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## A Neutron/X-Ray Diffraction, IR, and $^1\text{H}/^{29}\text{Si}$ NMR Spectroscopic Investigation of Armenite: Behavior of Extra Framework Ca Cations and $\text{H}_2\text{O}$ Molecules in Microporous Silicates

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The crystal chemistry of armenite, ideally  $\text{BaCa}_2\text{Al}_6\text{Si}_9\text{O}_{30}\cdot 2\text{H}_2\text{O}$ , 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  $\text{H}_2\text{O}$  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.  $^1\text{H}$  and  $^{29}\text{Si}$  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  $\text{H}_2\text{O}$  molecules and H-bonds to be determined. The diffraction results indicate Al/Si order in the framework. Four crystallographically independent Ca and  $\text{H}_2\text{O}$  molecule sites were refined, whereby both sites appear to have partial occupancies such that locally a Ca atom can have only a single  $\text{H}_2\text{O}$  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  $3410\text{ cm}^{-1}$  and by a single  $\text{H}_2\text{O}$  bending mode at  $1654\text{ cm}^{-1}$ . At 10 K four intense OH bands are located at  $3479$ ,  $3454$ ,  $3401$  and  $3384\text{ cm}^{-1}$  and two  $\text{H}_2\text{O}$  bending modes at  $1650$  and  $1606\text{ cm}^{-1}$ . The  $^{29}\text{Si}$  MAS NMR spectra show four resonances at  $-81.9$ ,  $-83.2$ ,  $-94.9$  and  $-101.8\text{ ppm}$  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  $^1\text{H}$  MAS spectra contain a single main resonance near  $5.3\text{ ppm}$  and a smaller one near  $2.7\text{ ppm}$ , which can be assigned to  $\text{H}_2\text{O}$  molecules bonded to Ca and a second  $\text{H}_2\text{O}$  type located in a partially occupied site, respectively. Bonding for the extra-framework “Ca-oxygen-anion- $\text{H}_2\text{O}$ -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  $\text{H}_2\text{O}$ , 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  $\text{H}_2\text{O}$  molecules and the aluminosilicate framework.