The fate of smectite in KOH solutions

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ABSTRACT

The aim of the present study was to investigate the detailed evolution of the SAz-1 smectite in 1 M KOH at 80 °C at a solid/liquid ratio of 1/80. AFM observations indicated no change in crystal size or shape. XRD measurements at 40% relative humidity revealed changes in expandability of the smectite. The (001) reflection profile of smectite was modeled using a trial-and-error approach. The results indicate that with increasing run time, the number of non-expandable layers with zero or one water layer increases and that the coherent scattering domain size of the smectite decreases. IR spectroscopy of the reacted smectite suggests that there is no change from the initial clay products. The dehydroxylation temperature showed a slight decrease from 619 to 605 °C. STA measurements demonstrated that the cis-vacant character of the octahedral sheet remained nearly unchanged throughout the experiment. Determination of the average layer charge showed a continuous increase from 0.32 to 0.42 eq/(Si/Al)O10, whereas the layer charge distribution indicated the appearance of high charged smectite layers with a charge of ~ 0.6 eq/(Si/Al)O10 and the disappearance of the low charged layers. XPS and SEM measurements indicated an increase of Al in the smectite samples. Isotope data support the theory of an internal diffusion mechanism by gradual changes in δ18O values.

From these data it appears that KOH solutions provoke a mineralogical change in the 2:1 layer of the smectite minerals that increases the layer charge by increasing the Al content. This mineralogical change does not involve dissolution/crystallization processes and then must show solid-state transformation of the clays at 80 °C.

Keywords: Smectite, illitization, solid-state transformation, KOH

INTRODUCTION

In 1997, at the end of a workshop dedicated to Victor Drits by the French Clay Group, Bernard Kübler proposed that it would be a great help if the speakers would give their definitions of vermiculite, high-charge smectite, and illite at the beginning of their talks. As a matter of fact, a look through the literature reveals that the terms used for expandable layers in the smectite-to-illite reaction are just operationally defined and, as such, they do not necessarily coincide with definitions from the nomenclature committee of the Association international pour l’étude des argiles. The aim of our study was to investigate the fate of smectite during a possible smectite-to-illite transformation. The question, then, is whether smectite is just a passive partner in the reaction giving the ingredients for the new phase illite? Or is illite perhaps smectite with a higher charge, and smectite collapse occurs only when K⁺ is supplied to the high-charge interlayer sites?

Chemical compositions of diagenetically altered shales, sandstones, or bentonites studied by Srodon et al. (1986), Nadeau and Bain (1986), Awillier (1993), and Cuadros and Altaner

(1998) indicate the formation of high-charge expandable layers together with the illitization process. The experimental illitization of smectite indicates that the proportion of high-charge layers increases followed by K fixation and subsequent illitization (Whitney and Northrop 1988). The high-charge but exchangeable layers are similar to the vermiculitic component described by Shutov et al. (1969) and Drits et al. (1997). As a result, a randomly interstratified illite/smectite (R0 I/S) mixed-layer structure has three components: one fully expandable (smectite), one partially expandable (vermiculite), and one non-expandable (illite). This means that the smectite-to-illite transformation must involve the vermiculitization of the smectite layers through the formation of high-charge, tetrahedrally substituted layers from the original clay (Drits 1985). Meunier et al. (2000) described this process as the vermiculitization of smectite interfaces. In their model, the low-charge montmorillonite is transformed into a high-charge vermiculite that remains partly expandable (one water layer or one ethylene glycol layer at 80% relative humidity) if the interlayer is not K⁺- or NH4+-saturated. A vermiculite interlayer leads to the formation of illite when K or NH4 is supplied. But how are smectite particles transformed during their transition to R0 I/S?

Two processes may control the reaction: solid-state transforma-

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