

A Neutron/X-Ray Diffraction, IR, and ¹H/²⁹Si NMR Spectroscopic Investigation of Armenite: Behavior of Extra Framework Ca Cations and H₂O Molecules in Microporous Silicates

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The crystal chemistry of armenite, ideally BaCa₂Al₆Si₉O₃₀·2H₂O, from Wasenalp, Valais, Switzerland was studied. Armenite typically forms in relatively low-temperature hydrothermal veins and fissures and has small pores containing Ca cations and H₂O molecules as extra-framework species. Single-crystal neutron and X-ray diffraction measurements were made on armenite from the above locality for the first time. IR powder spectroscopic measurements were made from room temperature (RT) down to 10 K. ¹H and ²⁹Si NMR measurements were made at RT. Attention was given to investigating the behavior of the extra-framework species and hydrogen bonding. The diffraction results show new features not observed before in published diffraction studies on armenite crystals from other localities. The neutron results also give the first static description of the protons, allowing bond distances and angles relating to the H₂O molecules and H-bonds to be determined. The diffraction results indicate Al/Si order in the framework. Four crystallographically independent Ca and H₂O molecule sites were refined, whereby both sites appear to have partial occupancies such that locally a Ca atom can have only a single H₂O molecule bonded to it through an ion-dipole interaction. The Ca cation is further bonded to six O atoms of the framework forming a quasi cluster around it. The IR spectrum of armenite is characterized in the OH-stretching region at RT by two broad bands at roughly 3470 and 3410 cm⁻¹ and by a single H₂O bending mode at 1654 cm⁻¹. At 10 K four intense OH bands are located at 3479, 3454, 3401 and 3384 cm⁻¹ and two H₂O bending modes at 1650 and 1606 cm⁻¹. The ²⁹Si MAS NMR spectra show four resonances at -81.9, -83.2, -94.9 and -101.8 ppm that are assigned to crystallographically different Si sites in an ordered structure, although their relative intensities deviate somewhat from those predicted for complete Al/Si order. The ¹H MAS spectra contain a single main resonance near 5.3 ppm and a smaller one near 2.7 ppm, which can be assigned to H₂O molecules bonded to Ca and a second H₂O type located in a partially occupied site, respectively. Bonding for the extra-framework “Ca-oxygen-anion-H₂O-molecule quasi-clusters” and also the nature of H-bonding in the microporous zeolites scolecite, wairakite and epistilbite are analyzed. The average OH stretching wavenumbers shown by the IR spectra of armenite and scolecite are, for example, not far removed from that observed in liquid H₂O, but greater than that of ice. What remains poorly understood in microporous silicates is how the ion-dipole interaction in quasi clusters affects H-bonding strength between the H₂O molecules and the aluminosilicate framework.