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A Crystal Chemical Investigation of Armenite, $BaCa_2Al_6Si_9O_{30}\cdot H_2O$: The Behavior of Extra Framework Ca Cations and H_2O Molecules in Microporous Silicates

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The crystal chemistry of armenite, ideally $BaCa_2Al_6Si_9O_{30}\cdot H_2O$, 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 H_2O molecules as extra-framework species.

Single-crystal neutron and X-ray diffraction measurements were made on armenite from Wasenalp for the first time. IR powder spectroscopic measurements were made from room temperature (RT) down to 10 K. ^1H and ^{29}Si NMR measurements were made at RT. Attention was given to investigating the behavior of the extra-framework species and hydrogen bonding. The neutron results also give the first static description of the protons, allowing bond distances and angles relating to the H_2O molecules and H-bonds to de determined. The diffraction results indicate complete Al-Si order in the framework and four crystallographically independent Ca and H_2O molecule sites. Both sites appear to have partial occupancies such that locally a Ca atom can have only a single H_2O 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. The IR spectrum of armenite is characterized in the OH-stretching region at RT by two broad bands at roughly 3470 and 3419 cm^{-1} and by a single H_2O bending mode at 1654 cm^{-1} and four intense OH bands at 10 K. The ^1H MAS spectra contain a single main resonance near 5.3 ppm and a smaller one near 2.7 ppm.

The extra-framework "Ca-oxygen-anion-H_2O-molecule quasi-clusters" and the nature of H-bonding in the microporous zeolites scolecite, wairakite and epistilbite were also 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 H_2O, 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 H_2O molecules and the aluminosilicate framework.