interpret this difference as related to the different type of energy dissipated during earthquakes (Doglioni et al., 2015a). In detail, (1) a joint effect of gravitational forces and pure elastic stress release governs extensional earthquakes, whereas (2) pure elastic forces control contractional earthquakes. Accordingly, normal faults operate in favour of gravity and seismicity lasts until gravitational equilibrium is reached (Doglioni et al., 2015b; Petricca et al., 2015). *Vice-versa*, thrusts act against gravity and the elastic energy dissipation is buffered by the gravitational force (Doglioni et al., 2015a). Finally, this comparative analysis of aftershock seismic sequences may provide to be useful for seismic hazard assessment and for the full understanding of long-term behaviour of ongoing seismic sequences.

Doglioni, C., Barba, S., Carminati, E., Riguzzi, F. (2015a): Fault on-off versus strain rate and earthquakes energy. Geosci. Front., 6, 265-276.

Doglioni, C., Carminati, E., Petricca, P., Riguzzi F. (2015b): Normal fault earthquakes or graviquakes. Sci. Rep., 5, 12110.

Petricca, P., Barba, S., Carminati, E., Doglioni, C. Riguzzi, F. (2015): Graviquakes in Italy. Tectonophys., 656, 202-214.

Shaw, B.E. (1993): Generalized Omori law for aftershocks and foreshocks from a simple dynamics. Geophys. Res. Letters, 20, 907-910.

Utsu, T. & Ogata, Y. (1995): The centenary of the Omori formula for a decay law of aftershock activity. J. Phys. Earth, 43, 1-33.

Technical session (Sponsors)

Air, soil, rocks, water: stable isotopes as the most versatile technique in geosciences

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Keywords: stable isotopes, geoscience, IRMS.

Isotope geochemistry is an aspect of geosciences based upon the study of natural variations in the relative abundances of isotopes of various elements. Variations in isotopic abundance are measured by isotope ratio mass spectrometry, and they can reveal information about the ages and origins of rock, air or water bodies, or processes due to a mixture between them.

Stable isotope geochemistry is largely concerned with isotopic variations arising from mass-dependent isotope fractionation.

The stable isotopes technique finds a large use in the geosciences field.

Carbon, nitrogen, hydrogen, oxygen and sulfur stable isotopes are the most important elements investigated throught IRMS technique in hydrology, petrology, geology, oceanography.

Elementar, as world leading company of analytical instruments for non-metallic elements like carbon, nitrogen, sulfur, hydrogen, oxygen can give an overview about the state of the art of the technology involved in such fields.

Explore the microcosmos - How modern X-ray fluorescence spectrometry solves analytical tasks in geological research

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Keywords: Wavelength dispersive X-ray fluorescence.

Microanalysis is a vital tool for researchers in geology and paleontology: Based on the elemental distribution in rocks, meteorites or fossils the origin of materials and the genesis of formations have been investigated and clarified. Different analytical technologies have emerged into this field: While electron microscopy based instruments are requiring extensive sample preparation and is limited with the maximum sample size, EDXRF technology are offering the capability of automation, little sample preparation and higher sample throughput. Advantage of SEM is the very high spatial resolution down to the nm range, EDXRF based methods are requiring special optics to achieve spot sizes around 50 µm. The detection limit of SEM is worse compared to EDXRF based methods, but EDXRF is limited in light element performance and spectral resolution.

Wavelength dispersive XRF has been widely used in industrial applications, but the beam path is optimal for bulk analysis due to the large spot sizes. New X-ray technologies and changes in the beam path are enabling to make use of the high spectral resolution and the optimal light element sensitivity reducing the spot sizes down to the 300 µm range.

This new WDXRF instrument has been used to analysis a range of different material, such as Fe-Ni-meteorite fragments from Arizona, minerals with rare earth element and fossils to show typical results. The technology will be compared with the established methods.

From the Empyrean platform to the Aeris benchtop: a few case studies related to PXRD applications

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Keywords: XRD, polymorphism, vanadate, arcanite, larnite.

Interplay between crystal structure and physical properties of minerals and related compounds is the key for the development of new materials for advanced applications.

Malvern-PANalytical are committed to provide state-of-the-art solutions covering both basic and advanced sample characterizations in ambient and non-ambient conditions (temperature, pressure, humidity, etc). In this talk we mainly report on the synthesis and the crystal structure determination of 2 new vanadates related minerals. $AgCaVO_4$ is a new material related to arcanite (β-K_2SO_4). Its crystal structure was determined from laboratory powder X-ray data (Nénert, 2017). Contrary to previously reported chemical compositions $AgBVO_4$ (B = Mg, Cd), this compound exhibits a distorted arcanite structure. Furthermore, we reported recently a new larnite related vanadate $NaSrVO_4$ exhibiting a complex phase diagram as a function of temperature (Nénert et al., 2017). This material is the first report for a $A^IB^{II}X^VO_4$ chemistry exhibiting the larnite structure. This is suggesting that the larnite structure can accommodate a richer chemistry that initially foreseen.

Nénert, G. (2017): Synthesis and crystal structure of the new vanadate $AgCaVO_4$: Comparison with the arcanite structure. Z. Kristallogr., in press, DOI: https://doi.org/10.1515/zkri-2017-2041.

Nénert, G., O'Meara P., Degen, T. (2017): Crystal structure and polymorphism of NaSrVO4: the first $A^IB^{II}X^VO_4$ larnite-related structure from X-ray powder diffraction data. Phys. Chem. Minerals, in press, DOI: 10.1007/s00269-017-0873-6.

X-ray microscopy as a correlative imaging technique

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Keywords: 3*D* imaging, microCT, *in situ*, correlative microscopy.

As X-ray microscopy is extended from the synchrotron community to the laboratory, correlation to other imaging techniques is vital for many reasons. Partly due to the need to show where the technique fits in the landscape of multi length scale imaging and partly to show the efficacy of the application by correlating similar imaging modalities. Furthermore *in situ* and 4*D* quantification of microstructural evolution under controlled environment as a function of time, temperature, chemistry or stress can be performed repeatable on the same sample, using practical specimen sizes ranging from tens of microns to several cm diameter, with achievable spatial imaging resolution from submicron to 50 nm. We will show through various applications from the fields of geosciences, as geology and paleontology, how X-ray microscopy complements existing technology, not replacing any technique, but adding further information to gain a deeper understanding of the scientific application.

Authors' Index

Authors are listed alphabetically: For each contribution, the page number and the session are given.
Communicating authors are highlighted in blue.

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