

Dehydration of Ca-montmorillonite at the crystal scale. Part I: Structure evolution

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ABSTRACT

The dehydration dynamics of the of the Ca-saturated <1 μm size fraction of SWy-1 (low-charge montmorillonite) were studied at the crystal scale under isothermal conditions using X-ray diffraction with a position-sensitive detector (XRD-PSD) in the 30–170 °C temperature range. A total of 630 XRD patterns were modeled between 30 and 125 °C using a trial-and-error approach based on the direct comparison of experimental and calculated XRD patterns. The proportion of layers with different hydration states (bihydrated, mono-hydrated, and dehydrated) were determined in the temperature-time space as well as small variations of layer thickness within each hydration state. The results showed that dehydration produces complex structures with heterogeneous hydration states, some of which are stable (not transient) and remain at the end of the experiment. The evolution of other structural parameters (interlayer water content, layer thickness fluctuation) was consistent with previous reports of smectite hydration. For bihydrated layers, the amount of water molecules per interlayer cation indicated the presence of water molecules both coordinated and non-coordinated to the interlayer cation. The transition from bi- to mono-hydrated layers produced the maximum structural heterogeneity, with (1) strong interlayer thickness fluctuation (in individual layers), and (2) the presence of several elementary mixed-layer structures. In contrast, the transition from mono-hydrated to dehydrated layers occurs homogeneously within layers. Finally, the decrease in thickness of mono-hydrated layers only implied the removal of some water molecules forming the hydration shell of the interlayer cation.

Keywords: Crystal structure, smectite-water, diffusion, water in smectite interlayer, order-disorder, mixed-layering, XRD data, smectite, montmorillonite