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Crystal structure interconnections in a family of hydrated phosphate-sulfates

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The phosphate-sulfate family incorporates several water-containing hypergene minerals with various structures. We determined the crystal structure of lately discovered [1] fibrous mineral arangasite, $[Al_2F(H_2O)_6(PO_4)(SO_4)]\bullet 3(H_2O)$ using single-crystal synchrotron diffraction at 100 K (a =7.073(1), b=9.634(2), c=10.827(2) Å, β=79.60(1)°, P2/a, Z=2). Its crystal chemical interpretation has allowed us to reveal some interesting features in a title group of compounds. The arangasite crystal structure is dominated by chains extending in the [100] direction and built of pairs of corner-shared Al octahedra joined through bridging F atoms and P tetrahedra. They alternate in the [001] with S tetrahedra forming layers parallel to the ac plane through a system of hydrogen bonds. Along [010] the complex layers are separated by layers of H_2O molecules. Hydrogen bonding serves here as the only mechanism providing linkage between the main structural fragments. The Al/ P chains are topologically identical to the chains built from Fe octahedra and P tetrahedra in the triclinic structure of destinezite, $Fe_2(OH)(PO_4)(SO_4)(H_2O)_6$ [2]. The repeating subunit of both chains consists of two octahedra and one tetrahedron sharing vertices. A main difference among the chains arises from their chemistry; Al octahedra in arangasite form pairs by sharing the F vertex of neighboring polyhedra, whereas pairs of Fe octahedra in destinezite are linked together through the oxygen vertex of an OH group. As a result, the larger size of the Fe octahedra compared to Al octahedra causes a larger c = 7.31 Å along the chain in destinezite. Additional SO_4 tetrahedra here are attached to these chains along their periphery through an oxygen vertex bridge with Fe octahedra. The monoclinic sanjuanite, $Al_2(PO_4)(SO_4)(OH)(H_2O)_9$ structure [3] is composed of Al/P chains, parallel to a = 6.11 Å. These chains are also built from three-member units that include corner-sharing pairs of octahedra connected by PO_4 tetrahedron, but they are not topologically equivalent to the chains in the arangasite and destinezite structures. Similar to arangasite, sulfate groups and H_2O molecules reside between chains in the sanjuanite structure with hydrogen bonding. Thus, similar the crystal chemical formulae of sanjuanite and arangasite differ with respect to the (OH) → F substitution, which results in contrasting unit cell parameters. Note, that the unit cell volume of sanjuanite, is twice as large as arangasite.

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