

## Introduction to the special issue on mineralogical crystallography

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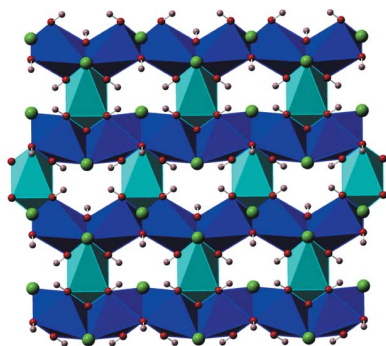
For many centuries crystallography and mineralogy were part of a single discipline, and it was impossible to separate one from the other. In fact even the early works of Theophrastus (*On Stones*) and Pliny's *Natural History* show that the beginnings of both sciences have the same roots. In fact, crystallography grew out of mineralogy because in Steno's time the only crystals available for study were those of minerals. In the XXth century, however, the two sciences went their separate ways, but even today crystallographic research is an important part of mineralogy and mineralogical research is still an important part of crystallography. The current issue of *Acta Crystallographica B* includes a special issue devoted to Mineralogical Crystallography and collects some important contributions that demonstrate the diversity of crystallographic ideas and methods developed to solve valuable issues in mineralogy.

There are some 5 500 (and growing) different mineral species known today (Pasero, 2018) compared with more than 1 200 000 biological species described so far! Some of these mineral species are rare and occur in only a few localities, whereas others crystallize in the range of millions of tons in the Earth's crust. The latter are called 'rock-forming minerals' and their study is of utmost importance for our understanding of the behaviour of rocks on and beneath the Earth's surface.

The first paper of the issue, written by Gagné *et al.* (2018), is devoted to theoretical aspects of bond-valence and bond-length calculations in rock-forming minerals. The authors found that *a priori* calculation of bond valences and bond lengths allows assessment of the strain in a specific structure and provides a way to examine the effect of bond topology on variation in observed bond lengths for the same ion pair in different bond topologies.

Most of the rock-forming minerals are oxygen-based, *i.e.* represent either oxides or oxysalts. However, there is an important group of ore minerals (*i.e.* those that are mined for specific elements such as Pb, Cu or Ni) that are based upon sulfur; these are sulfides and sulfosalts. The article by Bindi & Biagioni (2018) provides an interesting insight into the world of Cu- and Ag-rich sulfosalts, mostly based upon the original results obtained by the authors. Minerals of this group possess a number of interesting crystallographic phenomena such as structural disorder, commensurate and incommensurate modulations, highly variable coordination environments, twinning and polytypism. From the technological point of view, these minerals are of interest because of their ion-conducting properties.

Once upon a time, the discovery of a new mineral species was a considerable advance in science (especially when it was associated with the discovery of a new chemical element!). Today more than 100 new mineral species are described every year and their approval is the business of the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA) (Hatert *et al.*, 2018). What is of great interest is that very few of the newly discovered minerals have synthetic analogs, which means that the laboratories of Nature are in some aspects more ingenious than our own chemical laboratories. The point (or one of the points) is that the space and time scales of natural processes cannot be compared with those that we are able to model in laboratories. An example of the complex geological and mineralogical puzzles currently being worked on is pyrometamorphic rocks of the Hatrurim Complex in



the Negev Desert, Israel. A suite of chemically and structurally unusual minerals has been described there recently, and the third paper of the issue (Krüger *et al.*, 2018) is devoted to crystallography of yet another new mineral species from the Holy Land, aravaite,  $\text{Ba}_2\text{Ca}_{18}(\text{SiO}_4)_6(\text{PO}_4)_3(\text{CO}_3)\text{F}_3\text{O}$ . This mineral is unique in its chemical composition, as it contains at the same time silicate, phosphate and carbonate ions (there is not yet a single synthetic compound known with such a chemistry!). However, aravaite is also unique in its crystal structure that has a modular character [see the IUCr monograph by Ferraris *et al.* (2004) on the topic of modularity], and also represents an interesting case of disorder that leads to the appearance of diffuse scattering. The authors attempt to explain these features using modern crystallographic approaches.

Mineral-forming processes are not always large-scale in time and space and there are some environments, where mineral formation can be observed *in situ* by the open eye. Volcanic fumaroles, where mineral crystals form from hot volcanic gases, are currently active in several places on Earth. One such place which appears to be most productive recently is the Tolbachik volcano on the Kamchatka peninsula, Russia. Copper minerals that form in Tolbachik fumaroles are diverse in chemistry and structural features (96 minerals crystallizing in 80 structure types!), and the fourth paper in the issue (Pekov *et al.*, 2018) reviews their unusual and unique structural architectures. The authors separate these minerals into two groups according to the temperatures of their formation, which control their crystal-chemical properties. It is interesting that along with traditional cation-centred description, the authors, for a particular group of minerals, also use an anion-centred approach to aid structural interpretation.

Copper minerals have also received considerable attention recently due to their amazing magnetic properties. The atacamite group of minerals reviewed by Malcherek *et al.* (2018) possess a regular kagomé-type arrangement of  $\text{Cu}^{2+}$  ions, which behave as quantum spin liquids, showing geometrically frustrated states of the magnetic lattice. Since the first report on the experimental discovery of spin liquid state in ‘Zn-paratacamite’ (Shores *et al.*, 2005; note that the authors were guided by mineralogical information!), there have been a number of studies leading to many intriguing surprises that may result in new discoveries of topological and superconducting phases. It is, however, amazing that the basic architecture possessing such unusual physical properties was formed by natural forces far in advance of its synthesis under laboratory conditions.

Another class of natural materials that have found profound industrial applications are microporous crystalline materials such as zeolites, titano-, niobo- and vanadosilicates. In their contribution to the issue, Danisi and Armbruster (2018) report on a step-wise dehydration behaviour of VSH-13Na, a framework vanadosilicate structurally related to the minerals cavansite and pentagonite. By analogy with the latter two (Danisi *et al.* 2012, 2013), the authors observe the formation of new low and dehydrated phases, in which each new dehydrated state corresponds to a new structure type and

a new conformation state of an octahedral–tetrahedral framework.

The last paper of the issue (Huskić & Frisčić, 2018) opens up a new research agenda in mineralogical crystallography, namely, the previously underestimated connections between mineralogy and crystal engineering. In the Earth’s history, the origin of life was the starting point, when the evolution of our planet was strongly influenced by the evolution of the biosphere. The interactions between geo- and biospheres resulted in the formation of new hybrid mineral species incorporating both abiogenic and biogenic elements (see, for example, the recent discoveries of organic minerals: Chukanov *et al.*, 2015, 2018; Bojar *et al.*, 2017; Mills *et al.*, 2017). In many instances, these processes parallel research protocols used for the engineering of novel materials with functional properties. For instance, the recent paper by Huskić *et al.* (2016) reported on stepanovite and zhemchuzhnikovite, two minerals with metal–organic framework (MOF) structures. Many other interesting examples of such a parallelism are given by Huskić & Frisčić (2018) in their review. In our opinion, more attention should be paid to organic minerals and it is the task of mineralogists to look more closely at the structures formed at the interface between living and non-living matter.

Slightly less than 100 years ago, Vladimir Vernadsky wrote that ‘...there is a close connection between the general chemistry studied in our laboratories and the chemistry studied in the laboratories of the Earth’s crust. However, the latter provides a more grandiose picture of events, which differs from the former not only in scale, but also in complexity’ (Vernadsky, 1923). The unique character and richness of phenomena that we observe in the world of mineralogical crystallography is definitely a consequence of the evolution of the mineral kingdom that involves many factors and trends that are not reproducible under laboratory conditions (Hazen *et al.*, 2008; Grew *et al.*, 2017). The crystallographic studies of minerals are not only used to decipher the Earth’s history but also have many applications in material sciences and technology. This is why we believe that the discipline of mineralogical crystallography is alive and will see considerably more advances in the near future. We are grateful to the authors of the papers of this issue for their interesting and important contributions.

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