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Highlights and Breakthroughs

The crystallographic and petrogenetic significance of pegmatite phosphates

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Abstract: The paper describing the new phosphate mineral correianevesite, recently published by Chukanov et al. (2014), clearly demonstrates the importance of pegmatite phosphates. For material scientists, these minerals are a source of new structure types; for petrologists, they constitute valuable tools necessary to accurately determine the temperature conditions prevailing during pegmatite differentiation processes. **Keywords:** Phosphates, pegmatites, crystal chemistry, petrography, geothermometry

In rare-element pegmatites of the beryl-columbite-phosphates and spodumene subtypes (Černý and Ercit 2005), phosphates occur as black masses reaching several meters in diameter, enclosed in silicates. These minerals do not have any economic value; however, they are of first importance for mineralogists, petrologists, and for material scientists. Indeed, the geological environment of pegmatites is an extraordinary natural laboratory, in which a plethora of exciting phosphate structures crystallizes.

Such famous phosphates are those of the triphylite group, which exhibit the olivine structure. During the hydrothermal transformations affecting pegmatite phosphates, these minerals follow an oxidation process in which triphylite-lithiophilite [$Li(Fe^{2+},Mn^{2+})PO_4$] progressively transform to ferrisicklerite-sicklerite [$Li_{1-x}(Fe^{3+},Mn^{2+})PO_4$] and then to heterosite-purpurite [$(Fe^{3+},Mn^{3+})PO_4$] (Losey et al. 2004; Hatert et al. 2012). This oxidation mechanism, $Li^+ + Fe^{2+} = \square + Fe^{3+}$, was first described by Quensel (1937) and Mason (1941) on natural samples; 60 years later, Padhi et al. (1997) discovered the unique electrochemical properties of these compounds, which now allow their use as cathode material for Li-ion batteries. This example clearly demonstrates how the crystallography of pegmatite phosphates may induce the development of new advanced materials (Hatert 2012).

Another famous group of pegmatite phosphates are those of the alluaudite supergroup, which were investigated in detail by Hatert et al. (2000, 2003, 2005), Hatert (2008), and Rondeux and Hatert (2010). Their crystal structure contains two octahedral *M* sites generally occupied by Fe and Mn, while large cations as Na or Ca occur in the 8-coordinated *A* sites located in channels running along the *c* axis. The resulting formula is $A_{1-2}M(1)M(2)_2(PO_4)_3$, and the monoclinic space group is $C2/c$ (Hatert et al. 2000; Krivovichev et al. 2013). The presence of channels in alluaudite-type phosphates is responsible for their unusual properties, which make possible their use as catalysts (Kacimi et al. 2005) or as electrode material for Li-ion batteries (Trad et al. 2010).

The paper on correianevesite, recently published by Chukanov et al. (2014), is an excellent example of new phosphate mineral species description. The mineral was discovered in the Cigana pegmatite, Minas Gerais, Brazil; it belongs to the reddingite group, and shows an ideal formula $Fe^{2+}Mn^{2+}_2(PO_4)_2\cdot 3H_2O$. The structure of correianevesite is characterized by (100) octahedral layers containing Fe^{2+} and Mn^{2+}, and connected together by the PO_4 tetrahedra. Such new species descriptions may appear relatively useless for a majority of mineralogists, petrographers, and geochemists; however, they are of first importance since they constitute an inexhaustible source of new crystal structures. Moreover, a good knowledge of the petrography and of the stability fields of these minerals is the only way to understand complex pegmatite transformation processes, as recently shown by Baijot et al. (2012), who investigated the petrography of phosphate assemblages from the Sapucaia pegmatite, another famous Brazilian mine. In this paper, the authors depict a complete genetic sequence of phosphate minerals, from the magmatic and hydrothermal stages to the late meteoric alteration processes.

As mentioned by Fisher (1958) in his Presidential address at the 28th MSA meeting, the knowledge of phosphates at that time was comparable to that of silicates at the beginning of the 20th Century. The structural characterization of phosphate species was initiated by P.B. Moore in the 1970s, and the petrographic investigations of phosphate assemblages were initiated by F. Fontan, P. Keller, and A.-M. Fransolet (Fransolet et al. 1985, 1986). Nowadays, phosphate science has evolved towards experimental studies, as for example those by Hatert et al. (2006, 2011), that allowed to determine the stability fields of alluaudite-type phosphates, and to develop geothermometers based on the Na-content of triphylite. Such geothermometers are valuable tools to accurately estimate the temperatures that prevailed in pegmatites during the crystallization of phosphate minerals. This demonstrates again the crucial role of pegmatite phosphates, at the crossroads of material science and geology.

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