Commission on Inorganic and Mineral Structures

MINERALOGICAL CRYSTALLOGRAPHY AND ACTIVITIES OF THE INTERNATIONAL UNION OF CRYSTALLOGRAPHY COMMISSION ON INORGANIC AND MINERAL STRUCTURES

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Abstract

Understanding the crystal structures adopted by minerals and inorganic compounds necessitates bridging knowledge from the disciplines of mineralogy and crystallography with that developed in inorganic chemistry and materials science. The International Union of Crystallography (IUCr) Commission on Inorganic and Mineral Structures (CIMS) promotes scientific advancement at the interface of these four independent disciplines, a field of study often designated as 'mineralogical crystallography'. Here, based on a survey of relatively recent monographs and review articles, we present a brief non-exhaustive overview of this field, also highlighting a few new concepts and advancements which occurred recently.

Introduction

Mineralogical crystallography primarily encompasses the disciplines of mineralogy and crystallography, which are nowadays independent subject matters, although both were originally part of a single discipline and indistinguishable from one another [1].

There are currently ~5,500 mineral species known today, and ~100 new minerals are discovered yearly. An up-to-date list of discovered existing minerals and the approval of new species is directed by the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA) [2].

For inorganic compounds, the Inorganic Crystal Structure Database comprises 203,820 crystal structures as of December 2018 [3]. The structure types of many minerals are analogous to those of similar artificial inorganic compounds synthesizable in laboratory conditions. However, as recently pointed out [1], what is interesting is that very few of the newly discovered minerals have synthetic analogs, which implies that Nature has ways of making materials that are more inventive than those achieved in chemical laboratories.

Indeed, the specificity of mineral genesis is what differentiates the minerals and makes them unique. Clearly, the space and time scales of natural geological processes under which minerals are formed, are in no way comparable to those which can be achieved under artificial laboratory synthesis of materials.

In this spirit, as approved by action of the IUCr General Assembly (8 August 2002), according to its Terms of Reference, the IUCr-CIMS was then founded to promote and achieve the following aims:

To strengthen links and interactions among mineral, inorganic and materials scientists and between these scientists and the crystallographic community.

To promote the presence at the IUCr meetings of scientists working in 'inorganic-crystallographic' and 'geoscience-crystallographic' institutions.

To present at the same meetings common aspects of the inorganic structures independently from their natural or synthetic origin.

To favour the historical influence that mineral structures have played on developing inorganic materials of technological interest.

To promote and encourage the publication of inorganic and mineralogical papers in the Journals of the Union.

To promote the development and dissemination of methods, computing programs and databases of interest for the inorganic crystallographic community.

To promote and organise symposia of interest to the inorganic community on the occasion of the IUCr meetings, also in cooperation with other Commissions.

To promote and organise workshops and schools of interest to the inorganic community, also in cooperation with other Commissions.

In this short article, based on a survey of relatively recent monographs and review articles, a non-exhaustive overview of the field of mineralogical crystallography is presented, also highlighting a few new concepts and advancements which occurred recently.

Background on mineralogical crystallography

A few monographs on mineralogical crystallography have appeared in recent years [4, 5]. Ref. 4, titled "Mineralogical Crystallography", consists of Volume 19 of the EMU Notes in Mineralogy published together by the European Union of Mineralogy [6] and the Mineralogical Society of Great Britain and Ireland [7]. This is the latest volume in this series of short courses ("Schools") and accompanying review volumes [8], similar to the Reviews in Mineralogy and Geochemistry published by the Mineralogical Society of America [9]. In Ref. 4, the first chapter [10] provides a concise overview on structure description, interpretation and classification in structural mineralogy. The remaining chapters are then dedicated to recent advancements in the application of state-of-the-art methods and techniques for the structural analysis of mineral and inorganic compounds using powder X-ray diffraction [11], electron crystallography [12], and environmental mineralogical applications of total scattering and pair distribution function analysis [13]. In the final chapter, examples of natural substances with modulated, composite and quasicrystal structures are discussed with the concept of superspace described and then considered for elucidating the structural aspects of materials with such complicated structures [14].

In "Highlights in Mineralogical Crystallography" [5] a collection of review articles is presented with the focus on structural properties of minerals and synthetic analogues. Divided into seven chapters, this book includes: An introduction to the RUFF database [15] for structural, spectroscopic, and chemical mineral identification [16]; A systematic evaluation of the structural complexity of minerals [17]; *Ab initi*o computational modelling of mineral surfaces [18]; Implications of natural quasicrystals of meteoritic origin [19]; The potential role of terrestrial ringwoodite on the water content of the Earth's mantle [20]; Structural characterization of nanocrystalline bio-related minerals by electron-diffraction tomography [21]; The uniqueness of mayenite-type compounds as minerals and high-tech ceramics [22].

Taken together, despite not being completely exhaustive, the range of topics covered in Refs. 4 and 5 points to the vastness of the field of mineralogical crystallography. From the breadth of the scientific disciplines involved in the examples discussed in these two monographs, it is clear that mineralogical crystallography is an interdisciplinary subject matter at the interface of mineralogy, crystallography, inorganic chemistry and materials science – with boundaries expanding into the realm of crystal engineering, coordination chemistry and supramolecular chemistry, as will be pointed out below.

We would also like to attract the readers' attention to two other textbooks [23, 24] devoted to the crystallography of modular materials, where structural aspects of both mineral and inorganic structures are discussed in a common lens under the theme of advanced theoretical foundations for understanding the modular aspects of crystalline structures in general. The first one [ref. 23] is in fact the inaugural Volume 1 of the EMU Notes in Mineralogy which launched this series back in 1997. The second textbook [ref. 24] appeared only a few years later in 2004. These two monographs provide a convenient starting comprehensive treatment of theories and applications in the rapidly expanding field of the crystallography of modular materials, as applied to elucidate details of mineral and inorganic structures. Whereas molecules are the natural modules from which molecular crystalline structures are constructed, modular structures are those built from the assemblage of modules (blocks, rods, layers) which differ either in atomic composition or in their crystallographic position/orientation with respect to one another. Examples of modular structures include *e.g.* stacking polytypes, order-disorder structures, polysomatic and homologous series, cell-twins, *etc.* Unravelling the structure-building principles of modular structures found as both naturally-occurring and synthetic materials represents a current challenge in crystallography for both the experimental crystallographers and the theoreticians. Achieving a thorough understanding of the link between modular structures and their growth or genesis conditions may open a horizon for deeper petrological understanding of natural geological materials as well as the crystal engineering of man-made materials with fine-tuned properties.

Lastly, we note that a special issue on mineralogical crystallography recently appeared in the December 2018 printing of *Acta Crystallographica B*. In its introductory article [1], an elegant overview of the key concepts, results and highlights contained in the articles featured therein is presented. We will not repeat here nor provide a summary of the content of this special issue, but would like to emphasize that most of the topics exposed should be the object of specific keynote lectures, invited talks, and scientific micro-symposia at the upcoming 25th Congress of the IUCr in Prague, Czech Republic, 22–30 August 2020 [25].

Recent emerging concepts in mineralogical crystallography

We end this short article by highlighting briefly recent advancements which have resulted in important emerging concepts in mineralogical crystallography.

Data-driven approaches

The mining of large datasets and databases is now routinely applied in science, and data-driven approaches have become an essential component of various fields of research (*e.g.*, recommendation engines in materials sciences, data-driven optimization in engineering). The promotion and integration of data-driven discovery in crystallography, with primary focus on minerals, inorganic materials, and extended inorganic solids, is a topical area of research currently undergoing rapid expansion. It is expected that with the employment of large data resources, computationally-driven methods (*e.g.* multivariate analysis, pattern recognition), machine-learning guidance, and advanced analytical methods will be exploited leading to discovery of novel large-scale patterns in the solid state.

In the field of mineralogical crystallography, recent advances in this regard have given rise to new research avenues such as 'mineral evolution' [26], 'mineral ecology' [27] and 'mineral network analysis' [28]. Mineral evolution postulates that the mineralogy of terrestrial planets and moons evolves as a consequence of varied physical, chemical, and biological processes that lead to the formation of new mineral species. The novelty of this concept is that it raises questions such as what was the first the solid-state mineral species to exist in the Universe, and that the number and types of mineral species evolve through space and time in ways similar to what we are accustomed to think of for biological systems. From this postulate, as it involves the interplay of physical, chemical and biological processes (mostly) at the surfaces of planets and moons, it follows that certain factors of chance and necessity will contribute in determining mineral distribution and diversity, a concept called mineral ecology. It has been described [27] that four main factors contribute to the roles played by chance and necessity in determining mineral distribution and diversity: 1) crystal chemical characteristics, 2) mineral stability ranges, 3) the probability of occurrence for rare minerals, and 4) stellar and planetary stoichiometries in extrasolar systems. A fundamental goal of mineralogy and petrology is then to develop a deep understanding of the mineral phase relationships and their spatial and temporal evolution in rocks, ore bodies, sediments, and other natural polycrystalline materials existing on terrestrial planets and moons. Whereas traditional approaches for the analysis of the multi-dimensional chemical complexity of mineral assemblages have focused on experimental and theoretical considerations of 2-, 3-, or *n*-component systems as approximations to natural systems, network analysis of mineral systems [28] provides a new data-driven approach for understanding the complexity of multiphase mineral assemblage through space and time. By representing mineral species as nodes and coexistence of minerals as lines, network analysis provides a dynamic, quantitative, and predictive visualization framework for uncovering complex and otherwise hidden higher-dimensional patterns of diversity and distribution in mineral systems. This enables a dynamic visualization platform for higher-dimensional analysis of phase relationships, because topologies of equilibrium phase assemblages and pathways of mineral reaction series are embedded within the networks. Similar data-driven approaches are being applied in materials informatics to identify features (or descriptors) in the structure, chemistry and/or bonding for given chemical compositions in order to develop machine-learning based adaptive design for materials [29].

Organic minerals: a previously underestimated connection to crystal engineering

Recent analyses of crystal structures formed by organic minerals [30] reveal that they are naturally-occurring analogues of advanced synthetic materials such as coordination polymers and metal-organic frameworks (MOFs). This connection exposes a previously unrecognized contribution that the disciplines of crystal engineering, coordination chemistry and supramolecular chemistry may have in elucidating the structures of minerals.

From the point of view of mineralogical crystallography, this realization links the fields of mineralogy and geochemistry on one side, and modern materials chemistry and crystal engineering on the other. This recent unexpected discoveries of MOFs as minerals, further suggests that complex advanced organic materials, such as co-crystals, may also play an important role in the geology of planetary systems.

Such potential, and in some cases demonstrated geological significance of advanced organic and metal-organic materials, highlights a potential role for concepts of modern crystal engineering, notably coordination and supramolecular chemistry, in describing the composition and structures of organic minerals, a mineral class that has persistently resisted systematic classification.

Moreover, from these emergent connections between crystal engineering and geochemistry, it is clear that the two fields can learn from each other, to explore research questions such as: 1) the natural occurrence of advanced materials structures, including MOFs, coordination polymers, nanomaterials or co-crystals as minerals; 2) how recent advances in materials science can be used to predict new mineral structures, especially new carbon-based mineral species; and 3) the applications of geochemically-inspired processes, such as mineral weathering, mineral replacement reactions, or mechanochemistry, in the synthesis of advanced metal-organic materials.

In brief, the existence of metal-organic materials as organic minerals, as eloquently stated elsewhere [1], “opens a new research agenda in mineralogical crystallography”; “more attention should be paid to organic minerals and it is the task of mineralogists to look more closely at the interface between living non-living mater” to unravel this history.

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