

Heteropolymolybdates: structural relationships, nomenclature scheme and new species

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The molybdoarsenates betpakdalite, natrobetpakdalite and obradovicite and the molybdophosphates mendozavilite, paramendozavilite and melkovite typically occur as coatings of minute, poor-quality and/or complexly twinned crystals. Heretofore, the structure of only betpakdalite had been determined. In this investigation, we examined type material for all of these minerals, as well as similar material from other sources, in an effort to elucidate the interrelationships within this enigmatic family of minerals.

Comparative powder X-ray diffraction proved effective in identifying structurally related phases and obtaining refined cell parameters for those phases for which single-crystal studies could not be conducted. Electron microprobe analyses were performed for all species studied and optimal conditions for analysis were determined. These methods indicated that natrobetpakdalite, mendozavilite and melkovite are isostructural with betpakdalite and suggested that obradovicite has a closely related structure.

Single-crystal investigations yielded several new structure refinements and the solution of the structure of obradovicite. Although crystals of paramendozavilite were inadequate for collection of structure data, cell parameters were for the first time determined. Both the betpakdalite and obradovicite structure types are based upon frameworks containing four-member clusters of edge-sharing MoO₆ octahedra which link by sharing corners with other clusters, with Fe³⁺O₆ octahedra and with PO₄ or AsO₄ tetrahedra. The structures differ with respect to their linkages through the Fe³⁺O₆ octahedra, leading to substantially different, but closely related framework configurations. The cell parameters of paramendozavilite indicate that its structure may be related to those of betpakdalite and obradovicite. We suggest that these minerals be termed "heteropolymolybdates".

Besides the presence of As or P in the tetrahedral site (*T*) of the frameworks, the non-framework cation sites are key to discriminating different species with these structures. One generally smaller cation site (*B*) at a center of symmetry is octahedrally coordinated to H₂O molecules and two or more disordered, partially occupied, generally larger, cation sites (*A*) are coordinated to O atoms in the framework and H₂O molecules. The general formulas for minerals with either the betpakdalite or the obradovicite structure are the same: [A₂(H₂O)_{*n*}B(H₂O)₆][Mo₈T₂Fe³⁺₃O₃₀₊₇(OH)_{7-x}], where: *x* is the total charge of *A* + *B* and *n* is variable. Dominant cations noted in the *A* sites include K, Na and Ca and in the *B* sites Na, Ca, Mg, Cu and Fe. The various combinations that we identified define at least eight new heteropolymolybdate species.

We believe that a suffix-based nomenclature is most appropriate for the heteropolymolybdates with root names based upon the structure types and the *T* sites cations: betpakdalite (*T* = As), mendozavilite (*T* = P) and obradovicite (*T* = As); followed by two suffixes of the form: -*AB*, corresponding to the dominant cations in the two different types of non-framework cation sites. A new root name would be required for any new obradovicite structure species with *T* = P.

Our investigation of the paramendozavilite type specimen showed it to contain no paramendozavilite, but rather an apparently closely related new mineral. Another sample of paramendozavilite analyzed showed K > Na.

Qingheite-(Fe²⁺), Na₂Fe²⁺MgAl(PO₄)₃, a new member of the wylieite group

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Qingheite-(Fe²⁺), ideally Na₂Fe²⁺MgAl(PO₄)₃, is a new mineral species from the Sebastião Cristino pegmatite, Minas Gerais, Brazil [1]. It occurs as rims around frondelite grains, included in a matrix of quartz and albite. The empirical formula is (□_{0.65}Na_{0.35})(Na_{0.58}Mn²⁺_{0.40}Ca_{0.02})(Fe²⁺_{0.68}Mn²⁺_{0.32})(Mg_{0.72}Fe³⁺_{0.23}Fe²⁺_{0.05})(Al_{0.62}Fe³⁺_{0.38})[PO₄]₃, and the single-crystal unit-cell parameters are *a* = 11.910(2), *b* = 12.383(3), *c* = 6.372(1) Å, β = 114.43(3)°, *V* = 855.6(3) Å³, space group *P*2₁/*n*. Qingheite-(Fe²⁺) is the Fe²⁺ analogue of qingheite [Na₂MnMgAl(PO₄)₃], and belongs to the wylieite group of minerals. The mineral species and its name were approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (CNMNC-IMA) under the number 2009-076.

The crystal structure of qingheite-(Fe²⁺) has been refined, based on single-crystal X-ray diffraction data, to *R*₁ = 2.91 %. The basic structural unit is identical to that of other members of the wylieite group, and consists of kinked chains of edge-sharing octahedra stacked parallel to {101}. These chains are formed by a succession of M(2a)-M(2b) octahedral pairs, linked by highly distorted M(1) octahedra. Equivalent chains are connected in the *b* direction by the P(1), P(2a) and P(2b) phosphate tetrahedra to form sheets oriented perpendicular to [010]. These interconnected sheets produce channels parallel to *c*, channels that contain the large X sites. The X(1a) site is a distorted octahedron, whereas the X(1b) site can be described as a very distorted cube. The morphology of the X(2) site corresponds to a very distorted gable disphenoid with a [7+1] coordination, similar to the X(2) site of rosemaryite [2] and to the A(2)' site of the alluaudite structure.

The structural features of qingheite-(Fe²⁺) are compared to those of other wylieite-type phosphates: ferrosemaryite from the Rubindi pegmatite, Rwanda (□NaFe²⁺Fe³⁺Al(PO₄)₃, *R*₁ = 2.43 %, *a* = 11.838(1), *b* = 12.347(1), *c* = 6.2973(6) Å, β = 114.353(6)°) [3], rosemaryite from the Buranga pegmatite, Rwanda (□NaMnFe³⁺Al(PO₄)₃, *R*₁ = 4.01 %, *a* = 12.001(2), *b* = 12.396(1), *c* = 6.329(1) Å, β = 114.48(1)°) [2], wylieite from the Buranga pegmatite (Na₂MnFe²⁺Al(PO₄)₃, *R*₁ = 2.74 %, *a* = 11.954(2), *b* = 12.439(2), *c* = 6.406(1) Å, β = 114.54(1)°), and qingheite from the Santa Ana pegmatite, Argentina (*R*₁ = 2.65 %, *a* = 11.878(3), *b* = 12.448(2), *c* = 6.438(2) Å, β = 114.49(1)°). These new structural data indicate that Al is predominant on the M(2a) site in the investigated samples, not on the M(2b) site as observed in ferrowylieite [4]. The morphologies of the X(1a), X(1b), and X(2) crystallographic sites are also compared among the different minerals of the wylieite group.

- [1] Hatert, F. et al. (2010) *Eur. J. Mineral.*, **22**(3), 459-467. [2] Hatert, F. et al. (2006) *Eur. J. Mineral.*, **18**, 775-785. [3] Hatert, F. et al. (2005) *Eur. J. Mineral.*, **17**, 749-759. [4] Moore, P.B. & Molin-Case, J. (1974) *Am. Mineral.*, **59**, 280-290.