ACCADEMIA NAZIONALE DEI LINCEI

Conference

MINERALS AS TREASURE TROVE FOR SCIENTIFIC DISCOVERIES

15-16 FEBRUARY 2024

A B S T R A C T

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PROGRAMME

Minerals have been of great interest not only to nature scientists but to chemists and physicists too. The presence of impurities in natural samples and the ubiquitous variations in chemical composition may hamper the study of their physical properties but are an added value for geologists and material scientists. Huge database of chemical and structural data on minerals are now available, that may allow innovative research such as experience-based modeling and optimization of mineral properties and the recognition of mineral evolution in the solar system. This approach "from minerals to materials" avoids the trial-and-error method, often used in an exploratory synthesis, and may also be advantageous over computational predictions of thermodynamic stability that can be biased by inaccuracies of the computational methods.

Thursday, 15th February

14.30 Welcome addresses

15.00 Robert HAZEN (Carnegie Institution of Washington): *Data-driven discoveries in mineralogy*

15.30 Sergey KRIVOVICHEV (Saint Petersburg State University): *Minerals as a source of new ideas and inspiration for materials chemistry*

16.00 Roberta SESSOLI (Università di Firenze): *Superconductivity in minerals*

16.30 Coffee break

17.00 Davide DELMONTE (Istituto dei Materiali per l'Elettronica ed il Magnetismo (IMEM) - CNR Parma): *Ferroelectricity: the undisclosed secret in a fistful of crystals*

17.30 Giancarlo DELLA VENTURA (Università di Roma Tre): *Electrical conductivity in hydrous iron-bearing silicates*

18.00 Luca BINDI (Università di Firenze): *Minerals as first aperiodic compounds*

18.30 Ulrich SCHNEIDER (University of Cambridge): *Quantum simulation of aperiodic crystals*

19.00 Discussion

Friday, 16th February

9.00 John JASZCZAK (Michigan Technological University): *Natural van der Waals heterostructures*

9.30 Duccio FANELLI (Università di Firenze): *AI applied to the IMA list of minerals*

10.00 Cristian BIAGIONI (Università di Pisa): *Rare minerals as key to understand Earth's complexity*

10.30 Frank C. HAWTHORNE (University of Manitoba, Canada): *Decavanadates as minerals and as industrial materials*

11.00 Coffee break

11.30 Diego GATTA (Università di Milano): *Mineral wastes and minerals as critical raw materials*

12.00 Maura MANCINELLI (Università di Ferrara): *Zeolites and mineral engineering*

12.30 Alessandro GUALTIERI (Università di Modena e Reggio Emilia): *Minerals that changed everyday life*

13.00 Discussion, final remarks and outlooks

ROMA - PALAZZO CORSINI - VIA DELLA LUNGARA, 10
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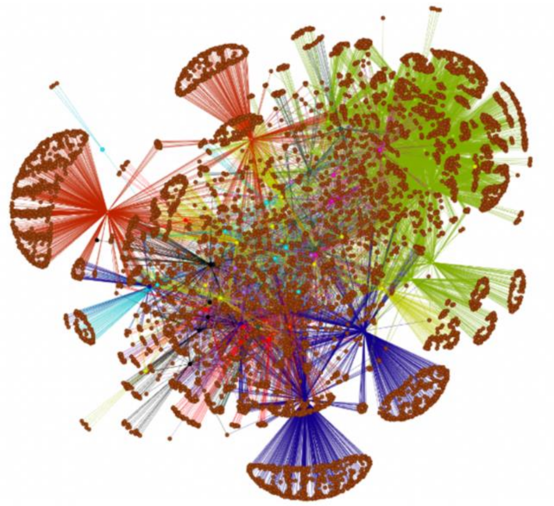
Fino alle ore 10 è possibile l'accesso anche da Lungotevere della Farnesina, 10
I lavori potranno essere seguiti dal pubblico anche in streaming
Online registration is required to attend the conference.
Until 10 a.m. access is also possible from Lungotevere della Farnesina 10.
The conference can also be followed by streaming.

L'attestato di partecipazione al convegno viene rilasciato esclusivamente a seguito di partecipazione in presenza fisica e deve essere richiesto al personale preposto in anticamera nello stesso giorno di svolgimento del convegno
The certificate of participation in the conference will be issued only following on attendance in presence and must be requested to the staff in charge on the same day of the conference.

Data-driven discoveries in mineralogy

Robert HAZEN (Carnegie Institution of Washington)

The story of Earth is a 4.5-billion-year saga of dramatic transformations, driven by physical, chemical, and biological processes. The co-evolution of life and rocks unfolded in an irreversible sequence of evolutionary stages. Each stage re-sculpted our planet's surface, while introducing new planetary processes and phenomena. This grand and intertwined tale of Earth's living and non-living spheres is coming into ever-sharper focus, thanks to advances in "mineral informatics"—a field that employs large and growing mineral data resources to tell the deep-time stories of our evolving planet. Minerals are remarkably information rich, holding dozens of trace and minor elements, scores of stable isotopes, solid and fluid inclusions, chemical zoning, twinning, exsolution, countless defects, and a host of optical, magnetic, electrical, and other properties. Every mineral specimen is a time capsule waiting to be opened—waiting to tell its story. This lecture will explore some of the advanced data analytical and visualization methods that are shining new light on the old field of mineralogy.



A network graph of more than 5700 mineral species connected to 57 modes of formation embeds the evolution of Earth's mineral diversity through more than 4.5 billion years. Colors link groups of minerals formed in similar ways. Of special note, green indicates minerals formed exclusively through biological processes.

Superconductivity in minerals

Roberta SESSOLI (Università di Firenze)

Superconductivity is a key property of a small selection of materials of large technological impact. Beyond their massive use to produce high-performance magnets, they are a key resource in quantum technologies as detectors and quantum logic units. They are also employed in nanoscience and coupled to other materials to form hybrid interfaces.
Nature is an unrivaled source of inspiration in many fields of research, including that on superconductors. In 2006, in an effort to the chemical-physical characterization of a selection of samples from the Museo di Storia Naturale (Università di Firenze) we magnetically investigated two samples of covellite (CuS) belonging to two important sulphide ores (e.g. Craig & Vaughan, 1994), Butte (Montana, USA) and Calabona (Sardinia, Italy) [1]. We found evidence that both mineral specimens exhibited a transition to superconductivity at the same temperature of the synthetic CuS compound investigated by H. K. Onnes in 1911 as one of the first superconductors [2].

Others extended the search for naturally occurring superconductivity among minerals to the Smithsonian Institution's National Museum of Natural History [3].
With the advent of artificial intelligence such demanding extensive surveys have recently been replaced by targeted investigations. Indeed, the mineralogical database provided by the International Mineralogical Association has been recently used as an unbiased training dataset in a Machine Learning approach in a joint effort with the Departments of Physics and Geological Sciences at the University of Florence. The study has allowed the identification of superconductivity in the synthetic analogs of michenerite, PdBiTe, and monchetundraite, Pd_2NiTe_2 [4].

[1] Di Benedetto, F.; Borgheresi, M.; Caneschi, A.; Chastanet, G.; Cipriani, C.; Gatteschi, D.; Pratesi, G.; Romanelli, M.; Sessoli, R. *Eur. J. Mineral.* **2006**, *18*, 283.
[2] Onnes, H. K. *Comm. Phys. Lab. Univ. Leiden, Nos*. **1911**, 119, 120, 122.
[3] Feder, T. *Physics Today* **2014**, *67*, 20.
[4] Pereti, C.; Bernot, K.; Guizouarn, T.; Laufek, F.; Vymazalova, A.; Bindi, L.; Sessoli, R.; Fanelli, D. *NPJ Comput. Mater.* **2023**, *9,* doi:10.1038/s41524-023-01023-6.

Ferroelectricity: the undisclosed secret in a fistful of crystals

Davide DELMONTE (Istituto dei Materiali per l'Elettronica ed il Magnetismo (IMEM) - CNR Parma)

This presentation aims to shed some light into a rare and fascinating property of the matter, Ferroelectricity. Among the wide class of dielectric materials (either natural or artificial), ferroelectrics constitute just a minimal subset due to severe crystallographic and electrical/electronic constraints which are needed to fulfil the necessary and sufficient conditions for the existence of such a phenomenology. Besides making a list of the main ore ferroelectric minerals, together with a series of artificial compounds (mainly, but not only, perovskites), and the principal technological applications in the field of electronics and energy, a deep analysis on the mechanisms at the basis of ferroelectricity is provided. Particularly, huge attention is paid for assessing the biggest issue which limits the observation and/or the physical understanding of ferroelectricity and thus its application i.e. the characterization of the hysteresis loop, especially when polycrystalline bulk systems are considered. Indeed, leakage character affecting real materials and intrinsic morphological/structural limitations have often led to fake interpretation of ferroelectricity in literature. For these reasons, basic experimental rules are here described as essential tools to face this challenge and to properly unveil such a precious and undisclosed secret.

Electrical conductivity in hydrous iron-bearing silicates

Giancarlo DELLA VENTURA (Università di Roma Tre)

Quasi one-dimensional (*1D*) and two dimensional (*2D*) minerals such as pyroxene, amphiboles and micas are relatively abundant in Nature and constitute ~25% of the Earth crust. Amphiboles and micas, in particular, also contain hydroxyl groups and are well known to contribute to the recycling of water during subduction and to the generation of arc magmatism (Schmidt and Poli, 1998). In this presentation I will summarize the experimental results obtained during the last decade *via* the fruitful collaboration of scientists from Italy, Germany and Canada; I will focus on the high-T behavior of riebeckite, a sodic amphibole with ideal stoichiometry $Na_2(Fe^{2+}_3Fe^{3+}_2)Si_8O_{22}(OH_2)$ considered as a proxy for Fe-rich hydrous silicates. At high-temperature, ferrous iron in riebeckite oxidizes to ferric iron via the $Fe^{2+} + OH^- = Fe^{3+} + O^{2-}$ reaction and without any structural breakdown. Fe oxidation couples with the delocalization of an electron and dissociation of the bonded OH^- anion to O^{2-} and H^+; in the presence of external oxygen, the latter may migrate out of the structure, combine with surface O^{2-} and be released as H_2O in the system. Under these conditions, the amphibole transforms into an oxo-phase thus remaining stable to very high-T; under reducing conditions, no Fe oxidation occurs, and the amphibole stability is reduced by 100 °C. Although relatively simple, the oxidation reaction has been shown by Della Ventura et al. (2018, 2023a) to be a complex and dynamical process, being reversible in a T range that depends on the amphibole composition (Mihailova et al., 2021, 2022; Bernardini et al., 2022, 2023). The important point here is that due to the above processes, Fe-amphiboles may develop both electron and ionic conductivity.

Convergent plate margins are the most important geologically active areas in the planet; in modern literature, these areas are termed "*Subduction Factories*" where materials from the seafloor, underlying subducting lithosphere and sediments eroded from the continents are recycled, giving rise to beneficial products, such as ore deposits and geothermal energy (e.g., Tatsumi and Kogiso, 2003; Arribas and Mizuta, 2018). These are also major sites of explosive volcanism, often associated with violent earthquakes. The geological process active in these areas depend on several factors, primarily the nature of the down-going slab and its thermal structure (a function of convergent rates, age of the sediments, rates of shear heating etc.) that ultimately control the metamorphic reactions and the dehydration processes at depth. Geophysical measurements show the occurrence of anomalous high-conductivity layers (HCL) in subduction zones at different depths, and these are typically associated with low-velocity layers where most of seismicity is generated (Peacock, 1996; Peacock and Wang, 1996; Kasaya et al., 2005; Syracuse et al., 2010). The explanation of HCL has been attributed to several different causes, including partial melting of crustal rocks, the presence of high-conductive fluids or minerals (graphite, metal oxides/sulfides) or thermal processes on Fe-bearing phases. Our research shows that one main explanation of these anomalies can be related to thermal enhancement of the electrical conduction *via* small-polaron hopping in Fe-bearing hydrous silicates augmented by H^+ diffusion occurring in oxidizing conditions. The thermal ranges of activation of the whole process can be elegantly followed via polarized Raman scattering, a technique widely accessible in Earth Science Laboratories that is both sensitive to phonon and electron states. This result represents an important aspect of our work, emphasizing to the Scientific Community the importance of Raman scattering in characterizing complex processes in a (relatively) straightforward way, opening the road to systematic experiments focused on the physical properties of common rock-forming minerals of geophysical interest.

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Minerals as first aperiodic compounds

Luca BINDI (Università di Firenze)

The 3D-periodic nature of crystalline structures has always been so strongly deep-rooted among the scientists that the abundant signals coming from Nature that seemed to pose doubts on this model were greeted with skepticism. The long-debated questions which arose from the analysis of the mineral calaverite ($AuTe_2$), which showed the presence of the so-called *satellite* reflections (surrounding the *main* reflections) in the diffraction patterns, posed the basis for the discovery of aperiodic crystals. *Aperiodic crystals* is a generic term including incommensurately modulated, composite and quasicrystal structures. Incommensurately modulated structures have an average three-dimensional periodic structure, but the atoms are periodically shifted from their average positions according to a modulation function with a period that is incommensurate with the periodicity of the basic structure. Composite modulated structures are aperiodic by construction and are described as intergrowths of two or more idealized periodic substructures. The unit-cell dimensions of these substructures have a mutually incommensurate ratio in at least one direction and, moreover, interactions between them lead to incommensurate modulations in these substructures. Quasicrystals are aperiodic by construction, present diffraction patterns with rotational symmetries that are incompatible with any translational invariance.
The Author will accompany the audience in a crystallographic excursion among the minerals that exhibits such aperiodicity. It will be also shown that most of the discoveries in aperiodic crystallography were done starting from material coming from the mineral kingdom, including the main steps in the elaboration of the superspace theory. The author will also discuss how aperiodic crystals are an example of how sometimes being too uncritical of conventional wisdom may hinder research and progress in understanding the marvels of this world and beyond.

Natural van der Waals het

John JASZCZAK (Michigan Technological University)

Following the experimental realization of graphene in 2004 there has been an explosion of interest in layered and low-dimensional van der Waals materials of a multitude of compositions and structures, including but going beyond just graphene. Engineered heterostructures of van der Waals materials enable structural, electronic, magnetic, and chemical properties to be tailored for applications ranging from memory devices to optoelectronic- and bio- sensors. A variety of natural van der Waals materials, including complex heterostructures exist and provide insights, inspiration, and physical building blocks for the fabrication of new engineered heterostructures. This talk will provide an overview of some natural van der Waals materials, ranging from graphite and molybdenite to franckeite and merelaniite, and discuss some of their properties in the context of engineering desired properties in this class of materials.

AI applied to the IMA list of minerals

Duccio FANELLI (Università di Firenze)

Finding new superconductors constitutes a complex task, which relies on individual experience and intuition. To overcome these limitations, an approach to supervised classification (tag a given material as superconducting) and regression (quantify the associated critical temperature) of superconductive materials is proposed which builds on the DeepSet technology, a peculiar neural network implementation. The employed network receives as input information on the atomistic description of the examined material. Feature engineering is carried out self-consistently, with no a priori imposed bias. The extracted features are combined linearly and provide a handy and immediate proxy of the chemical propensity to superconductivity (as well as of the impact of each element on the ensuing critical temperature). The trained algorithm was applied to search for possible superconducting minerals, scanning the IMA catalogue. A list of minerals identified as putative superconductors was extracted by the trained network. Given the rarity of the selected minerals and their occurrence only as micron-sized grains, we carried out a systematic experimental characterisation of the magnetic properties of their synthetic analogues. Remarkably enough, we concluded that the synthetic equivalent of michenerite and monchetundraite were found to exhibit superconducting transitions with critical temperatures in good agreement with those predicted by the algorithmic approach.

Rare minerals as key to understand Earth's complexity

Cristian BIAGIONI (Università di Pisa)

Currently, more than 6000 mineral species are known. Among them, a dozen of mineral species may seem to be sufficient to achieve a first picture of the Earth's dynamics. However, this picture is still incomplete, as rare mineral species give important insights about the complexity of our planetary home, in some cases revealing huge gaps in our understanding of geological processes. This awareness promoted a renewed interest in the study of rare minerals, as clearly evidenced by several studies published in the last decade and by the increasing number of new mineral species described since 2010. Rarity in mineralogy is due to several reasons, related to physical-chemical constraints as well as to sampling bias. Some case-studies, based on the own experience of the author, are discussed, also stressing the implications of these investigations. In particular, the outstanding role of mineralogical crystallography in deciphering the complex crystal chemistry of rare minerals, allowing the extraction of geological information from these unusual compounds, is stressed. Even if the study of rare minerals could seem to be interesting for geoscientists only, in some cases the accurate examination of mineral assemblages, with the characterization of the rare accessory minerals, could highlight unexpected geochemical anomalies. Rare minerals can thus be considered as details in the picture of the

Earth's dynamics, making it more perfect. And, as Leonardo Da Vinci (1452–1519) stated, "*details make perfection, and perfection is not a detail*".

Key-words: rare minerals, mineralogical crystallography, crystal chemistry.

Mineral wastes and minerals as critical raw materials

Diego GATTA (Università di Milano)

Modern and sustainable use of mineral resources is expected to follow the basic principles of the so-called "circular economy", which transforms the dominant model of "linear economy", persisting since the onset of the Industrial Revolution, into a circular one. To date, there are more than 100 diverse definitions of "circular economy" in the literature. However, some key words and objectives can be elucidated: *One of the most important objectives of the circular economy is to reduce the environmental impact of resource consumption, through a radical reshaping of all processes across the life cycle of products, and with a minimization of waste generation. A circular economy can provide opportunities to generate well-being, growth and jobs.* Different countries are currently adopting diverse protocols to promote the application of circular economy concepts for a sustainable growth. In the European Union, for example, a recent important step is the «Critical Raw Materials Act» (CRMA), published by the European Commission on March 2023, in order to ensure secure and sustainable supply chains for the EU's green future. The CRMA 2023 contains a careful analysis of raw materials supply chains in EU, along with a list of "Critical Raw Materials" (CRMs, 34 entries) recognized by the European Commission. With respect to the previous list of CRMs published on 2020, the new entries are: feldspars (as industrial minerals), arsenic, copper, manganese and vanadium.
Borates are recognized among the CRMs, with a criticality that reflects their supply chain: one unique non-EU country, Turkey, provides *ca.* 98% of this mineral commodity in the EU. Currently, the average cost of borates in EU is *ca.* 340 Euro/t, and the average consumption is *ca.* 51 kt/y. In EU, borates are mainly used and transformed in glass technology (55%), frits and ceramics (17%), fertilizers (15%), chemical manufacture (4%), metallurgy (4%) and construction materials (4%). Focusing on the construction materials field, borates are mainly used to produce lightweight components (due to the low density of borates) and neutron absorbers (due to the high neutron absorption capacity of ^{10}B). In this presentation, I will show preliminary results on the production and characterization of a hybrid-composite material made by a mixture of Sorel cement and a B-bearing mineral waste (rich in the hydrous borate colemanite, $CaB_3O_4(OH)_3 \cdot H_2O$). Such a composite material proved to act as an efficient radiation-shielding material for thermal, epithermal and fast neutrons. With respect to the most common ordinary Portland cements, Sorel cements (also called "magnesium oxychloride cements") require a drastically lower production energy; therefore, they are more sustainable. In addition, the use of B-rich mineral waste, instead of virgin material, is aligned with the concepts of the "circular economy". We prove that the final product, in the form of tiles of panels, can also be easily fabricated.

Zeolites and mineral engineering

Maura MANCINELLI (Università di Ferrara)

Fundamental connections exist among material composition, minerals, and crystallography, intricately contributing to shaping contemporary industry and addressing environmental challenges. Mineralogy encompasses a broad spectrum, including mineral definition, origin, structure, impurities, internal structure, properties, and their diverse impacts on the environment and applications in modern industry. Crystallography, a cornerstone in mineralogical studies, is essential for comprehending the structure of

crystals. It outlines principles governing various crystal structures, their determination methods, and applications in scientific fields like metallurgy, materials science, ceramics, physics, and chemistry.
The essential connections between mineralogy, crystallography, and industry offer insights into sustainable solutions for water management and environmental challenges. The potential of environmentally friendly materials, such as zeolites, in removing pollutants from water bodies and serving as gas sensors is highlighted owing to their hydrophilic/hydrophobic characteristics, water stability, and resistance to chemical solutions and thermal heating. The focus is on molecular sieves, which, with unlimited structural and chemical variations, find applications in catalysis, adsorption, sensing, and various industrial processes.

Minerals that changed everyday life

Alessandro GUALTIERI (Università di Modena e Reggio Emilia)

The presentation reports examples of discoveries in the field of mineralogy that have significantly impacted human life, blooming numerous areas of science and technology. In the past, discoveries were usually accomplished in a random or empirical way or based on practical experience, with the major driving force given by the (increasing) needs of Mankind ("*Necessity is the mother of invention*", as Plato said). Since the industrial revolution, discoveries have been the outcome of a systematic approach based on the advance of scientific knowledge.
Examples of mineralogy-related discoveries for industrial applications, health and environment are discussed, with a window open for the future opportunities in a sustainable changing world. The presentation is focussed on asbestos, a mineral that had certainly changed many people's everyday life. In fact, exposure to this natural carcinogen has caused at least 2 million deaths worldwide in the last 24 years. The presentation will show that Mineralogy is a powerful tool for the understanding of the very nature and properties of natural materials and that the development of new analytical methods is an incredible boost to go beyond the existing limits and paradigms of knowledge. As far as asbestos is concerned, the strong acquired scientific background permits scientists now to devise geo-inspired (or mineralogy-inspired) safe substitutes of asbestos.