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Rehydration of dehydrated-dehydroxylated smectite in a low water vapor environment

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Abstract

Thermal analysis experiments in the environment of an extremely low water vapor concentration provide insight into the first steps of the rehydration mechanism in smectite when completely dehydrated and the interlayer region is collapsed. The relative structural and compositional controls on dehydration and rehydration reactions are compared from a well-characterized suite of samples that vary with respect to chemical composition, octahedral and tetrahedral substitution, octahedral cation site vacancy, and degree of dehydroxylation. Techniques including multi-cycle heating-cooling thermogravimetric analysis and nitrogen gas adsorption on various smectite samples preheated at different temperatures followed by rehydration at ambient conditions were used to characterize the interaction of water molecules with completely dehydrated montmorillonite, beidellite, and nontronite smectite types.

Beidellite with high-Al^{3+} tetrahedral substitution results in electrostatically undersaturated basal oxygen atoms that exert strong repulsion between the tetrahedral sheets of adjacent 2:1 layers. The interlayer region of dehydrated or dehydroxylated beidellite is capable of being spontaneously rehydrated even in low water vapor environments. In completely dehydrated montmorillonite and nontronite, the external surface area of the crystallites is a primary control on water adsorption at low humidity when the molecules form a shell around the exchangeable cations present on external surfaces. The potential of montmorillonite and nontronite to reopen a collapsed interlayer is significantly lower than beidellite because of their crystal-chemical features that result in 2:1 layer and interlayer cation attraction. With increasing water vapor partial pressure, the hydration potential of interlayer cations provokes a reopening of the interlayer. In a dehydroxylated nontronite, the undersaturated residual oxygen atom strongly bonds the interlayer cation within the ditrigonal ring of the tetrahedral sheet, resulting in a permanent interlayer collapse.

The specific surface area calculated from a conventional N_2 gas adsorption measurement using the BET model represents the external surface area of a dehydrated smectite crystallite and can be converted into the mean crystallite thickness. The mean crystallite thickness of a completely dehydrated smectite increases with an increase in preheating temperature.

Keywords: Beidellite, BET, dehydroxylation, montmorillonite, nontronite, rehydration, thermogravimetry