Interstratified kaolinite-smectite: Nature of the layers and mechanism of smectite kaolinization

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ABSTRACT

This study aims to contribute to a better understanding of the nature and evolution mechanism of interstratified clay minerals. We examined the <2 μm or <0.2 μm size fraction of interstratified kaolinite-smectite (K-S) formed by hydrothermal and hydrogenic alteration of volcanogenic material from a Tortonian clay deposit (Almería, Spain), a weathered Jurassic bentonite (Northamptonshire, England), and a weathered Jurassic bentonite (Northamptonshire, England). The methods used were X-ray diffraction analysis (XRD) of random and oriented preparations, thermogravimetry, chemical analysis, and 29Si MAS nuclear magnetic resonance. The proportions of kaolinite and smectite in K-S (%K) were determined by fitting the XRD patterns of ethylene-glycol-saturated samples with patterns calculated with the NEWMOD computer program. The obtained range of compositions is 0–85% K. A comparison of the results from the various techniques showed non-linear relationships, indicating that the layers in K-S are complex and hybrid in nature. The smectite-to-kaolinite reaction is a solid-state transformation proceeding through formation of kaolinite-like patches within the smectite layers. The process consists of several non-simultaneous stages: (1) removal of parts of the tetrahedral sheet, resulting in formation of kaolinite-like patches; (2) layer collapse to ~7 Å where the kaolinite-like patches are sufficiently large; (3) Al for Mg substitution in the octahedral sheet, simultaneous or slightly delayed with respect to layer collapse, causing a layer-charge decrease and loss of interlayer cations; (4) Si for Al replacement in the tetrahedral sheet and further loss of interlayer cations. Iron remains in the kaolinite or is lost at the latest stages of the process.

Keywords: Crystal structure, kaolinite-smectite, solid-state transformation, TGA, XRD

INTRODUCTION

Phyllosilicates are ubiquitous in the Earth’s crust. They may be transformed into other phyllosilicates through a sequence of intermediate interstratified phases. Mixed-layer phyllosilicates are critical in many processes (e.g., soil formation, diagenesis, plant growth) and, therefore, they are relevant and fundamental to science and economics. Despite the considerable body of literature on these mineral phases, there is still debate on the nature of the individual layers and what their transformation mechanisms are.

In contrast to phyllosilicate end-members, mixed-layer phases are composed of two or more different layer types that coexist within crystals. The classic interpretation of the nature of mixed-layering assumed that the layers of the interstratification were identical to the end-member species (Weaver 1989). However, several studies of illite-smectite have provided evidence for the existence of “polar layers” (Lagaly 1979; Altaner et al. 1988; Cuadros and Linares 1995; Jakobsen et al. 1995; Stixrude and Peacor 2002), i.e., layers in which the two tetrahedral sheets have different chemical compositions, one smectite-like and the other illite-like, resulting in the two tetrahedral sheets across every interlayer having the same character, smectite-like or illite-like. The implications of this finding are significant because it suggests that the centers of the building process in mixed-layer phyllosilicates are the interlayers, not the layers.

Two mechanisms are usually proposed for phyllosilicate transformation through mixed-layer phases: (1) conversion in the solid-state by atom rearrangement with the interlayer as the main route for atom diffusion in and out the structure; (2) dissolution of the original mineral and crystallization of the new structure. Evidence for both mechanisms has been reported (solid-state transformation of illite-smectite: Cuadros and Altaner 1998; Lindgreen et al. 1991, kaolinite-smectite: Amouric and Olives 1998; Hughes et al. 1993, biotite-vermiculite: Środoń 1999, and dissolution-crystallization of illite-smectite: Inoue et al. 1988; Środoń et al. 2000, kaolinite-smectite: Środoń 1980; Delvaux et al. 1989, glauconite-smectite: Buatier et al. 1993). It seems that the solid-state transformation mechanism prevails in weathering environments. In diagenetic and hydrothermal environments, the occurrence of either solid-state transformation or dissolution-crystallization appears to be largely controlled by fluid/rock ratio, with a high ratio favoring dissolution-crystallization. In our view, the solid-state transformation mechanism is more consistent with a polar layer structure and the central role of the interlayer in the reaction, because it suggests that the reaction occurs in the limited tetrahedral-interlayer-tetrahedral region, rather than affecting entire crystals, as dissolution would do.

The purpose of the present study was to investigate the possible layer polarity of kaolinite-smectite (K-S) and the mechanism of K-S formation and evolution. We chose to examine K-S because the very different structure (1:1 vs. 2:1) and composition...