The crystal structure of mineral magadiite, Na$_2$Si$_{14}$O$_{26}$(OH)$_2$·8H$_2$O

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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$_{12}$O$_{22}$(OH)$_{16}$]·6H$_2$O 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 $P2_12_12_1$ (No. 43) converged to residual values of $R_{Bragg} = 0.031$ and $R_B = 0.026$ 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$_1$ 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$_2$O)$_{6/1.5}$] octahedra are intercalated between the silicate layers extending along (110) and (T10). 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/silox) 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$_2$O)$_{6/1.5}$] octahedra, are closely related to the structure of Na-RUB-18.

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

Introduction

Occurrences and properties of magadiite

Magadiite is a mineral known since 1967 (Eugster 1967) and is named after Lake Magadi, Kenya, the location of the initial mineral discovery. Later, other occurrences of magadiite emerged: Trinity County, California, U.S.A. (McAtee et al. 1968); Mont Saint-Hilaire, Canada (Horváth and Gault 1990); Lake Chad, Chad (Maglione 1970); Alkali Lake, Oregon, U.S.A. (Rooney et al. 1969); and Aris phonolites, Windhoek, Namibia (Hudson Institute of Mineralogy 1993–2020) to name a few. Magadiite typically precipitates from saline brines of alkaline lakes, which contain large amounts of soluble silica. According to Jones et al., “high concentrations of SiO$_2$ can be attributed to reaction of waters with silicates, and subsequent evaporative concentration accompanied by a rise in pH” (Jones et al. 1967). In addition, carbonates, halides, sodium silicates, zeolites,feldspars, iron oxides, quartz, and garnet manifest in these deposits as impurities. This fact is attributed to the reaction between the volcanic rocks and brines, which also cause the formation of halite, gaylussite, calcite, villiaumite, stromianite, fluorite, and mirabilite from residual brines (Rammlmair 2000).

The type locality of magadiite is Lake Magadi, Kajiado County, Kenya. Lake Magadi is a saline, alkaline lake that is fed by alkaline hot springs and saturated brines with high concentrations of sodium carbonate. The lake is the most saline of all the lakes in the Eastern Rift Valley and is surrounded by a closed basin at 603 m above sea level. The lake is periodically dry, except for brine pools near the margins, containing a vast deposit of trona (Eugster 1969).

The idealized chemical composition as given by Hans Eugster in 1967 is Na$_2$Si$_{14}$O$_{26}$(OH)$_2$·6H$_2$O. Magadiite is a soft (Mohs hardness = 2), white, transparent mineral. The experimental density is 2.17 g/cm$^3$; the crystals are birefringent with a biaxial indicatrix and a mean refractive index of 1.48 (Eugster 1967). It appears as white masses of very small plate-like crystals and is often associated with quartz and kenyaite.

The water content of magadiite is obviously quite variable...