Crystal chemistry of the tsumcorite-group minerals. New data on ferrilotharmeyerite, tsumcorite, thometzekite, mounanaite, helmutwinklerite, and a redefinition of gartrellite

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Abstract: The general formula for the tsumcorite-group minerals is Me(1)Me(2)(XO₄)(OH,H₂O)z; Me(1) = Pb, Ca, Na, and partly Bi; Me(2) = Fe, Mn, Cu, Zn, Co, Ni, and partly Al; X = P, As, V, S. Out of this group the minerals ferrilotharmeyerite, tsumcorite, thometzekite (sulfatian), mounanaite, helmutwinklerite, gartrellite and zincian gartrellite were investigated regarding optical properties, morphology, chemical composition, infrared and Mössbauer spectroscopy, and crystal structure. Crystal symmetry is either (i) triclinic in the case of an ordered occupation of two Me(2) sites, (ii) triclinic due to ordering of the hydrogen bonds in the case of species with 2 water molecules per formula unit or (iii) monoclinic in the other cases. Cell parameters were refined from X-ray powder data; powder patterns are given for thometzekite (sulfatian), mounanaite, helmutwinklerite, gartrellite and zincian gartrellite. Mössbauer measurements confirmed the iron in ferrilotharmeyerite, tsumcorite, gartrellite and zincian gartrellite to be completely trivalent. Electron microprobe analyses showed that at least partial solid solution is common for the Me(2) and less frequent for the X and Me(1) site. In addition to homovalent substitutions [e.g. Zn²⁺ ↔ Cu²⁺ or (AsO₃)³⁻ ↔ (PO₄)³⁻] there are 3 heterovalent exchange mechanisms with a coupled substitution involving OH/H₂O groups: (i) on the Me(1) site, e.g. [(Ca)²⁺(H₂O)]²⁺ ↔ [(Bi)³⁺(OH)]²⁺, (ii) on the Me(2) site, e.g. [(Zn,Cu,Co, Ni)²⁺H₂O]²⁺ ↔ [(Fe,Al,Mn)³⁺(OH)]²⁺, and (iii) on the X site, e.g. [(AsO₄)³⁻(H₂O)]³⁻ ↔ [(SO₄)⁵⁻(OH)]³⁻.

Crystals of ferrilotharmeyerite, tsumcorite, thometzekite (sulfatian), and mounanaite have monoclinic symmetry, space group C2/m. The crystal structures were investigated by single-crystal X-ray diffraction. The structural data for tsumcorite given by Tillmanns & Gebert (1973) were confirmed, for the other minerals isotypy is proved. Infrared absorption spectra indicate two independent and strong hydrogen bonds. In particular, there is no evidence for protonated arsenate groups. The chemical formulas of ferrilotharmeyerite and lotharmeyerite (for analogy reasons) have to be revised on a 10 oxygen basis to Ca(Fe⁹⁹,Zn)₂(AsO₄)₂(OH,H₂O)₂, and Ca(Mn⁹⁹,Zn)₂(AsO₄)₂(OH,H₂O)₂, respectively.

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