Interlayer Structures of the Two-Layer Hydrates of Na- and Ca-Vermiculites

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Abstract: The three-dimensional order shown by the two-layer hydrates of Na- and Ca-vermiculite, prepared from Mg-vermiculite from Llano, Texas, has enabled clear, two-dimensional Fourier projections of their interlayer structures to be obtained. Structure factor calculations were made in space group C2 and with unit-cell dimensions of a = 5.358 Å, b = 9.232 Å, and β = 96.82 ° for Na-vermiculite c = 14.96 Å and for Ca-vermiculite c = 15.00 Å. In Na-vermiculite the interlayer cations are octahedrally coordinated to water molecules with the sodium-water polyhedra only located between the triads of oxygen atoms forming bases to tetrahedra in adjacent silicate layers. In Ca-vermiculite the interlayer cations are in both octahedral and 8-fold (distorted cubic) coordination with water molecules. The octahedrally coordinated Ca ions are between the bases of tetrahedra in adjacent silicate layers, but the 8-fold coordinated Ca ions are between the ditrigonal cavities. In both Na- and Ca-vermiculite some water molecules are drawn from planar networks appreciably towards the ditrigonal cavities. The three-dimensional order observed for these vermiculites contrasts with the stacking disorder reported for Mg-vermiculite from Llano. The distinct crystallographic behavior of Na^{+}, Ca^{2+}, and Mg^{2+} in the hydration layers of Llano vermiculite probably depends on cation sizes and field strengths, together with the need to achieve local charge balance near the sites of tetrahedral Al-for-Si substitution.

Key Words: Crystal structure • Fourier projection • Hydrates • Interlayer cation • Vermiculite

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