Mineralogical School of the
National Mineralogical Group (GNM) and
Italian Society of Mineralogy and Petrology (SIMP)

GNM-SIMP School, Bressanone 2018, 12th - 15th February

BOOK OF ABSTRACTS

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Physical properties of minerals:

how and why to dive into their knowledge

Bressanone (BZ), 12-15 February 2018

Aims and Scope

The National Mineralogical Group (GNM) of the Italian Society of Mineralogy and Petrology (SIMP) is pleased to announce the Mineralogical School: *"Physical properties of minerals: how and why to dive into their knowledge"*.

The school is open to students of master degree programs, PhD students and young researchers from universities and research institutions, classified in the subject area of Earth Sciences, Material Sciences, Natural and Environmental Sciences, Chemistry and Physics. The School will be focused on the physical properties of solid/crystalline materials – optical, thermodynamic, electrical, magnetic and mechanical – highlighting the relationships among those properties and the crystal structures, the size vs surface as well as the microstructure in them.

Types of materials – minerals, semiconductors, metals, glasses, orientationally disordered crystals, defective solids, and more – will be introduced and their main physical properties will be described. These themes will be approached by a theoretical and analytical point of view and some applications/implications to geological and material science themes will be followed.

The school is based on a number of lessons, which will be complemented by exercises, worked examples and learning self-assessment. Students will be continuously monitored by a selected and restricted panel of teachers, who are expected to attend the school all the time, and to provide an up-to-date and complete framework of knowledge and investigation methods on the selected topics.

Participants to the School have been encouraged to present their research work in a dedicated poster session. The abstract of the 19 submitted poster are collected here.

Besides, the abstract of the 12 lessons are included here. The slides of the presentations are available at https://www.socminpet.it/SIMP/GNM/lezioni_brix.htm

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CHARACTERIZATION OF TRANSITION METAL ION-BASED LDHs SYNTHESIZED *VIA* CO-PRECIPITATION METHOD

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Layered Double Hydroxides (LDHs with general formula: $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2(A^{n-})_{x/n}]\cdot yH_2O)$ belong to the so-called anionic clay class. Their crystal structure is characterized by stacking of positively charged brucite-like octahedral layers (where different cation types can coexist) alternated with interlayer domains of water molecules and anionic groups (Bellotto *et al.*, 1996; Drits & Bookin, 2001). The peculiar structural and chemical features make LDHs promising materials for several technological applications (*e.g.*, catalysis, pollutants sorption and drug delivery) (Cavani *et al.*, 1991; Rives *et al.*, 2013; Bi *et al.*, 2014). Considered excellent catalytic precursors, CuFeLDH compounds are quite difficult to synthesize (the possible occurrence of Jahn-Teller effects being one of the main causes; Atanasov *et al.*, 1994). In order to overcome these synthesis troubles, novel hydrotalcite-like precursors having different proportion of Ni^{2+}, Cu^{2+} and Fe^{3+} cations have been obtained through the co-precipitation method. The obtained compounds allowed to carefully investigate: 1) the effects generated by the crystallization of mixed oxides at high temperature (catalytic tests are performed on calcined materials), and 2) to understand the oxidative depolymerization of lignin β-O-4 and β-β model oligomers (Dutta *et al.*, 2014). The amount of cations after precipitation have been estimated through EDX (Energy Dispersive X-ray) analysis. Besides, each sample has been calcined at 300, 400, 500 and 600 °C and analyzed through *ex situ* X-Ray powder diffraction in order to obtain information on the oxides formation. Rietveld refinements (GSAS software; Larson & Von Dreele (1994) on both uncalcined and calcined samples provided information about: 1) type and percentage of present phases, 2) cell parameters, and 3) possible structural defects. Results on uncalcined samples revealed: 1) the occurrence of 100% LDH phase, and 2) a strong dependence of LDH crystallinity to the II/III cations ratio. On the other hand, qualitative and quantitative analysis carried out on calcined samples highlighted that the crystallization of NiO and CuO oxides occurs at almost 300°C, while spinel phases (*i.e.*, magnetite, trevorite and cuprospinel) are detected only above 500°C. Furthermore, unit-cell refinements highlighted that lattice parameters, at each investigated temperature, scaled with the phase fraction of the each phase detected within the analyzed samples as well as the different II/III cations ratio.

REFERENCES

Atanasov, M., Zotov, N., Friebel, C., Petrov, K., Reinen, D. (1994): *J. Solid State Chem.*, **108**, 37-45.

Bellotto, M., Rebours, B., Clause, O., Lynch, J., Bazin, D:, Elkaïm, E. (1996): *J. Phys. Chem.*, **100**, 8527-8534.

Bi, X., Zhang, H., Dou, L. (2014): *Pharmaceutics*, **6**, 298-332.

Cavani, F., Trifirò, F., Vaccai, A. (1991): *Catal. Today*, **11**, 173-301.

Drits, V.A. & Bookin, A.S. (2001): *in* "Layered double hydroxides: present and future", V. Rives, ed. Nova Science Publ., New York, 41-100.

Dutta, S., Wu, K.C.W., Saha, B. (2014): *Catal. Sci. Technol.*, **4**, 3785-3799.

Larson, A.C. & Von Dreele, R.B. (1994): Los Alamos Natl. Lab. Report, 86-748.

Rives, V., Del Arco, M., Martín, C.V. (2013): *J. Contr. Release*, **169**, 28-39.

MANGANESE OXIDES AS ENVIRONMENTAL INDICATORS AND THEIR ROLE IN THE SPREAD OF TOXIC ELEMENTS

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Manganese oxides/hydroxides are very important geomaterials, resulting from the linkage of the MnO_6 octahedra, to form layer and tunnel structures that can accommodate large cations and water molecules (Post, 1999). They occur typically as cryptocrystalline and fine-grained mixtures of different Mn-phases and additional minerals such as carbonates, silicates and Fe oxides/hydroxides. These features make their identification and proper characterisation a challenge by standard X-ray diffraction methods because of their poor crystallinity. Therefore, a multi-methodological approach is mandatory to get to a proper characterisation of Mn-samples.

Variations in the Earth oxidizing conditions during geological ages affect their occurrences: deposits first started to form in the Late Archaean, related to the development of few oxygen oases, while large scale deposition started from the Early Proterozoic. During the Phanerozoic the manganese deposits reflect the intermittently oxidizing and reducing conditions of the hydrosphere (Roy, 1997). Manganese oxides are widespread all over the world: on the ocean floor they form hydrothermal crusts associated with the black smokers activity, or hydrogenous nodules and crusts; also they form continental deposits, associated with hydrothermal activity and weathering and sedimentary processes. Their formation and distribution are strongly controlled by fluids conditions (*p*H, *E*h, chemistry and so on) and circulation as well as by microbial activity, as a consequence each environment has its own typical manganese oxides paragenesis. They also develop an high specific surface area and a low Point of Zero Charge (generally less than 3; McKenzie, 1981; Oscarson *et al.*, 1983), so they can easily adsorb arsenic and heavy metals from the environment, controlling their partitioning between rocks, soils, and aqueous systems. Moreover, their wide occurrences (over time and space) allows their use as environmental indicators, in fact, nodules and crusts constitute a very powerful geological record. Therefore, by a proper mineralogical characterization, it is possible to recognize the environmental changes occurring over time (changes in *p*H, *E*h and fluids chemistry conditions), and unravel their role in the spreading of elements potentially toxic for human health and the environment.

REFERENCES

McKenzie, R.M. (1981): *Austr. J. Soil Res.*, **19**, 41-50

Oscarson, D.W., Huang, P.M., Liaw, W.K., Hammer, U.T. (1983*): Soil Sci. Soc. Am. J.*, **47**, 644-648.

Post, J.E. (1999): *Proc. Natl. Acad. Sci. USA*, **96**, 3447-3454.

Roy, S. (1997): *in* "Manganese mineralization: Geochemistry and mineralogy of terrestrial and marine deposits", K. Nicholson, J.R. Hein, B. Buhn, S. Dasgupta, eds. *Geol. Soc. London*, **119**, 5-27.

IN SITU TIME-RESOLVED SYNCHROTRON POWDER DIFFRACTION STUDY OF ZSM-5 ZEOLITES WITH DIFFERENT ALUMINUM CONTENT: STABILITY AND STRUCTURAL CHANGES UPON HEATING

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One of the most remarkable, and dramatically variable from one compound to another, properties of zeolites is their response to heating for both their characterization and application. Such a characteristic entails stability, phase transformations, rate and temperature of dehydration and rehydration (Alberti & Martucci, 2005, 2011; Cruciani, 2006). Detailed and accurate information on the thermal stability of microporous zeolite are still scanty and, occasionally, controversial or unreliable. In this work, the step by step thermal dehydration process of four ZSM-5 zeolites with different Si/Al ratio (SAR), has been studied *in situ* by synchrotron radiation powder diffraction. Samples of ZSM-5 were prepared starting from the following reactants mixture: TPABr (98%, Fluka), NaOH (97%, Carlo Erba Reagenti), $Al(OH)_3$ (98%, Fluka), precipitated silica gel (100%, Merck) and distilled water (Migliori *et al.*, 2014). In order to achieve different Si/Al ratio in the sample, the molar composition of the starting gel was changed by varying the amount of Al_2O_3 in the following starting mixture: $0.08Na_2O–0.08TPABr–xAl_2O_3–SiO_2–20H_2O$ where x ranges from 0.01 to 0.02 (*i.e.*, the Si/Al [mol/mol] is equal to 21, 30, 51, 84, respectively; Migliori *et al.*, 2014). The time-resolved experiment was performed at the MCX beamline at Elettra. For this study, powder samples of ZSM-5 were placed in a quartz-glass capillary using a gas blower to control the sample temperature. The evolution of the structural features was monitored through 36 structure refinements in the temperature range from 25 to 800°C by full profile Rietveld analysis.

Structural characterisation of samples having different Al content revealed no significant differences in the thermal stability. High temperature experiments confirm that all ZSM-5 maintain their crystallinity within the investigated T-range. On the contrary, the beta angle variation was found to be affected by the Si/Al ratio. Specifically, the higher the Silicium content the greater the beta angle. Lattice parameters vary continuously on increasing temperature, with a strong change in their evolution close to the temperature at which the monoclinic to orthorhombic phase transition takes place ($T \approx 100°C$).

Finally, a negative volume expansion associated with the temperature increase was observed in all investigated ZSM-5 samples.

REFERENCES

Alberti, A. & Martucci, A. (2005) *in* “Oxide based materials”, A. Gamba, C. Colella, S. Cosuccia, eds. *Studies Surf. Sci. Catal.*, **155**, 19-43.

Alberti, A. & Martucci, A. (2011): *Microp. Mesop. Mater.*, **141**, 192-198.

Cruciani, G. (2006): *J. Phys. Chem. Solids*, **67**, 1973-1994.

Migliori, M., Aloise, A., Giordano, G. (2014): *Catal. Today*, **227**, 138-143.

TEMPERATURE-INDUCED DESORPTION OF TOLUENE CONFINED ON Y ZEOLITE: *IN SITU* SYNCHROTRON XRD POWDER DIFFRACTION

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In this work the capability of Y commercial high silica zeolite (HSZs), for the removal of toluene (TOL) from aqueous solutions was investigated by in situ synchrotron powder diffraction. Toluene, was purchased as analytical standards from Sigma-Aldrich with a purity of 99.9%. Highly dealuminated Y hydrophobic zeolite was provided by Tosoh Corporation [FAU topology (Baerlocher *et al.*, 2007), code HSZ - 390HUA, SiO_2/Al_2O_3 molar ratio = 200] in its hydrogen form and used as received. All data collections were carried out in situ at the ID22 high resolution powder diffraction beamline (European Synchrotron Radiation Facility, ESRF, Grenoble, France) from room temperature up to 600°C. Thermogravimetric (TG) and differential thermal analysis (DTA) of Y loaded zeolite was performed in constant air flux conditions using the Netzsch STA 409 PC LUXX®-simultaneous TG/DTA thermogravimetric balance with a heating rate of 10°C/min, from room temperature (RT) to 600°C. Adsorption isotherm and kinetics of toluene on Y zeolite was determined from batch tests. This kind of information is crucial for designing and optimizing the regeneration treatment of such microporous material. Toluene molecules occupy one crystallographic independent and partially occupied site and statistically can assume six different orientations. Rietveld analysis demonstrated that the adsorption/desorption process occurred without any significant zeolite crystallinity loss, but with slight deformations in the channel apertures. The evolution of the structural features monitored by full profile Rietveld refinements revealed a phase transition ($Fd\text{-}3 \rightarrow Fd\text{-}3m$) at about 70°C. The evolution of unit-cell parameters during TOL desorption was continuously observed, thus indicating a negative thermal expansion process.

The refined occupancies revealed that TOL content decreases rapidly up to 110°C; complete desorption was achieved at ≈ 190°C. Rietveld refinement indicated the presence of co-adsorbed water molecules whose refined bond distances highlight the occurrence of organic contaminant and hydrophobic zeolite interactions mediated *via* H_2O. The crystallographic sites attributed to the water molecules decrease their occupancies more gradually than toluene and are completely emptied between 410 and 430°C.

This result is in good agreement with the TG and DTA tracks that shows a first weight loss associated to the elimination of species (water and/or TOL) weakly bonded to the surface ($T < 100°C$, weight loss 5%). A second more conspicuous weight loss (about 12%) occurs at higher temperatures, due to the elimination of TOL and/or H_2O molecules trapped within the zeolite pores. This result is in very good agreement with the extraframework content given by the refined occupancies and with the saturation capacity determined by the adsorption isotherms.

REFERENCES

Baerlocher, C., McCusker, L.B., Olson, D.H. (2007): Atlas of zeolite framework types, 6th ed. Elsevier, Amsterdam, 404 p.

TRACE ELEMENTS PROFILES AND MINERALOGICAL CHARACTERIZATION OF ANDRADITES (DEMANTOID VARIETY) FROM THE MINE OF SA SPINARBEDDA, DOMUS DE MARIA (CAGLIARI)

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Demantoid is considered one of the brightest gemstones, and its name is derived from the German demant, meaning "diamond-like". In particular, its name makes reference to the characteristics of this gem: brilliance and brightness. Demantoid belongs to the garnets family as a nesosilicate with the general formula $X_3Y_2(SiO_4)_3$. Chemically, the X site can be occupied by divalent cations (Ca^{2+}, Mg^{2+}, Fe^{2+}, Mn^{2+}) while the Y site usually host six-fold coordinated trivalent cations, as Al^{3+}, Fe^{3+}, Cr^{3+}, Ti^{4+} (Novak & Gibbs, 1971). Until now, these gems have been found only in few areas: Madagascar, Namibia, Ural Mountains (Russia), Iran, Pakistan and Canada. In Italy, isolated demantoid crystals have been recovered only in the Val Malenco (Sondrio) and in Montjovet (Aosta). The samples analysed in this work have been found by chance in an abandoned mine of Sa Spinarbedda (Domus de Maria, Cagliari) (Fig. 1). Due to their unusual location, it has been decided to proceed with a complete characterization in order to verify their truly belonging to the demantoid class. After a previous gemmological analysis, chemical and mineralogical characterization were carried out using a combined approach through LA-ICP-MS and X-ray powder diffraction techniques. Firstly, gemmological analysis has highlighted the high refraction index (> 1.81), which is typical of demantoid variety. Moreover, he chemical features, which has confirmed the demantoids compositional complexity, has revealed the low Cr content (~ 8 ppm) in all analysed samples.. The chemical data obtained have been also compared with the chemical composition of Namibian and Madagascar demantoids reported by the literature (Fig. 2): this comparison has been suggested by the presence of the same skarn matrix (Bocchio *et al.*, 2010). Finally, the Rietveld refinement, performed using the GSAS method (Larson & Von Dreele, 1994), has confirmed the demantoid structure and the presence of isomorphic substituents in both X and Y sites. In light of these results, it is possible to conclude that Sardinia can be added to the demantoids deposits traditionally cited by the literature.

Fig. 1 – Sa Spinarbedda demantoid samples.

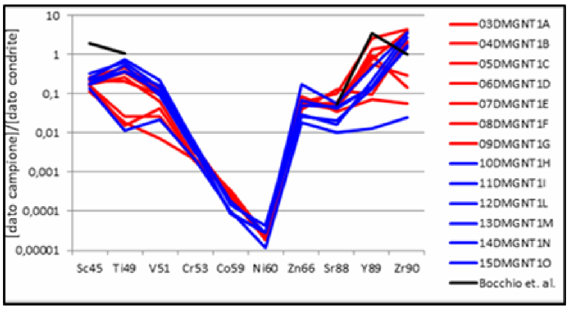

Fig. 2 – Spider diagram of the trace elements present in the analysed samples.

REFERENCES

Bocchio, R., Adamo, I., Diella, V. (2010): *Can. Mineral.*, **48**, 1205-1216.
Larson, A.C. & Von Dreele, R.B. (1994): Los Alamos Natl. Lab. Report, 86-748.
Novak, G.A. & Gibbs, G.V. (1971): *Am. Mineral.*, **56**, 791-823.

REDUCTION OF ELECTRICAL CONDUCTIVITY IN AIR EXPOSED TNO FILMS

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Nb-doped anatase TiO_2 is a viable candidate for replacing indium-tin-oxide (ITO), and fluorine-tin-oxide (FTO) as a transparent electrode in several technological applications like: flat panel displays, thin film amorphous silicon solar cells or dye-sensitized solar cells (Furubayashi *et al.*, 2005). We have produced transparent and conducting Nb-doped anatase TiO_2 films (TNO) at high deposition rate (tens of nm per minute) by reactive DC magnetron sputtering from metal targets. High deposition rate is obtained by an active control of the oxygen gas flow in order to stabilize the impedance of the plasma discharge (Oka *et al.*, 2014). Highly conductive (resistivity in the 10^{-3} $\Omega\cdot$cm range) Nb-doped TiO_2 thin films have been obtained by thermal treatment (600°C) in reductive atmosphere (high vacuum) (Tao *et al.*, 2014). The exposure of the films to ambient condition, has been found to play a crucial role in determining the resistivity of the material. In particular, air exposure in the tens of hours range has a dramatic effect on the film resistance. The resistivity of the film increases by one order of magnitude or more, depending on the thickness of the film, with a power-law behaviour. Scanning electron microscope (SEM) characterization reveal the presence of fractures in TNO films. SEM images show that the number and magnitude of fractures is proportional to the duration of the exposure of TNO to ambient condition. X-ray Photoelectron Spectroscopy analysis show a re-oxidation of the surface of TNO after ambient exposure. In order to understand if the increase of resistivity of TNO, after ambient exposure, is due to the re-oxidation of the TNO film or to the formation of fracture we performed cathodoluminescence (CL) measurements. CL reveals that the stoichiometry of the bulk TNO films reduced in vacuum, did not significantly change upon air exposure. It can be concluded, that the fractures increase the resistivity of the films.

REFERENCES

Furubayashi, Y., Hitosugi, T., Yamamoto, Y., Ina-ba, K., Kinoda, G., Hirose, Y., Shimada, T., Hasegawa, T. (2005): *Appl. Phys. Lett.*, **86**, 252101.

Oka, N., Sanno, Y., Jia, J., Nakamura, S., Shigesato, Y. (2014): *Appl. Surf. Sci.*, **301**, 551-556.

Tao, J., Pan, H., Wong, L.M., Wong, T.I., Chai, J.W., Pan, J., Wang, S.J. (2014): *Mater. Res. Express*, **1**, 015911.

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A NATURAL NANOSPONGE: CRYSTAL-FLUID INTERACTIONS IN LAUMONTITE

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Laumontite, $|(Ca_{4-x}Na_x)K_x(H_2O)_n|\cdot[Al_8Si_{16}O_{48}]$, space group *C*2/*m*, is one of the most common natural zeolite occurring in a wide range of geological environments, including sedimentary deposits, deep-sea sediments and in sedimentary deposits related to oil reservoirs. Remarkbly, 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. However, laumontite 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, a number of studies investigated, mainly *via* X-ray powder diffraction, 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 the 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 valuable considering the fact that laumontite is one of the most common zeolite in the oceanic basalts and, thereby, it can be a an important H_2O-carrier in the very first kilometers of the subduction zones. Moreover, it is worth to note that the *KV* of leonhardite is a critical parameter needed in order to model the thermodynamic stability of this mineral in geological environments of economic relevance (*i.e* deposits related to oil reservoirs). 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 base 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.

REFERENCES

Coombs, D.S., Ellis, A.J., Fyfe, W.S., Taylor, M. (1959): *Geochim. Cosmochim. Acta*, **7**, 53-107.
Fridriksson, T., Bish, D.L, Bird, D.K (2004): *Am. Mineral.*, **88**, 277-287.
Lee, Y., Hrilja, A.J., Vogt, T. (2004): *Phys. Chem. Minerals*, **31**, 421-428.
Neuhoff, P.S. & Bird, D.K. (2001): *Mineral. Mag.*, **65**, 59-70.
Yamazaki, A., Shiraki, T., Nishido, H., Otsuka, R. (1991): *Clay Science*, **8**, 79-86.

THE HIGH PERFORMANCE SOLIDIFICATION/STABILIZATION (HPSS) PROCESS: A NEW PERSPECTIVE FOR THE REMEDIATION OF CONTAMINATED SOILS

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Nowadays, despite the environmental protection policies that control and regulate the release of pollutants in the different matrices, the contamination originated from past anthropic activities remains an issue. Brownfields, which are abandoned industrial areas often located nearby city centers, are in many cases affected by soil contamination (Alker *et al.*, 2000), especially due to heavy metals. Since soil and sediments are the last receptacles for this kind of pollutants, they tend to persist in the environment, posing potential toxicity problems (Alloway, 1990). Landfill disposal has often been an obligatory choice, both because of the large volume of materials to be treated and for the type of contaminants, though generating a considerable amount of wastes and increasing soil consumption.

In the context of less impacting strategies for soil recovery, in line with the circular economy recommendations, the High Performance Solidification/Stabilization (HPSS) process for soil and sediments is able to reduce both the environmental and economic costs posed by land reclamation. With this recently improved technology, soil is removed from the ground and treated on site with the addition of a binder, Portland cement. When properly formulated, this blend, composed for the most part of contaminated soil and a little percentage of cement, is able to immobilize the inorganic contaminants present. Before the binder hardens, the mixture is submitted to a granulation step. The result is a centimeter-sized pellet material, characterized by good mechanical properties (Ferrari *et al.*, 2010) and a higher handling potential. This valuable product can be used as a filling material directly in the restored area, or recycled for other applications, *e.g.*, as aggregate in non-structural concrete, thanks to its low leaching of contaminants.

Recently, a former agriculture supply cooperative located in Bagnolo Mella (BS, Italy) has been submitted to the HPSS technology. There, the sulfuric acid manufacturing in operation in the first half of the XXth century, now results in a high concentration of lead and arsenic in soil. A laboratory investigation, simultaneous to the real-scale treatment applied on site, permits to analyze the mechanisms regulating the immobilization of the target elements. This represents an opportunity for a refinement of the formulation and of the set-up of the entire process.

REFERENCES

Alker, S., Joy, V., Roberts, P., Smith, N.J. (2000): Environ. Plann. Man., 43, 49-69.

Alloway, B.J. (1990): Heavy metals in soils. Blackie, Glasgow, 339 p.

Ferrari, G., Artioli, G., Parisatto, M. (2010): International Solidification/Stabilization Technology Forum, Sydney, 14-18 June 2010, 193-203.

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STRUCTURE OF NATURAL AND NH_4-EXCHANGED SASBACH FAUJASITE: A SINGLE CRYSTAL STUDY

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The interest for the environmental, industrial and technological applications of Si-rich zeolites is very high (Arletti *et al.*, 2012). Among the large pore zeolites, faujasite is one of the most exploited. This work is aimed to provide detailed structural information on natural and NH_4-exchanged faujasite before using this zeolite for dealumination tests, targeting obtaining large single crystals of all-silica faujasite (Fantini *et al.*, 2018).

Faujasite from Sasbach [$Na_{13.64}K_{0.87}Mg_{10.46}Ca_{8.89}Sr_{0.34}(Al_{51.95}Si_{139.57})O_{384}\cdot 272.29H_2O$; s.g. $Fd\text{-}3m$; a = 24.6906(2) Å] was chosen being one of the most Si-rich natural samples(Rinaldi *et al.*, 1975). Single-crystal X-ray diffraction structural refinements of both natural and NH_4-exchanged samples are reported and discussed (Fig. 1). In natural faujasite, the localization of almost all the extraframework species – never reported before in literature – was successful. The ammonium and water molecule sites were localized in the NH_4-exchanged sample. Ammonium cations are located in two extraframework sites originally occupied by cations in natural faujasite.

REFERENCES

Arletti, R., Martucci, A., Alberti, A., Pasti, L., Nassi, M., Bagatin, R. (2012): *J. Solid State Chem.*, **194**, 135-142.

Fantini, R., Arletti, R., Pastero, L., Quartieri, S., Di Renzo, F., Cámara, F., Vezzalini, G. (2018): *Eur. J. Mineral.*, **30**, 515-523.

Rinaldi, R., Smith, J.V., Jung, G. (1975): *N. Jb. Miner. Mh.*, **1975**, 433-443.

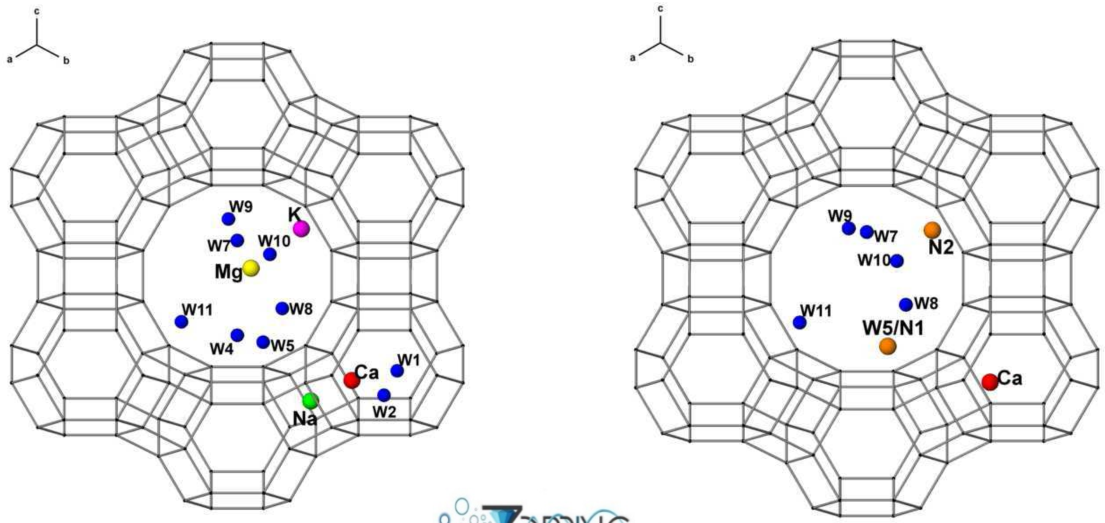

Fig. 1 – Structure of FAU(left) and of FAU-NH_4 (right) viewed along [111].

POTENTIALLY TOXIC ELEMENTS IN SERPENTINE SOILS AND BEDROCKS: A CASE STUDY FROM VOLTRI MASSIF OPHIOLITES

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Serpentine soil is a general term used to describe soils derived from a wide range of ultramafic rocks, including peridotites and their metamorphic equivalents (serpentinites). Serpentine soils are typically characterised by very high PTEs contents (particularly Cr, Ni, and Co), commonly exceeding residential and industrial concentration limits according to Italian and international laws.

The aim of this study is to determine how lithological, structural and textural characteristics of ultramafic bedrocks may affect distribution and fate of PTEs in serpentine soils during weathering processes. In particular, we focused on the serpentine soil profiles from the HP-LT metaophiolite of the Voltri Massif (Ligurian Alps). The studied bedrocks are represented by ultramafic rocks with various degree of metamorphic overprint and different structural features (*i.e.*, partially serpentinized peridotites, massive antigorite-serpentinites, antigorite-serpentine schist, serpentinite schist with actinolite-chlorite rich interlayers).

The mineralogy and mineral chemistry of the main phases were analysed by SEM-EDS, EMPA-WDS, XRPD with synchrotron X-ray sources and Rietveld refinement (GSAS software). The bulk chemistry (major, minor, and trace elements) was analysed in situ and in laboratory *via* Field Portable-EDXRF, ICP-MS, and ICP-AES.

In the bedrock, PTEs-bearing phases are represented mainly by Fe and Ti oxides (spinel group minerals, ilmenite and rutile) with subordinate silicates (*i.e.*, serpentine group minerals, olivine, pyroxenes and chlorite). In spinels, Cr, Ni, and Co concentrations progressively decrease with the serpentinization degree of the rocks. Conversely, Ti and V concentrations increase significantly in serpentinite schist with actinolite-chlorite rich interlayers. Spinel compositions are also correlated to the different textural or microstructural feature where they occur (porphyroclast, recrystallized porphyroclast, re-oriented trail).

Along the studied soil profiles, the major PTEs-bearing minerals are derived from the bedrock and are represented by serpentine group minerals, magnetite, chlorite, olivine, and pyroxene. They show a significant increase of weathering from the parent rock toward the superficial horizons in all sites. The authigenic phases are subordinated and mainly represented by low-crystalline Fe-oxyhydroxides and oxides, with minor amount of clay minerals. The main PTEs-bearing phases are represented by magnetite, ilmenite and Cr-magnetite; also, rutile and Ni sulphides constitute an important source of PTE, but they are only an accessory phase.

More than 90% of the PTEs in the soil profiles is represented by: Cr, Ni, Co, Cu, Zn, and V. Soils are generally depleted in Cr, Ni, and Co and enriched in Cu, Zn and V with respect to the bedrocks. As expected in such primitive soils, both the mineralogy and the chemistry are compatible with the bedrock, and seem to be controlled mainly by the serpentinization degree and metamorphic re-equilibration, as much as by the rock texture and proximity with other lithologies.

PRELIMINARY CHEMICAL AND MINERALOGICAL ANALYSES OF TWO ORDINARY CHONDRITES FROM DRAA VALLEY, ZAGORA (MOROCCO)

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The two rock-type meteorites, named 2C and 3D, were discovered in 2010 in the desert of Morocco near the city of Zagora. Microtextural features were observed using optical and scanning electron microscopes whereas mineral chemical compositions were obtained with EDS semi-quantitative analyses. Mineralogical characterizations and major and trace elements analyses were performed with XRD, DTG and XRF, ICP-MS, respectively. Both meteorites belong to the Chondrites Group.

2C chondrite is formed by silicate portion (85% vol), composed by chondrules, individual grains of olivine, pyroxene, rare plagioclase and fine grain-matrix; the metallic portion is scarce (10% vol). The chondrules vary in size (250 µm to 1 mm across) and in petrographic types (BO, POP, RP, GOP and Criptocrystalline (Scott & Krot, 2014). The metallic portion is constituted by Fe-Ni alloy (8% vol) and Fe-Ni-sulfurs (2% vol). The sample is crosscut by secondary (fluid/melt?) veins (up to 5 % vol).

3D meteorite is similar to 2C in terms the silicate portion (80% vol), but shows less chondrules and olivine and pyroxene grains. The chondrules (BO, PP, PO and GOP; Scott & Krot, 2014) are not well defined, generally fractured with evident mosaic texture. The metallic portion (up to 20% vol) is made of Fe-Ni alloy (kamacite-taenite phase group), and Fe-Ni-Cu-Sulfurs.

2C and 3D chondrites show similar DTG profiles with endothermic reaction peak at 300°C (Fe oxidation); only the 3D chondrite, records an evident esothermic peak at 450°C, testifying for sulfur contents larger than 2C chondrite. The XRD results show the same mineralogical composition of the two chondrites, with (forsteritic) olivine, Ca-poor pyroxenes and (albitic) plagioclase as the most abundant silicates. Kamacite (low temperature) and taenite (high temperature). Troilite, chromite and goethite (probably terrestrial alteration phase) are identified as the main matrix components. Irrespectively to the textural types, olivine in 2C chondrite have Fa contents from 17.45 to 25.59; predominant enstatitic pyroxenes (Mg# 81-89) with low to very low CaO and Al_2O_3 contents (0.4-0.8 wt% and 0.1 wt% respectively). The olivine compositions suggest a low petrological type (presumably 3). The Fe-Ni alloy are close to the kamacite endmember (Fe 94.05-98.38 wt% and Ni 1.62-5.60 wt%).

The few analyzed olivines of 3D chondrite are more forsteritic (Fa: 12.51-14.94) than those of 2C chondrite, coherent with a higher petrological type (presumably 4-6). The metallic matrix is formed by equally contents of Ni rich (Ni > 7%) and Ni poor kamacites; Fe-sulfurs generally contain small Cu abundances (0.9 wt%).

On the basis of Fe/Ni-Fe/Mg elemental ratios both 2C and 3D chondrites may be classified as H-type chondrites (Bischoff *et al.*, 1993), whereas the preliminary mineral chemistry so far obtained indicate 3 to 6 as petrological types (Huss *et al.*, 2006).

REFERENCES

Bischoff, A., Palme, H., Ash, R.D., Clayton, R.N., Schultz, L., Herpes, U., Stöffler, D., Grady, M.M., Pillinger, C.T., Spettel, B., Weber, H., Grund, T., Endress, M., Weber, D. (1993); *Geochim. Cosmochim. Acta*, **57**, 1587-1603.

Huss, G.R., Rubin, A.E., Grossman, J.N. (2006): *in* “Meteorites and the Early Solar System II”, D.S. Lauretta & H.Y. McSween Jr., eds. University of Arizona Press, Tucson, 567-586.

Scott, E.R.D. & Krot, A.N. (2014): *in* “Treatise on Geochemistry, Vol. 1”, A.M. Davis, ed. Elsevier, Amsterdam, 65-137.

CRYSTAL STRUCTURE AND HYDROGEN BONDING IN EPSOMITE FROM FORNOVOLASCO, APUAN ALPS, TUSCANY (ITALY)

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Epsomite is the Mg end-member of a group of orthorhombic heptahydrate sulfates having general formula $M^{2+}(SO_4)\cdot 7H_2O$ (where M = Mg, Zn or Ni). These minerals typically occur in evaporitic deposits, in saline lakes as precipitates, or in weathering zones of coal and ore deposits (Jambor *et al.*, 2000). Recently, epsomite has been recognized in the Martian soils and in the icy moons from the outer Solar System (Bobocioiu & Caracas, 2014).

The crystal structure of synthetic $Mg(SO_4)\cdot 7H_2O$ was solved and then refined using neutron as well as X-ray diffraction (Baur, 1964; Ferraris *et al.*, 1973; Calleri *et al.*, 1984). The present study aims at refining the crystal structure of epsomite using a natural specimen from Fornovolasco (Apuan Alps, Tuscany, Italy), comparing these results with those previously achieved on synthetic analogues.

Epsomite occurs as mm-long colorless prismatic crystals or as thin needles up to more than 1 cm long, associated with pyrite and other sulfates such as melanterite, pickeringite, magnesiocopiapite, wilcoxite, and gypsum.

Preliminary EDS chemical analyses revealed the occurrence of Mg, Fe, and S as the only elements with $Z > 8$ above the detection limit.

The Raman spectrum of epsomite in the region between 400 and 1200 cm^{-1} is dominated by bands arising from the SO_4 group vibrations. The strongest band occurs at 984 cm^{-1} and is related to the symmetrical SO_4 stretching ν_1. Three weaker bands at 1061, 1099 and 1145 cm^{-1} can be assigned to the antisymmetrical SO_4 stretching mode ν_3. The bending modes of the SO_4 group are represented by bands at 444 (ν_2 mode) and 614 cm^{-1} (ν_4 mode). The occurrence of H_2O groups is confirmed by the occurrence of bending and stretching vibration of O–H bonds.

Epsomite crystallizes in the space group $P2_12_12_1$, with unit-cell parameters a = 11.8664(2), b = 12.0150(2), c = 6.8598(1) Å, V = 978.03(4) Å^3, Z = 4. The crystal structure of epsomite has been refined to $R1$ = 0.021 on the basis of 3418 reflections with $F_o > 4\sigma(F_o)$. In agreement with qualitative EDS chemical analysis, which show detectable amounts of Fe, the refinement of the site occupancy factor (s.o.f.) at the *Mg* site points to an occupancy ($Mg_{0.92}Fe_{0.08}$).

The crystal structure of epsomite can be described as formed by undulating layers of SO_4 groups and Mg-centered octahedra coordinated by H_2O groups. The hydrogen bond system is described in detail and plays a fundamental role in the crystal structure of epsomite. Since six out of the seven H_2O groups belong to the Mg^{2+}-centered polyhedra, the chemical formula of epsomite should be correctly written as $Mg(H_2O)_6(SO_4)\cdot H_2O$.

REFERENCES

Baur, W.H. (1964): *Acta Crystallogr.*, **17**, 1361-1369.
Bobocioiu, E. & Caracas, R. (2014): *Am. Mineral.*, **99**, 1126-1220.
Calleri, M., Gavetti, A., Ivaldi, G., Rubbo, M. (1984): *Acta Crystallogr.*, **B40**, 218-222.
Ferraris, G., Jones, D.W., Yerkess, J. (1973): *J. Chem. Soc. Dalton Trans.*, **1973**, 816-821.
Jambor, J.L., Nordstrom, K.D., Alpers, C.N. (2000): *Rev. Mineral. Geochem.*, **40**, 303-350.

INSIGHTS ON MINERALOGICAL, ENVIRONMENTAL AND NORMATIVE ISSUES IN THE NATURALLY OCCURRING ASBESTOS (NOA) MANAGEMENT: IDENTIFICATION AND QUANTIFICATION BY SEM-EDS AND SYNCHROTRON RADIATION X-RAY MICROTOMOGRAPHY

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Asbestos Containing Materials (ACM), declared harmful to health, have been banned in Italy by Law N° 257 of 27/03/1992 and afterwards in the entire European Community. However, anthropogenic and natural processes contribute to the continuous production of Elongated Mineral Particles (EMP) of amphibole and serpentine, releasing fibres in heterogeneous and unpredictable concentrations in the environment. The asbestos classification system defined by M.D. 06/09/1994 is generic, subjective and not always applicable to amphiboles that can take either a prismatic or fibrous habitus. Even fibrous antigorite is similar for morphology to its polymorph chrysotile and therefore it is not easily distinguishable. Moreover, despite the known carcinogenic nature of asbestos, prismatic amphibole and cleavage fragments are not yet univocally regulated as asbestos in many countries. The aim of this work is to provide solutions to social and environmental problems by using unconventional techniques for asbestos detection.

Firstly, a comparison among Italian normative methods for asbestos quantification in massive lithotypes (five samples of metamorphic rocks potentially containing serpentine and/or amphibole asbestos were selected) was carried out by SEM-EDS. Despite the D.P.R. 13 June 2017, no. 120, the same normative permits to use the previous decree (M.D. 161/2012) for projects approved before 08/22/2017. Comparing the sample preparations (milling of a representative sample fraction) and calculation of asbestos fibres concentration, it emerged that on the whole, the results according to M.D. 161/2012 could decrease the concentration from 80 to 50% compared with total asbestos analyses (M.D. 06/09/1994 and D.P.R. 13 June 2017, no. 120). So fibres concentration depends on the initial concentration (mineralogical composition) but also on the technical processes (*e.g.*, grinding, sample preparation) that the rock undergoes.

Secondly, morphological studies have been performed by Synchrotron Radiation X-ray microtomography (SR X-ray μCT) in order to understand if asbestos phase are affected by modifications during the comminution. Preliminary results highlight that fibers could have a critical counting dimension (length > 5 μm, diameter < 3 μm, length:diameter 3:1) as result of the comminution even if the pristine crystal has an acicular habitus. Moreover SR X-ray μCT technique could help to discriminate cleavage fragments from the fibers.

The final aim will be to carry out a second cycle of microtomography analysis on the samples that have undergone grinding, and to address detailed TEM analysis, in order to develop precise and repeatable protocols to be transferred to the qualitative and quantitative assessment of asbestos risk at national and international level.

GROUNDWATER REMEDIATION: WHAT DOES MINERALOGY HAVE TO DO WITH IT?

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Toxic metal release, transport and dispersion into the biosphere have a direct impact on the environment and human health. Hexavalent Chromium (CrVI) is a highly toxic agent that acts as a carcinogen, mutagen, and teratogen in biological systems, so the reduction of this pollutant in soils and water to acceptable levels is of vital importance.

This work is part of a much more extensive project aimed at: on one hand, to test adsorption ability of naked colloidal maghemite (γ-Fe_2O_3) nanoparticles called SAMNs (Surface Active Maghemite Nanoparticles) on highly polluted industrial groundwater; on the other hand to stress the role of the mineralogical control on the release of toxic metals in soils and water. SAMNs are superparamagnetic maghemite nanoparticles characterised by excellent colloidal stability not requiring any superficial modification or coating process, high surface-area-to-volume-ratio, low toxicity and strong absorption ability (Magro *et al.*, 2016). The ex-Stoppani site (Cogoleto, NW Italy) is investigated: the production of sodium dichromate, chromic acid and basic chromium sulphate and subsequent disposal of millions of tons of Chromite Ore Processing Residues(COPRs) in all the area caused the release of a high quantity of CrVI in percolating water. Preliminary, but auspicious, results in the mineralogical characterisation of COPRs through Micro-Raman Spectroscopy (Thermo Scientific DXR Raman Microscope) are shown. Only micro-Raman analysis of untreated COPR samples, after granulometric separation (71, 50, 20 µm), revealed the presence of chromate phases such as sodium chromate (Na_2CrO_4) and crocoite ($PbCrO_4$). Previous mineralogical and minero-chemical characterisation of soils, performed through X-Ray powder diffraction (XRPD) and scanning electron microscopy (SEM), showed the typical mineralogic composition of COPRs (Hillier *et al.*, 2003; Chrysochoou & Dermatas, 2006). No CrVI-phases (*i.e.*, $PbCrO_4$ and Na_2CrO_4) were found; this could be due to solubilization during sample preparation.

The removal efficiency of SAMNs in respect of CrVI it was tested on industrial groundwater from 9 wells varying the *p*H of the solution between 3.0 and ~8.0 and SAMNs concentration of 10 $g \cdot L^{-1}$. CrVI concentration was determined using Cary 60 UV-Vis Spectrophotometer using the 1,5 dyphenilcarbazide method (Petala *et al.*, 2013). From these tests emerged that SAMNs are very promising for the remediation of industrial groundwater: they can remediate water with very high concentrations of CrVI (~22 mg/L) with only two treatments. *p*H of the solution is a crucial factor: the amount of CrVI removed reach about 99% at *p*H of 3.0 after two treatments, while this amount decreases to ~ 60% at the natural *p*H of the sample (~ 8.0).

REFERENCES

Chrysochoou, M. & Dermatas, D. (2006): *J. Hazard. Mater.*, **2006**, 20-33.

Hillier, S., Roe, M.J., Geelhoed, J.S., Fraser, A.R., Farmer, J.G., Paterson, E. (2003): *Sci. Total Environ.*, **308**, 195-210.

Magro, M., Domeneghetti, S., Baratella, D., Jakubec, P., Salviulo, G., Bonaiuto, E., Venier, P., Malina, O., Tuček, J., Ranc, V., Zoppellaro, G., Zbořil, R., Vinello, F. (2016): *Chem. Eur. J.*, **22**, 14219-14226.

Petala, E., Dimos, K., Douvalis, A., Bakas, T., Tucek, J., Zbořil, R., Karakassides, M.A. (2013): *J. Hazard. Mater.*, **261**, 295-306.

ADSORPTION OF S-METOLACHLOR IN WATER SOLUTION USING DIFFERENT ZEOLITES TOPOLOGY: A COMBINED DIFFRACTOMETRIC AND CHROMATOGRAPHIC STUDY

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The release of emerging contaminants in environmental matrixes represents one of the most important emergencies in the last years. In particular, pesticides and herbicides are frequently detected in the water bodies, causing adverse effect for human health and the aquatic ecosystem. S-Metolachlor is an organic compound included in the herbicides class, often present in both ground and surface water. Due to its bioaccumulation capacity in food and its potential carcinogenicity for human, the removal of this chemical from water matrix is of relevant interest concern. For this reason, in this work we studied the possibility to remove S-Metolachlor by means the adsorption technique using different kinds of synthetic materials. The materials used are constituted by different zeolites topologies (Braschi *et al.*, 2010; Pasti *et al.*, 2013) (MFI, FAU, BEA) characterised by different SiO_2/Al_2O_3 oxide-ratio (from 25 to 280 SAR). The samples (ZSM-5, 424AS, β and Y zeolites) were investigated by chromatographic (High Performance Liquid Chromatography - HPLC) before and after S-Metolachlor adsorption. The adsorption capacity of selected samples from aqueous solution was evaluated in different S-Metolachlor concentration range (5, 20 and 100 ppm). A contact time of 1 and 24 hours was employed. Among the tested zeolites, the best performance was achieved by Y zeolite sample. This sample was analysed by diffractometric (X-Ray Powder Diffraction - XRPD) and thermogravimetric (TG) techniques. The obtained results highlighted that S-Metolachlor was almost adsorbed by Y zeolite until 100 ppm. The maximal amount of S-Metolachlor adsorbed was 20% DW of dry zeolite weight, as remarked by thermogravimetric analyses. The refined unit cell parameters, using Rietveld method, showed variations in respect of the unload Y sample. This evidence suggest that S-Metolachlor molecules are adsorbed in Y super-cage. In light of these results, the effective of Y as S-Metolachlor adsorber was demonstrated and it is possible to conclude that Y zeolite may be suitable for remediation of herbicide-polluted waters.

REFERENCES

Pasti, L., Sarti, E., Cavazzini, A., Marchetti, N., Dondi, F., Martucci, A. (2013): *J. Separ. Sci.*, **36**, 1604-1611.
Braschi, I., Blasioli, S., Gigli, L., Gessa, C.E., Alberti, A., Martucci, A. (2010): *J. Hazard. Mater.*, **178**, 218-225.

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OXYGEN ISOTOPIC ANALYSIS OF MINEO (SICILY, ITALY) PALLASITE

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Pallasites are stony-iron meteorites essentially composed of olivine [$(Mg,Fe)_2SiO_4$] with a metallic portion covering one-third of the total volume1 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 (11-14wt%) 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; and 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 $\delta^{18}O = 2.33 \pm 0.30$, 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.

REFERENCES

Boesenberg, J.S., Delaney, G.S., Hewins, R.H.J. (2012): *Geochim. Cosmochim. Acta*, **89**, 134-158.
Buseck, P.R. & Goldstein, J.I. (1969): *Geol. Soc. Am. Bull.*, **80**, 2141-2158.
Stephan, T. (2001): *Planet. Space Sci.*, **49**, 859-906.

DRUGS ADSORPTION STUDY FROM AQUEOUS SOLUTIONS *VIA* SYNTHETIC MICROPOROUS MATERIALS: CHROMATOGRAPHICAL AND STRUCTUCTURAL CHARACTHERIZATION

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In recent years, molecules such as the analgesics, anti-inflammatories, antiepileptics, β blockers, etc. have been identified as environmental pollutants usually found in the aquatic environment.

For instance, he non-steroidal anti-inflammatory drugs (NSAIDs) are widely used as generic painkillers and in addiction with antibiotics and other pharmaceutical compounds represent one of the most important pollutants class for water bodies (Löffler *et al.*, 2005; Braschi *et al.*, 2010). As a matter of fact, many drugs taken for both human and veterinary therapy are excreted without being metabolized. These active metabolites persist in the surface water due to the ineffective treatment plants (Tolls, 2001) and have been caused negative effects in the aquatic fauna. However, the possible adverse effects on human health remain to be ascertained. In this work the adsorption of ketoprofen (KTP), hydrochlorothiazide (HTC) and atenolol (ATN) are investigated. Different drugs concentration at different *p*H condition from water solution were adsorbed by beta (BEA) and Ultra Stable Y (FAU) zeolites samples with different silicon/aluminum oxide ratio (Beta 25 SAR, Beta 360 SAR, USY 200 SAR and USY 360 SAR). This study was conducted in order to verify NSAIDs adsorption capacity of the selected materials and the possible release of these drugs from saturated samples as function of pH variation. The adsorption of KTP, HTC and ATN from aqueous solution on zeolites was evaluated using static approach and the isotherm data was elaborated employing the Langmuir model. The total amount of adsorbed drugs was also evaluated by thermal analysis and the information regarding the structural modification undergoes on the saturated samples was obtained by X-ray powder diffraction technique. The results obtained from these complementary techniques highlight that Beta 25 SAR and Y 200 SAR showed the highest drugs adsorption capacity.

REFERENCES

Braschi, I., Blasioli, S., Gigli, L., Gessa, C.E., Alberti, A., Martucci, A. (2010): *J. Hazard. Mater.*, **178**, 218-225.
Löffler, D., Römbke, J., Meller, M., Ternes, T.A. (2005): *Environ. Sci. Technol.*, **39**, 5209-5218.
Tolls, J. (2001): *Environ. Sci. Technol.*, **35**, 3397-3406.

WATERSHEDS AS COMPLEX DISSIPATIVE GEOCHEMICAL SYSTEMS: STABILITY, VARIABILITY AND RESILIENCE. THEORY AND PRACTICAL APPLICATIONS

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The research project we present will be carried forward during a PhD course in Earth Sciences, started this academic year and supported by ARPAT (Environmental Agency of Tuscany) and Tuscany Region (Borsa da Piano Strategico di Ateneo, Prot. n. 116487). It is well know that most geological systems behave as dissipative and self-organising structures. They are open, dynamic, consist of numerous components and develop in nonlinear branch, far from equilibrium. Watershed systems are not an exception. A general feature of these systems is robustness and resilience (Dai *et al.*, 2015). They can be relatively insensitive to perturbations and have a strong capacity to restore themselves after changes (Scheffer *et al.*, 2012). Reasons for this fault-tolerance are that self-organization is facilitated by randomness, while the stabilizing effect of feedback loops guarantee resilience. Although in general there will still be exchange of matter and energy between systems and surrounding, the organization is determined purely internally. Thus, the system is thermodynamically open, but organizationally closed. Such system has properties can be described only by the probability laws that govern the joint behaviour of the chemicals and related environmental variables (van Rooij *et al.*, 2013). If this dynamics has to be captured, a multidisciplinary statistical-geochemical approach is needed. Moreover, the relative nature of concentrations should be taken into account since the constrained simplex is the sample space for statistical analysis (Aitchison, 1986). Unfortunately this is not always the case.

The aim of the project is to investigate the statistical properties of geochemical landscapes in the watersheds of Tuscany to decipher the dynamics of natural/anthropogenic processes. To achieve the target numerical information contained in the regional GEOBASI repository will be used and implemented adding: 1) sampling campaigns and experimental data (concentrations of main and trace components, isotopes) from selected natural conditions, 2) statistical graphical-numerical tools, oriented on a space-time basis 3) correlation with soil use, morphology, lithology, rain, runoff.

REFERENCES

Aitchison, J. (1986):The statistical analysis of compositional data. Chapman & Hall, London, 416 p.

Dai, L., Korolev, K.S., Gore, J. (2015): *Proc. Natl. Acad. Sci.*, **112**, 10056-10061.

Scheffer, M., Carpenter, S.R., Lenton, T.M., Bascompte, J., Brock, W., Dakos, V., van de Koppel, J., van de Leemput, I.A., Levin, S.A., van Nes, E.H., Pascual, M., Vandermeer, J. (2012): *Science*, **338**, 344-348.

van Rooij, M.M.J.W., Nash, B.A., Rajaraman, S., Holde, J.G. (2013): *Frontiers Physiol.*, **4**, 1-16.

RE-CLASSIFICATION OF THE SINNAI METEORITE

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We report here new data set of bulk and mineral major and trace element analyses of the Sinnai meteorite which fell in southern Sardinia, on February 19th 1956.

The SINNAI meteorite is currently classified as H6-petrological type. The 18 mol% Fa content in olivine (as reported in an unreferenced note) is the only chemical parameter to support this classification. On the basis of the new chemical data and textural and physical characteristics, Sinnai meterorite is currently under investigation for a potential reclassification from H6 to H3 petrological type.

We based our revision on SEM-EDX and EMP-WDX analyses of new thin section and mirrored chip sample. About 4.5 g of meteorite chips were powdered and homogenized in order to investigate bulk chemistry. Major and trace element concentration were obtained by XRF and ICP-MS. Petrographic analysis of the fragment showed a moderate shock stage (S3) for the presence of clinoenstatite lamellae and opaque shock with feeble oxidation (W1). The meteorite consists of rounded chondrules (ca. 64 vol%) up to 1.0 mm in size, large olivine and sub-calcic pyroxene crystals, a fine-grained matrix (ca. 20 vol%) and a metallic portion. CAIs and AOAs are not observed.

The matrix is made up of olivine, pyroxene, rare plagioclase, and even more rare merrillite and apatite. The metallic portion (ca. 16 vol%) consists of predominant Fe-Ni alloy and Fe sulphides. In chondrules, the average Fa content is 15.7 mol% whereas in the matrix it is 12.1 mol%. The dominant pyroxene is low-Ca pyroxenes (Wo: 0.4-2.5 mol%). Glassy patches in chondrules occur associated with plagioclase crystallites (An: 11-22) and rarer tiny phosphates (Na_2O = 2.74-3.20 wt%). Glasses are rich in CaO (1.65-4.00 wt%), and rather poor in FeO (0.62-5.50 wt%) and MgO (0.75-16.4 wt%). Fe-Ni alloy is formed by kamacite (Ni = 0 4.3 and 6.7 wt%) and taenite (Ni: 31.0 and 53.1 wt%).

On the basis of Mg/Si (0.906) and Al/Si (0.083) ratios, we grouped the Sinnai meteorite as Ordinary Chondrite, undistinguishable between H, L and LL (Bonadiman *et al.*, 2016). Comparing with the average H normalised chondrite REE+Y geochemistry (Troiano *et al.*, 2011), this meteorite shows moderate REE enrichment. These new data suggest a new classification as H group, 3 petrographic type, 8 subtype, S3 shock stage and W1 weathering grade (Brearley & Jones, 1988).

REFERENCES

Bonadiman, C., Cruciani, G., Franceschelli, M. Marchi, M., Tarocco, C., Colombetti, P., Bhandari, N., Sinha, N., Rubinetti, S., Romero, A., Tassinari, R., Lunari, C. (2016): 2nd European Mineralogical Conference, Rimini, Italy, 11-15 September 2016, abstr., 459-460.

Brearley, A.J. & Jones, R.H. (1998): *in* “Planetary materials”, J.J. Papike, ed. *Rev. Mineral.*, **36**, 3.1-3.398

Troiano, J., Rumble III, D., Rivers, M.L., Friedrich, M.J. (2011): *Geochim. Cosmochim. Acta*, **75**, 6511-6519.

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Abstract delle lezioni

LONG- *VS.* SHORT-RANGE PROPERTIES ALONG BINARY SOLID SOLUTIONS: THE INTERPLAY BETWEEN X-RAY DIFFRACTION AND ABSORPTION SPECTROSCOPY

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La parte teorica della lezione si svilupperà a partire dai concetti fondamentali riguardanti le soluzioni solide (più dal punto di vista geochimico/cristallochimico che da quello termodinamico). Enfasi verrà posta alla comprensione della struttura cristallina di minerali e analoghi di sintesi attraverso la variazione composizionale (principalmente attraverso la sostituzione isormorfa di cationi in coordinazione tetraedrica e ottaedrica con metalli di transizione), richiamando quindi il concetto di “cristallochimica comparativa”. Le tecniche d’indagine saranno la diffrazione di raggi X (principalmente da polveri, pochi cenni) e la spettroscopia per riflettanza diffusa (particolare spettroscopia UV-VIS utilizzata con campioni in polvere). Saranno fornite nozioni addizionali sull’utilizzo di altre spettroscopie “elemento selettive” (come quelle di assorbimento di raggi X, XAS) accreditate di modelli più accurati per ottenere informazioni strutturali (coordinazione, distanze di legame, etc.). Al fine di confrontare direttamente dati strutturali derivanti dalla diffrazione (osservazioni a lungo-raggio) e dalla spettroscopia DRS (osservazioni a corto-raggio) ci si avvarrà di nozioni introduttive sulla teoria del campo cristallino (CFT). Il possibile “mismatch” fra distanze di legame medie e locali sarà poi misurato attraverso il modello semiempirico del rilassamento strutturale.

La seconda parte della lezione verrà dedicata alla discussione di alcuni casi studio di interesse mineralogico-applicativo.

A CONTINENT ENTRAPPED INSIDE A MINERAL

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Le inclusioni di fuso silicatico in fenocristalli di rocce effusive sono uno strumento ampiamente utilizzato in petrologia magmatica da almeno quattro decenni. Tuttavia, solo di recente è stata scoperta la presenza di analoghe inclusioni in minerali peritettici di rocce di alto grado metamorfico (migmatiti e granuliti). Queste inclusioni sono policristalline, con un diametro generalmente < 20 μm e contengono quarzo, plagioclasio, feldspato alcalino, biotite, muscovite e minerali accessori. Considerando la paragenesi mineralogica e le dimensioni dei cristalli, questa tipologia di inclusione è stata nominata “nanogranitoide”. Le inclusioni nanogranitoidi rappresentano piccole porzioni di fuso anatettico prodotto dalla fusione incongruente di rocce crostali. Il seminario presenterà i) le diverse modalità di intrappolamento di inclusioni di fuso silicatico in sistemi magmatici e metamorfici, ii) le metodologie di analisi microstrutturale e chimica delle inclusioni nanogranitoidi, e iii) le loro principali applicazioni petrologiche.

COLLECTING HIGH TEMPERATURE SINGLE CRYSTAL DIFFRACTION DATA ON MINERALS AND PROXIES: HOW AND WHAT FOR

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La lezione inizierà con una introduzione al concetto di condizioni estreme di temperatura e motivazione dello studio dei minerali in queste condizioni, sulla base del tipo d'informazione che si può ottenere in uno esperimento di diffrazione in alta temperatura. Segue una giustificazione della scelta della diffrazione di cristallo singolo sulla diffrazione da polvere, assieme ad un breve ripasso dei concetti di geometria della diffrazione che introduce ai dettagli tecnici della raccolta dei dati in condizioni di alta temperatura (e bassa temperatura). Verrà di seguito fatta una breve esposizione dei diversi tipi di dispostivi per riscaldare i cristalli montati su un goniometro in modo da ottenere dati di intensità diffratte in condizioni variabili di temperatura (fiamma aperta, combustione, riscaldamento elettrico diretto, radiazione, flusso di gas riscaldato/raffreddato, laser). Saranno discussi i dettagli riguardanti alla montatura del cristallo compatibilmente con condizioni di alta e bassa temperatura, così come la calibrazione della temperatura dei cristalli durante gli esperimenti. Per completezza, vengono discussi recenti accorgimenti per poter raggiungere simultaneamente condizioni esperimentali di alta pressione e alta temperatura.

Gli effetti della temperatura sui materiali cristallini verranno brevemente descritti: espansione termica del reticolo cristallino (equazioni empiriche e fisiche; ellissoide di deformazione); moto termico degli atomi (descrizione e influenza della temperatura sui dati di diffrazione) e relative correzioni necessarie in condizioni di alta temperatura.

La lezione termina con alcuni esempi di studi in condizioni di alta/bassa temperatura che illustrano la necessità di raccolta di dati accurati e descrivono le transizioni di fase distorsive e i fenomeni de deidratazione.

ELASTIC PROPERTIES OF MINERALS: THEORY AND PRACTICE

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Le proprietà elastiche caratterizzano le proprietà allo stato solido dei materiali e la loro conoscenza può dare informazioni fondamentali per le scienze che vanno dalla geologia all'ingegneria dei materiali alla medicina.

In questo talk, dopo un accenno alla definizione delle proprietà elastiche dei materiali, l'attenzione verrà focalizzata sulle definizioni delle equazioni di stato e quindi alle variazioni di densità dei minerali nonché sulle deformazioni di volume isotrope (nei cristalli cubici) e anisotropi (per gli altri sistemi cristallini).

Verranno mostrati alcuni metodi sperimentali (tecniche per esperimenti *in situ*, visto il carattere elastico delle deformazioni) per la determinazione dei parametri che entrano nella definizione di tali grandezze, quali il K (bulk modulus e le sue derivate), come anche le diverse equazioni di stato che possono essere impiegate (Murnaghan, Birch-Murnaghan, Vinet) per interpretare i dati raccolti.

Verranno descritti diversi tipi di transizioni di fase che portano a discontinuità nella densità e nei parametri elastici all'aumentare della pressione. Verranno mostrati alcuni software per il trattamento dei dati in alta pressione e verranno risolti esercizi insieme ai partecipanti.

A concludere, una serie di esempi dal mondo delle Scienze della Terra e delle scienze dei materiali mostreranno le tante implicazioni e applicazioni, dalla nano alla mega scala, che possono essere estratte dalla conoscenza della proprietà elastiche dei cristalli in generale, e dei minerali in particolare.

EPR SPECTROSCOPY AND MAGNETOMETRY OF MINERALS: INSIGHTS TO CRYSTAL CHEMISTRY

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L'obiettivo della lezione è quello di esplorare le relazioni che intercorrono tra proprietà magnetiche di uno ione di un metallo di transizione e la struttura ospite. Da un lato le proprietà paramagnetiche di uno ione in un determinato sito rispondono a specifiche istanze indotte dal campo cristallino, e, *vice versa*, lo studio delle proprietà magnetiche contribuisce ad identificare la localizzazione di un elemento all'interno di uno dei siti disponibili. La lezione includerà cenni sulla distribuzione *short-range* di ioni magnetici in siti prossimali.

I contenuti specifici includono:

- introduzione alla spettroscopia EPR: interazioni principali (zeeman, iperfine, fine, spin-orbita); spin pari e dispari; ioni concentrati; EMR; gerarchia delle interazioni ed EPR in multifrequenza;
- principi di magnetometria: suscettività magnetica di ioni di TE o REE; relazioni di Curie e Curie-Weiss; trattamento microscopico, equazioni di Van Vleck e di Bleaney-Bowers;
- richiami di teoria del campo cristallino: la soluzione one-electron; la soluzione multielectron e i termini; diagrammi energetici per ioni di TE.

Verranno infine discussi esempi applicativi allo studio di minerali.

RAMAN SPECTROSCOPY IN EARTH SCIENCES

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La spettroscopia Raman è una spettroscopia vibrazionale che misura la variazione tra la lunghezza d'onda di una luce monocromatica incidente e quella diffusa in modo anelastico dal campione analizzato. Permette, quindi, di ottenere informazioni soprattutto sulla struttura del campione e, in misura minore, sulla sua composizione chimica. È una tecnica analitica non distruttiva, che permette di analizzare sostanze allo stato solido, liquido o gassoso, che non richiede una particolare preparazione del campione e che consente di ottenere analisi in tempi rapidi. Nella configurazione "micro", cioè con strumento annesso ad un microscopio ottico, è possibile ottenere analisi *in situ* su volumi di circa 5 μm^3 e di analizzare campioni presenti all'interno di mezzi trasparenti.

Le principali applicazioni nelle Scienze della Terra sono: identificazione di minerali e di fasi amorfe; caratterizzazione della loro struttura e, talora, della loro composizione chimica; identificazione e determinazione di specie poliatomiche e della composizione e della densità di fasi gassose in inclusioni fluide e vetrose.

ELECTROCHEMICAL PROPERTIES OF MINERALS

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Le batterie al litio sono, ad oggi, i dispositivi di accumulo di energia più studiati per applicazioni di piccola e media scala come smartphone, computer, telecamere, bici elettriche e ciclomotori. Alla base dei continui tentativi di migliorare le loro densità di energia e di potenza c'è il bisogno di ottenere dispositivi efficienti, affidabili, leggeri, e competitivi di stoccaggio di energia per espandere i settori di trasporto pubblico/privato e per l'accumulo di energia derivante da fonti di energia rinnovabile. In questo contributo discuteremo degli studi strutturali di analoghi sintetici di minerali utilizzabili nei catodi e negli anodi di batterie al litio ricaricabili. In particolare, discuteremo l'importanza della spettroscopia di assorbimento dei raggi-X (XAS) per studiare la localizzazione strutturale e lo stato di ossidazione di droganti (solitamente metalli di transizione) in tre materiali ($LiFePO_4$, ZnO e SnO_2), concentrando l'attenzione sia sulla struttura dei materiali di partenza, sia sull'evoluzione dello stato di ossidazione degli elementi di transizione durante i cicli di carica/scarica.

MICRO AND MESOPOROSITY OF INORGANIC MATERIALS: ION EXCHANGE PROPERTIES

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Nel corso di questa lezione verranno descritte le caratteristiche peculiari di alcune tipologie di materiali porosi, con particolare attenzione verso quelli classificati dall'International Union of Pure and Applied Chemistry (IUPAC) come microporosi e mesoporosi. La prima parte della lezione verterà sulla descrizione delle caratteristiche peculiari di questi, quali: (a) la presenza di canali e/o gabbie (pori) con dimensioni variabili, ma che comunque risultano comprese nell'intervallo 3÷20 Å; (b) la carica negativa della struttura dovuta a difetti di carica nelle impalcature, normalmente compensata da controcationi localizzati nelle aperture e dotati di elevata mobilità; (c) la presenza nei pori di acqua. Da queste deriva l'estrema efficacia dei materiali porosi come scambiatori ionici e il loro impiego, anche massivo, in processi di recupero ambientale e nell'industria. Esempi di applicazioni della capacità di scambio ionico saranno quindi oggetto della seconda parte della lezione, finalizzata in particolare alla comprensione delle relazioni tra porosità, scambio cationico e applicazioni nell'industria e dell'ambiente.

ELECTRON CRYSTALLOGRAPHY: IMAGING AND DIFFRACTION

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Lo studio cristallografico delle strutture atomiche dei minerali richiede radiazioni con lunghezze d'onda minori rispetto a quelle tipiche della luce visibile. I raggi X sono da sempre la radiazione più utilizzata, e grazie ad essi sono state determinate le strutture di milioni di fasi sia naturali che sintetiche, sia inorganiche che organiche o biotiche (DNA, proteine, etc.). Nonostante il suo indiscusso successo, la diffrazione da raggi X può essere applicata solamente su cristalli singoli di alcuni micrometri. Per cristalli più piccoli l'unica alternativa è quella di far diffrangere polveri policristalline, schiacciando così l'informazione su un'unica dimensione. Nel caso di materiali a grana sub-micrometrica, una valida alternativa è costituita dall'utilizzo di una radiazione di elettroni accelerati tramite un microscopio a trasmissione elettronica (TEM), i quali hanno un'interazione più forte con la materia e consentono pertanto l'analisi di volumi molto ridotti. Gli elettroni hanno anche il vantaggio di poter essere facilmente focalizzati per formare immagini ad altissima risoluzione che permettono una visualizzazione diretta del campione a scala atomica o sub-atomica. Nel campo della diffrazione elettronica, si è poi affermata negli ultimi anni una nuova tecnica denominata Electron Diffraction Tomography, che ha permesso lo studio di materiali finora non descrivibili tramite raggi X, con la localizzazione anche di atomi leggeri quali gli idrogeni. In questa lezione verranno descritte brevemente le tecniche più comuni di immagine e diffrazione elettroniche e verranno forniti esempi specifici relativi alla loro applicazione alle Scienze della Terra.

SINGLE CRYSTAL X-RAY DIFFRACTION: A POWERFUL ANALYTICAL TOOL

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Nella lezione saranno affrontati i seguenti argomenti:

- teoria della diffrazione dei raggi X da parte dei reticoli cristallini, in cui verrà introdotto il concetto di reticolo reciproco;
- aspetti geometrici ed aspetti energetici della diffrazione dei raggi X, mediante la descrizione delle equazioni di Laue e dell'equazione di Bragg, in cui verrà introdotto il concetto di fattore di struttura.

Seguiranno alcuni esempi volti a descrivere il tipo di informazioni che si possono ottenere mediante l'analisi di minerali in diffrazione di raggi X:

- calcolo dell'intensità della diffrazione da una struttura reale;
- come si legge un raffinamento strutturale (coordinate atomiche, distanze di legame, poliedri di coordinazione);
- verifica del corretto posizionamento degli atomi di idrogeno (bond valence balance);
- confronto tra formula chimica e formula strutturale (es: nuovo minerale ferri-kaersutite);
- informazione cristallografica e informazione cristallochimica a confronto (es.: apatiti di arsenico);
- varianti di una stessa topologia: effetti sulle intensità della diffrazione (es.: gruppo della nefelina).

PHYSICAL PROPERTIES OF MINERALS: PAST, PRESENT AND FUTURE

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La lezione, di carattere generale, introduce alla tematica della Scuola.

Verrà focalizzata l'attenzione sull'anisotropia delle proprietà fisiche dei materiali cristallini e sulle relazioni con la simmetria delle strutture. Il tema dell'anisotropia delle proprietà fisiche verrà affrontato con un approccio quantitativo e così da fornire il necessario "background" per l'apprendimento proficuo di quanto verrà discusso nelle lezioni successive.

In generale nei solidi cristallini le proprietà fisiche variano a seconda della direzione in cui vengono misurate e per descrivere adeguatamente tali variazioni sono necessari i tensori. I tensori sono semplici espressioni matematiche usate per descrivere le proprietà fisiche, generalizzazione di scalari e vettori. Lo scopo è di acquisire familiarità con l'espressione tensoriale, come possano essere costruiti e come possano essere utilizzati per dare risposte numeriche ai problemi.

L'analisi delle fonti bibliografiche permetterà di sottolineare il ruolo che le proprietà fisiche dei materiali cristallini ha avuto, ha e avrà nello studio dei problemi interessanti le Scienze della Terra e dei materiali.

INDUSTRIAL MINERALS IN THE SPOTLIGHT: OPTIMIZING THEIR ENVIRONMENTAL PERFORMANCE FOR SUSTAINABLE DEVELOPMENT

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Cemento, argille e altri minerali industriali rappresentano manufatti essenziali nella società moderna. La necessità di tagliare l'impatto ambientale associato ai processi industriali per la produzione di questi materiali non dovrebbe penalizzare l'impulso alla crescita e allo sviluppo infrastrutturale, soprattutto nei confronti delle economie in via di sviluppo. Questa lezione fornisce una panoramica sulle proprietà di bulk e di superficie di questa classe di minerali e di come queste controllano le proprietà macroscopiche come resistenza meccanica, reologia e durabilità. Alcune tecniche analitiche utilizzate per determinare tali proprietà vengono qui illustrate, assieme a possibili soluzioni per mettere a punto la performance di questi materiali, al fine di convergere verso un design di materiali da costruzione eco-compatibili.

Sessione poster