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The crystal structure of mineral magadiite, $Na_2Si_{14}O_{28}(OH)_2 \cdot 8H_2O$

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Abstract

Magadiite from Lake Magadi was structurally analyzed based on X-ray powder diffraction data. The idealized chemical composition of magadiite is $Na_{16}[Si_{112}O_{224}(OH)_{16}] \cdot 64H_2O$ per unit cell. The XRD powder diffraction pattern was indexed in orthorhombic symmetry with lattice parameters a_0 = 10.5035(9) Å, b_0 = 10.0262(9) Å, and c_0 = 61.9608(46) Å. The crystal structure was solved from a synthetic magadiite sample in a complex process using 3D electron diffraction combined with model building as presented in an additional paper. A Rietveld refinement of this structure model performed on a magadiite mineral sample in space group *F2dd* (No. 43) converged to residual values of R_{Bragg} = 0.031 and R_F = 0.026 confirming the structure model. Physico-chemical characterization using solid-state NMR spectroscopy, SEM, TG-DTA, and DRIFT spectroscopy further confirmed the structure. The structure of magadiite contains two enantiomorphic silicate layers of, so far, unknown topology. The dense layers exhibit no porosity or micro-channels and have a thickness of 11.5 Å (disregarding the van der Waals radii of the terminal O atoms) and possess a silicon Q^4 to Q^3 ratio of 2.5. 16 out of 32 terminal silanol groups are protonated, and the remaining groups compensate for the charge of the hydrated sodium cations. Bands of edge-sharing $[Na(H_2O)_{6/1.5}]$ octahedra are intercalated between the silicate layers extending along (110) and ($\bar{1}$10). The water molecules are hydrogen bonded to terminal silanol groups with O···O distances of 2.54–2.91 Å. The structure of magadiite is slightly disordered, typical for hydrous layer silicates (HLS), which possess only weak interactions between neighboring layers. In this respect, the result of the structure refinement represents a somewhat idealized structure. Nevertheless, the natural magadiite possesses a higher degree of structural order than any synthetic magadiite sample. The structure analysis also revealed the presence of strong intra-layer hydrogen bonds between the terminal O atoms (silanol/siloxy groups), confirmed by ^{1}H MAS NMR and DRIFT spectroscopy. The surface zone of the silicate layers, as well as the interlayer region containing the $[Na(H_2O)_{6/1.5}]$ octahedra, are closely related to the structure of Na-RUB-18.

Keywords: Sodium silicate, structure determination, characterization, layer silicate, Rietveld