Oral presentation

Three-dimensional electron diffraction (3DED) and energy-dispersive X-ray spectroscopy (EDS) as innovative methods to resolve and refine crystal structures in Earth Sciences

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Crystal-chemical investigation of mineral phases is an essential step in Earth Sciences to shed light on genetic processes occurring in different geological environments. Single-crystal or powder X-ray diffraction and electron microprobe are generally applied to determine the structure and the chemical composition of crystalline phases. These analytical techniques are the best for providing high-quality crystal-chemical data, but their use is limited to pure samples or to grains several tens of µm across. Therefore, it is difficult to characterize µm-sized and sub-µm materials included in rocks. Only recently has the development of protocols to collect three-dimensional electron diffraction (3DED) data [1] and of software able to perform dynamical refinements [2] been available to confidently determine and refine crystal structures of sub-micrometric phases. Although the associated structural residual ranges 10-20%, electron diffraction represents an innovative and powerful method to obtain crystallographic information. Nonetheless, its application is still limited in the Earth Sciences.

Here we present some excellent examples of new mineral phases resolved *ab initio* and refined through EDS and 3D electron diffraction data. The *holotype* crystals occurred as sub-micrometric to micrometric inclusions in corundum in chromitites from the Luobusa ophiolite (Tibet, China) and in garnet in eclogites from the Bohemian Massif (Germany). The new minerals in the Luobusa samples to be reported here are *jianmuite* [3] and a Ti^{3+}-rich calcium amphibole [4]. Jianmuite is a Zr-Al-Ti oxide (ideally $ZrAl_3Ti_6O_{16}$), crystallizing in the tetragonal I-4 space group with a= 10.367 Å and c= 9.812 Å. This mineral phase has a chemical composition similar to carmeltazite ($ZrAl_2Ti_4O_{11}$) [5], but with a completely different crystal structure. Jianmuite was also detected in the Allende meteorite, sample USNM 3510-5 [3]. The Ti^{3+}-rich calcium amphibole crystallizes with typical amphibole crystal structure (monoclinic $C2/m$ space group) [4], but has incorporated an unusual amount of Ti^{3+} cations for a terrestrial mineral [4]. We also report two new mineral phases found in crystallized melt inclusions, i.e., nanogranitoids, in garnet from the Bohemian Massif, namely *pfaffenbergite* (previously known as "phase 412") and "phase 430" [6]. Pfaffenbergite, ideally $KNa_3(Al_4Si_{12})O_{32}$, crystallizes in the hexagonal $P6/mcc$ space group with a= 10.258 Å and c= 14.775 Å. Pfaffenbergite is the Na-analogue of wodegongjieite ($KCa_3(Al_7Si_9)O_{32}$) [7], a mineral recently found as an inclusion in corundum in a chromitite from the Luobusa ophiolite (Tibet, China). "Phase 430", ideally $K_2Ca_3(Al_8Si_{34})O_{84}$, crystallizes in the hexagonal $P6/mcc$ space group. This mineral consists of a feldspathoid-like tetrahedral framework with a completely new topology.

The identification of these mineral phases will provide additional information for understanding the crystallization conditions and environment of the phases included in the corundums in Luobusa chromitites and in nanogranitoids in garnets from the Bohemian Massif. It is our opinion that these pioneering studies will pave the way for a more comprehensive characterization of the geologic processes in similar environments where micrometric mineral inclusions have been found.

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