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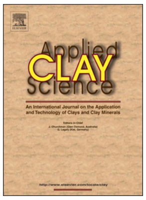

Research paper

Rehydroxylation in smectites and other clay minerals observed in-situ with a modified thermogravimetric system

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A B S T R A C T

Dehydroxylation-rehydroxylation experiments were performed on various dioctahedral aluminous 2:1 layer clay minerals using the precise thermogravimetry (TG) system equipped with a continuous N_2 gas flow enriched with H_2O vapor of controlled concentration. The setup and rehydroxylation conditions applied are specifically sensitive to study in-situ rehydroxylation of smectites with various octahedral compositions and vacancy, saturated with counterions in various sizes and valences. Under the conditions applied, the pyrophyllite structure does not rehydroxylate, illite shows a minor ability to rehydroxylate, and smectites present an entire range of potential rehydroxylation, from remaining in the completely dehydroxylated state to an almost complete rebuild of the octahedral sheet.

The mass gained during single- or multi-isotherm rehydroxylation matches the mass lost during the subsequent (secondary) dehydroxylation. In smectites, the Al-pyrophyllite-like arrangement is preferentially rehydroxylated, but at higher degrees of rehydroxylation, OH groups in other octahedral arrangements are also rebuilt. Among the temperatures tested, smectites and illite rehydroxylate most intensively during isothermal heating at 400 °C (H_2O content = 0.28 mol H_2O/m^3), which is the onset temperature of dehydroxylation of their rehydroxylated forms. The smectites capability to rehydroxylate comes from an interplay of the counterions' size, the tetrahedral substitution in the 2:1 layers, and the negative charge generated in the former-octahedral sheet that controls the ability of cations to move from the surface of the tetrahedral sheet or from the octahedral sheet back to the interlayer.

The conventional $(\text{time})^{1/4}$ power law and the logarithmic kinetic models of rehydroxylation produced good fits of the experimental data. Calculation of activation energies (E_a) for the rehydroxylation reaction produced values from 30 kJ/mol to 173 kJ/mol, highly dependent on the interlayer cation, 2:1 layer structure, and the experimental protocol. The kinetic models developed for rehydroxylation at temperature near ambient remain valid for the experiments up to 400 °C. At 500 °C the mechanism of rehydroxylation is influenced by other factors.

1. Introduction

Upon heating, firing, explosion, earthquake tectonic friction, or meteoritic impact shock clay minerals dehydroxylate (Hirono and Tanikawa, 2011; Gavin et al., 2013; Clegg et al., 2012; Hamilton and Hall, 2012). Dehydroxylation proceeds by the liberation of a water molecule formed by two adjacent OH groups, leaving a remaining residual oxygen atom (O_r) in the structure:

$$(OH)_{2n} \Rightarrow nH_2O + nO_r \qquad (1)$$

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

In the 2:1 layer silicates, the newly formed water molecule passes through the ditrigonal cavity in the tetrahedral sheet and diffuses through the interlayer space out of the crystallite (Gualtieri and Ferrari, 2006). If the interlayer space is not wide enough for H_2O to migrate, as is the case for micas, collapsed smectites, or pyrophyllite, or if the ditrigonal cavity is blocked by interlayer cations, the molecule reacts back with the residual oxygen i.e. the structure is rehydroxylated (Stackhouse et al., 2004; Molina-Montes et al., 2010). This process repeats until the temperature increases to the point at which the total motion energy of newly formed H_2O molecules is high enough to overcome the attractive interlayer forces (Drits et al., 2012a, 2012b).

Eq. (1) is entirely true only for dioctahedral 2:1 layer species, where the presence of octahedral vacancy allows the reaction to proceed. The dioctahedral structural arrangement transforms into a five-fold coordinated bipyramidal structure but the tetrahedral sheets sandwiching the former-octahedral sheet remain intact. Dehydroxylation of trioctahedral 2:1 and 1:1 layer clay minerals, however, is associated

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with simultaneous breakdown of the layer structure thus the dehydroxylated phases no longer resemble a phyllosilicate (Drits et al., 2012a; Drits and Derkowski, 2015 and references therein).

During heating, dioctahedral 2:1 layer clays dehydroxylate at temperatures between 300 °C and 800 °C, while trioctahedral ones require temperatures of at least 700 °C (e.g. Vedder and Wilkins, 1969; Kawano and Tomita, 1991a; Kuligiewicz and Derkowski, 2016). The actual temperature of the dehydroxylation of dioctahedral species depends on the type of octahedral vacancy (usually >600 °C for *cis-vacant*, <600 °C for *trans-vacant*), crystallite thickness, and the octahedral cation composition (Drits et al., 2012a). Differential thermal analysis (DTA) and differential scanning calorimetry (DSC) experiments on clay minerals showed that at the temperature usually much higher than the temperature of dehydroxylation, and always above 800 °C, dehydroxylated dioctahedral 2:1 layer minerals undergo structure breakdown and new phases are formed (Guggenheim and Koster van Groos, 2001; Che and Glotch, 2012).

When submerged in water or exposed to water vapor, dehydroxylated clays rehydroxylate. Rehydroxylation is primarily controlled by the ability to rehydrate as the H_2O molecules have to enter the octahedral sheet through a ditrigonal cavity after migrating via interlayer space, in a direction opposite to that of H_2O gradient during dehydroxylation. Therefore, rehydration after dehydroxylation (Kawano and Tomita, 1991b; Emmerich et al., 2001) can be a proxy for rehydroxylation because the same initiating mechanism is required for both processes (Derkowski et al., 2012a, 2012b). Except Fe-rich 2:1 layer clays, all rehydroxylated dioctahedral 2:1 layer minerals have a *trans-vacant* arrangement of octahedral cations, regardless of their initial octahedral vacancy, while the Al-pyrophyllite type octahedral arrangement seems to be the preferred site for rehydroxylation (see Derkowski et al., 2012a and references therein).

Due to expandability, structural variability, and cation exchange properties, smectites are unique minerals to test the influence of interlayer opening as well as the size and occupancy of interlayer cations (counterions) on dehydroxylation and rehydroxylation of 2:1 layer clay minerals. Small dehydrated interlayer cations enter ditrigonal cavity and bind to the residual oxygen of the dehydroxylated layer (Emmerich et al., 1999; Muñoz-Santiburcio et al., 2012). The bond strength between O_r and the counterion, and the ability to break that bond, that results in moving the cation back to the interlayer (Kawano and Tomita, 1991b; Emmerich et al., 2001) seems to control the capability of rehydroxylation.

Qualitative study of rehydroxylation in smectite is readily available by X-ray diffractometry (via rehydration tests; Kawano and Tomita, 1991b; Emmerich et al., 2001) or Infrared Spectroscopy (IR; Vedder and Wilkins, 1969; Clegg et al., 2012; Derkowski et al., 2012a), especially in-situ when using temperature chambers. Although dehydroxylation can also be quantified by both of these common methods (Malhotra and Ogloza, 1989; Drits et al., 2011, 2012b), thermogravimetry remains the most precise and independent approach (Drits et al., 2012a).

Using multi-cycle heating and cooling thermogravimetric (TG) experiments Derkowski et al. (2012a) showed that all Al-rich dioctahedral smectites rehydroxylate spontaneously even under extremelly low moisture content occurring in a TG chamber and that the adsorbed H_2O molecules reconstruct OH groups, while ideal montmorillonites (no tetrahedral charge) resist rehydroxylation. Following Kawano and Tomita (1991b) and Emmerich et al. (2001), those authors observed a role of interlayer cations in the rehydroxylation potential. Although Derkowski et al. (2012a) did not control the environment of rehydroxylation in the TG chamber, trends observed in numerous experiments suggested that in-situ observations of rehydroxylation could be used semi-quantitatively and linked to certain smectite structures.

Smectite and interstratified illite-smectite minerals are common in raw clays used to produce ancient and modern ceramic. Combined with gravimetry under controlled environment, rehydroxylation has been used as a valuable tool for archeological dating of ancient ceramic artifacts (RHX dating). In the dating procedure, a rehydroxylated fraction of a material and the rate of rehydroxylation in the given material have to be determined in laboratory experiments. Subsequently, the values are substituted into an assumed long-term kinetic model, which returns time elapsed from the firing of a clay (e.g., Wilson et al., 2009; Hamilton and Hall, 2012). The reaction rate is a function of the reaction temperature and the actual state of the material subjected to rehydroxylation, which are controlled by the raw clay composition and the clay firing temperature (Tosheva et al., 2010; Hall et al., 2013; Le Goff and Gallet, 2014; Gallet and Le Goff, 2015). The mechanism of ceramics rehydroxylation is still under debate and the crystallographic explanation of the process is lacking (Hamilton and Hall, 2012).

Recent developments in thermal analysis allow quick and accurate quantitative in-situ dehydroxylation-rehydroxylation tests in a controlled environment, distinguishing rehydroxylation from rehydration, and providing insight into the mechanism of rehydroxylation in 2:1 layer clays. The present study aims at testing the rehydroxylation potential and kinetics of dioctahedral smectites with various octahedral sheet compositions and counterions, using the TG technique, in order to determine how these species fit the currently known models of rehydroxylation.

2. Materials

Three dioctahedral smectite samples from the Clay Minerals Society's (CMS) Source Clay Repository were selected to represent different octahedral compositions, layer charge, and charge location, namely: high-charge Mg-rich montmorillonite SCa-3 (designated as “Otay” hereafter), a low-charge *cis-vacant* (*cv*) beidellitic montmorillonite SWy-2, and a medium-charge *trans-vacant* (*tv*) beidellite SBId-1 (for classification see Emmerich et al., 2009). Standard chemical treatment and centrifugation methods were used to separate a <0.1 μm size fraction from the beidellite and SWy-2 bulk samples, and a <1.0 μm fraction from the Otay bulk sample (Jackson, 1969). These fraction sizes allowed obtaining the least non-smectite impurities, which was tested by XRD. The SBId-1 beidellite fraction contains minor fine-crystallite kaolinite with some smectitic interlayers. Each separated fraction was split into portions that underwent multiple saturation with Cs^+, K^+, Li^+, Ca^{2+}, or La^{3+}, followed by dialysis in deionized water to remove excess salt and drying at 60 °C (Steudel and Emmerich, 2013). The saturation procedure allows controlling the interlayer counterions composition in smectites.

The natural smectites were complemented by a high-defect KGa-2 and low-defect KGa-1 kaolinites from the CMS repository, pyrophyllite from Shokozan Mining Co. (Japan), and RM30 a Mg-poor *tv* 1*M* illite from the Silver Caldera, San Juan Mountains, CO, USA (Drits et al., 2012a, 2012b; Drits and Derkowski, 2015).

3. Methods

Smectites reach their maximum potential of rehydroxylation when dehydroxylated to at least 70% (Derkowski et al., 2012a). To keep samples able to rehydroxylate, the maximum temperature reached in the primary dehydroxylation run needs to be lower than the temperature at which the dehydroxylated 2:1 layer structure breaks down, assuming that after the structure breakdown a sample is no longer a 2:1 layer mineral. Following the works of Guggenheim and Koster van Groos (2001) and Che and Glotch (2012), who used experimental conditions similar to the present study, the temperature of 800 °C was adapted as the upper limit for dehydroxylation that ensures that no structure breakdown occurs.

The experiments were performed using the TA Discovery thermal analyzer (TA Instruments, USA) equipped with an infrared thermal chamber allowing fast and precise heating and cooling. TG weighing