

4.4. Phosphates

The crystal chemistry of natural and synthetic beryll phosphates

Frédéric Hatert,^{1,*} Fabrice Dal Bo^{1,2} and Yannick Bruni¹

¹Laboratory of Mineralogy, University of Liège B18, B-4000 Liège, Belgium

²University of Oslo, National History Museum, Postboks 1172, Blindern, 0318 Oslo, Norway

* fhatert@uliege.be

Only 30 natural beryll phosphates are reported in the literature, occurring mainly in granitic pegmatites and resulting from the reaction of beryl with P-bearing hydrothermal solutions. The formation of these minerals is highly dependent upon the pH, temperature, availability of specific alkali cations, and Be:P ratio of the solution. Despite their low abundance, beryll phosphate minerals crystallize in many structure types, characterized by different polymerization degrees of the BeO₄-PO₄ tetrahedra; these compounds form chain structures (fransoletite, väyrynenite), sheet structures (herderite, uralolite), framework structures (hurlbutite, babefphite, beryllonite), structures containing clusters of tetrahedra (gainesite), and even zeolite-type structures (pahasapaite). The crystal chemistry of the beryll phosphates is exciting, as their structures are similar to those of aluminosilicates and borosilicates; these analogies can be explained by the Pauling bond-valence rule. Indeed, the O atoms shared by Be and P in beryll phosphates, by Al and Si in aluminosilicates, and by B and Si in borosilicates, receive exactly the same Pauling bond-valence sum of 1.75.

Dal Bo et al. (2014) performed extensive hydrothermal experiments starting from the M²⁺Be₂P₂O₈ compositions (M²⁺ = Ca, Sr, Pb, Ba), in order to better understand the crystal chemistry and the stability of beryll phosphates. Between 200 and 600°C, and under acidic or basic conditions, the synthesized compounds show the same structure types, without any phase transition. CaBe₂P₂O₈, SrBe₂P₂O₈, and PbBe₂P₂O₈ crystallize in space group *P2₁/c* (*a* = 7.81-8.09, *b* = 8.80-9.02, and *c* = 8.31-8.42 Å, β = 90.12-90.51°), and show a paracelsian-type structure composed of a framework of corner-sharing BeO₄ and PO₄ tetrahedra. These tetrahedra are assembled in four- and eight-membered rings showing the typical UUDD and DDUDUUDU patterns, respectively (U = tetrahedron pointing up, and D = tetrahedron pointing down). The M²⁺ cations occur in distorted 7+3-coordinated polyhedra located in the eight-membered ring. BaBe₂P₂O₈ crystallizes in space group *P6/mmm* (*a* = 5.028(1) and *b* = 7.466(1) Å), and its crystal structure consists of double layers of tetrahedra, which contain both Be and P in a 1:1 ratio. Inside the layers, the (Be,P)O₄ tetrahedra form six-membered rings by sharing corners. The Ba atoms are located in very regular 12-coordinated polyhedra and connect two successive double layers. CaBe₂P₂O₈ and SrBe₂P₂O₈ are isostructural with the minerals hurlbutite and strontiohurlbutite, respectively [Rao et al., 2014], whereas BaBe₂P₂O₈ is the synthetic analogue of minjiangite [Rao et al., 2015].

These last years, three new Ba-bearing beryll phosphates were described in pegmatitic environments, showing exciting crystal structures. Minjiangite is a phyllophosphate, discovered in the Nanping No. 31 pegmatite, Fujian Province, China; it is the first example of a mineral showing a mixed occupancy of 0.5 P + 0.5 Be on the same tetrahedral site [Rao et al., 2015; Dal Bo et al., 2014]. Wilancookite, (Ba,K,Na)₈(Ba,Li,□)₆Be₂₄P₂₄O₉₆·32H₂O, forms tiny rhombododecahedral crystals deposited on moraesite fibres from the Lavra Ponte do Piauí pegmatite, Minas Gerais, Brazil; its crystal structure (*I23*, *a* = 13.5398(2) Å) is identical to those of pahasapaite and of synthetic zeolite RHO [Hatert et al., 2017]. More recently, a new species was submitted to the IMA-CNMNC under number 2019-011; it was discovered in the Vilatte-Haute pegmatite, Limousin, France, and shows the ideal formula BaCa[Be₄P₄O₁₆]·6H₂O. This beryll phosphate, which crystallizes in space group *P2₁/c* (*a* = 9.4958(4), *b* = 13.6758(4), *c* = 13.4696(4) Å, β = 90.398(3)°), shows a zeolite framework identical to that of phillipsite; it is the third known zeolite-type phosphate.

The structural similarities between aluminosilicates and beryll phosphates would necessitate a classification of these mineral species into subclasses; such a classification scheme is elaborated herein.

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