Nature of rehydroxylation in dioctahedral 2:1 layer clay minerals

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ABSTRACT

Rehydroxylation of the previously dehydroxylated dioctahedral 2:1 layer clay mineral occurs preferentially in specific sites within the former octahedral sheet. The rehydroxylation of dehydroxylated Al-rich and Al,Mg-rich 2:1 layers occurs as trans-vacant (tv) structural arrangements, regardless of whether the initial structure was tv or cis-vacant (cv). In nontronite (Fe-rich 2:1 layer clay), the dehydroxylate pseudo-cv structure is probably directly reconstructed into the rehydroxylated cv structure without migration of octahedral cations. Rehydroxylation occurs preferentially in the R3+·O-R3+ former octahedral structural arrangements (O = residual oxygen) over R2+·O-R (R = R3+ or R2+ = Al3+, Fe3+, or Mg2+, Fe2+). In the case of the R2+ octahedral substitution, the interlayer cation is attracted to the electrostatically undersaturated residual oxygen of the R3+·O-R arrangement, which blocks the ability of water molecules to pass through the ditrigonal cavity and rehydroxylate the previously dehydroxylated local arrangement. The pyrophyllite-like type of octahedral R2+·O-R3+ arrangements, formed due to the lack of tetrahedral substitution and resulting in the absence of interlayer cations, is thus favored for rehydroxylation over the mica-like R3+·O-R2+ arrangements where Al occurs in the tetrahedral sheet. The valence of the interlayer cation and the charge density of the 2:1 layer clay mineral, which controls the interlayer cation content, also affect the degree of rehydroxylation. Dehydroxylated 2:1 layer minerals with a high-rehydroxylation potential, including beidellite and illite, use all the adsorbed water molecules that persist above 200 °C for rehydroxylation; the water vapor from the ambient environment also becomes a source of H2O molecules for rehydroxylation. The high demand for water molecules to use for rehydroxylation results in a noticeable gain of mass in the temperature interval between 200 and 350 °C even during heating.

Keywords: Rehydroxylation, dehydroxylation, beidellite, montmorillonite, illite, aluminoceladonite, pyrophyllite

INTRODUCTION

Dehydroxylation

Dioctahedral 2:1 layer clay minerals have the characteristic structure of a sheet of octahedrally coordinated cations shared between two sheets of tetrahedrally coordinated cations. The octahedral sheet comprises three symmetrically independent cation sites differing in their arrangement of OH groups and O atoms coordinating octahedral cations. In the trans octahedra, the OH groups occupy opposite apices, whereas in the cis octahedra, the OH groups form a shared edge. Dioctahedral smectite structures may be pure trans-vacant (tv) or cis-vacant (cv) and comprise interstratified cv and tv layers (Tsipursky and Drits 1984). According to these authors, the beidellite and nontronite series has only a tv structure, whereas montmorillonite in which the layer charge is generated in the octahedral sheet may have either a cv or tv structure, but the cv montmorillonite occurs more commonly. Aluminoceladonite is considered to have a tv structure, similar to a most common illite; however, pure cv illite has been recognized in several environments along with cv illite fundamental particles in mixed-layered illite-smectite (Zviagina et al. 1985; Drits et al. 1993; Reynolds and Thomson 1993; McCarty and Reynolds 1995; Drits et al. 2006, 2010; Drits and Zviagina 2009).

During gradual heating over a broad temperature range (e.g., 25–1000 °C), 2:1 layer clay mineral structures exhibit two distinct mass-loss effects that emit water molecules. The low-temperature (≤250 °C) thermogravimetric (TG) effect is caused by the dehydration of adsorbed water molecules. However, in pure smectite, some of the water molecules adsorbed on interlayer cations persists even above 400 °C (El-Akkad et al. 1982; El-Barawy et al. 1986). The high-temperature TG effect from dehydroxylation occurs between 350 and 800 °C because of the liberation of a water molecule formed by two adjacent OH groups that leaves one residual oxygen atom in the structure:

\[(\text{OH})_n \rightarrow n \times \text{H}_2\text{O} + n \times \text{O} \]  \hspace{1cm} (1)

where n is the number of water molecules eliminated during dehydroxylation.