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

INTRODUCTION

Smectite is a clay mineral that occurs in many surface environments, both terrestrial and marine, frequently as one of the main mineral components. The expandability properties of its interlayer space and the resulting large surface area make it a main control of the physical and chemical behavior of the environments where it is found. Thus smectite is important in many applications; e.g., in agriculture (to retain and release water and nutrients), in civil engineering (for controlling ground properties), for industrial applications (making use of the large active surface area), in the construction of waste repositories (providing impermeable barriers to retain pollutants), including those for nuclear waste containment, etc. However, as smectite reacts quickly to changing environmental conditions, it can display a wide range of structural states that can depend strongly on cation exchange, temperature, or relative humidity (RH). Such modifications involve differences in hydration/dehydration states that can alter significantly the properties of smectite. Indeed, the change in volume that results from dehydration can cause a dramatic modification of the bulk texture of the material, induce the formation of cracks, and lead to a strong alteration of water migration paths. Thus dehydration will reduce the efficiency of a smectite waste barrier and could lead to fluid and pollutant flows in and out of a repository. In this respect, the establishment of a realistic model of smectite behavior requires a good understanding of the organization of water and its hydration/dehydration mechanism occurring at each scale of observation. At the crystal scale, smectite structure most often exhibits, within the same crystallite, layers with different interlayer water configurations (Cases et al. 1992, 1997; Bérend et al. 1995; Cuadros 1997; Calarge et al. 2003; Ferrage 2004; Michot et al. 2005; Ferrage et al. 2005a, 2005b, 2007). This effect can be quantified by comparing X-ray diffraction (XRD) profiles with patterns calculated assuming a random interstratification of layers exhibiting different hydration states (Ferrage 2004; Ferrage et al. 2005a, 2005b, 2007).

This paper reports on a detailed characterization of the structural dehydration process of a calcium-saturated low-charge montmorillonite reference sample (The Clay Mineral Society Source Clay, SWy-2). In part I of the present study, we assess the evolution of the smectite structure subjected to dehydration between 25–125 °C by systematically comparing the experimental XRD patterns with calculated models, to obtain the proportion of layers with defined hydration states. Additional structural parameters, such as the thickness of hydrated layers and the water content, are also assessed. The obtained evolution of structural parameters will be used in part II of this paper to propose a kinetic model of smectite dehydration that can be used for the prediction of structural changes of this mineral.