

Supplemental Discussion to
“Nature of rehydroxylation in dioctahedral 2:1 layer clay minerals”
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In the initial review of the manuscript ‘Nature of rehydroxylation in dioctahedral 2:1 layer clay minerals’ several significant questions were raised about the nature of dehydroxylation in dioctahedral clay minerals. A comprehensive discussion on this issue is beyond the scope of the primary paper, but may be valuable in the understanding of the dehydroxylation and rehydroxylation processes for some readers. The following supplemental discussion corresponds to the questions raised and forms an extended reference to the discussion in the paper.

Homogenous vs. heterogeneous dehydroxylation of dioctahedral 2:1 layer silicates

Guggenheim et al. (1987) and Guggenheim (1990) developed a commonly accepted model describing the dehydroxylation reaction of pyrophyllite and related dioctahedral 2:1 layer silicates as a heterogeneous process. According to this model, the main factor affecting the thermal stability of the octahedral sheet is the Al-OH bond strength. The formation and loss of the first portion of H₂O molecules in the octahedral sheet of the 2:1 layer increases the strength of the bonds between the octahedral cations and hydroxyl oxygen of the OH groups remaining in the layer. Because it was assumed that the intermediate structures are stable, it was concluded that complete dehydroxylation did not proceed spontaneously. Therefore, higher temperature and activation energy are required to form a new portion of H₂O molecules in the layer from the intermediate semi-dehydroxylated structure. This model has been evoked to explain the broad dehydroxylation temperature range.

Using pyrophyllite as a simplest structural model for dioctahedral 2:1 layer silicates, various researchers (e.g. Stackhouse et al. 2004; Sainz-Díaz et al. 2004; Molina-Montes et al. 2008a, b) applied quantum mechanical calculations to simulate the occurrence of a great variety of intermediate structures formed during the dehydroxylation reaction and assumed they are stable phases. Therefore, those authors also suggested that the dehydroxylation of pyrophyllite and related dioctahedral 2:1 phyllosilicates is a heterogeneous reaction. For example, Wang et al. (2002) observed two ν (OH) bands at 3690 and 3702 cm⁻¹ in the IR spectrum of the dehydroxylated pyrophyllite sample and concluded that those bands originate from the intermediate pyrophyllite dehydroxylation phase, which is in agreement with the models by Guggenheim et al. (1987) and Sainz-Díaz et al. (2004). However, the intermediate phase model is not the only explanation for this IR observation. Perez-Rodriguez et al. (2010) also found the same new ν (OH) bands in the IR spectrum of dehydroxylated pyrophyllite as did Wang et al. (2002), but only after extensive rehydroxylation under high temperature and water-saturated conditions. There were no new IR bands observed after dehydroxylation with increasing temperature. Therefore the new ν (OH) bands found in the pyrophyllite studies by Wang et al. (2002) and Perez-Rodriguez et al. (2010) clearly resulted from rehydroxylation.

The apparently stable intermediate semi-dehydroxylated pyrophyllite phase, suggested by Guggenheim et al. (1987) and Guggenheim (1990) and predicted based on quantum mechanical calculations, has never been confirmed by experiments involving kinetic analysis and structural transformations of natural samples. Perez-Rodriguez et al. (2010) and Drits et al. (2011b) conducted thermal experiments along with careful structural analysis, but did not find any evidence of stable intermediate structure derivatives during pyrophyllite dehydroxylation of.

Using different kinetic analysis approaches, Perez-Rodriguez et al. (2010) and Drits et al. (2011a) showed that the activation energy of dehydroxylation is independent of the progress of the reaction. These authors independently found that the broad temperature interval of pyrophyllite dehydroxylation is related to particle size distribution, which agrees with the results of Perez-Maqueda et al. (2004). Moreover, the partial dehydroxylation of pyrophyllite follows a homogeneous, zero-order kinetic reaction (Drits et al., 2011b). Using quantum mechanical calculations, Molina-Montes et al. (2010), came to the conclusion that intermediate semi-dehydroxylate derivatives are not stable and rehydroxylation is highly favorable, which is consistent with the experimental studies. A new experimental study with data from a wide variety of clay structures by Drits et al. (in review) challenges the intermediate structural model of dehydroxylation for all dioctahedral Al-rich 2:1 layer clay structures. This study recognizes it is possible that the dehydroxylation reaction in dioctahedral 2:1 layer silicates could be heterogeneous. However, at present the only clear experimental (negative) evidence about the occurrence of intermediate semi-dehydroxylated phases that may occur in 2:1 layer silicates is with pyrophyllite. In the present paper interpretations about a heterogeneous or a homogenous dehydroxylation, reaction is not attempted.

The expression “semi-dehydroxylate structure” is a descriptive term that is commonly used in publications about models of dehydroxylation in dioctahedral 2:1 layer silicates. These models refer to a semi-dehydroxylate structure that forms when dehydroxylation progresses during heating isothermally or at a constant rate. However, such a structure can also form for example when dehydroxylated layers regain some OH from the environment during cooling following the maximum dehydroxylation temperature. In the present study, progressive rehydroxylation produced semi-dehydroxylated structures that are locally rehydroxylated, and resulted in the coexistence of R-O_r-R and R-OH-R arrangements within the same layer. This rehydroxylation mechanism needs to be distinguished from the formation of an intermediate semi-dehydroxylate phase formed during progressive dehydroxylation (Guggenheim et al., 1987; Stackhouse et al., 2004; Sainz-Díaz et al., 2004; Molina-Montes et al., 2008a, b). However, semi-dehydroxylated structures may form from these mechanisms at the same time during localized rehydroxylation that competes with progressive dehydroxylation (Molina-Montes et al., 2010; Perez-Rodriguez et al., 2010). This concept requires further studies.

The ν (OH) frequencies of rehydroxylated specimens.

Important evidence to consider regarding an intermediate semi-dehydroxylated vs. rehydroxylated structure is that samples heated beyond the temperature of complete dehydroxylation and then allowed to rehydroxylate have ν (OH) IR frequencies from OH groups that must have reformed during the rehydroxylation process, and could not be from an intermediate semi-dehydroxylated structure formed during dehydroxylation. For example, at a heating temperature of 800°C the S037 pyrophyllite dehydroxylates completely and any remaining non-dehydroxylated portion left would have to be from *cv* layers (Drits et al., 2011 b). However, the ν (OH) frequency at 3675 cm⁻¹, of the major OH band that occurs in the rehydroxylated pyrophyllite, corresponds to the *tv* portion of S037 pyrophyllite which dehydroxylates completely at temperatures much lower than 800°C (Drits et al., 2011a,b). Therefore, these ν (OH) frequencies in the FTIR spectrum from the rehydroxylated pyrophyllite in this study cannot be from an intermediate semi-dehydroxylated phase formed during dehydroxylation but instead the evidence indicates that these ν (OH) bands are from the

formation of a rehydroxylated *tv*-structure, as with all other 2:1 layer clay structures examined in this study.

The semi-dehydroxylated structures formed during localized rehydroxylation, have both R-O_r-R and R-OH-R arrangements within the same layer. The rehydroxylated R-OH-R groups may be different from those in the initial sample, because the reformed OH groups are separated by the vicinal R-O_r-R groups. If the non-rehydroxylated portions of a structure affect the bond strength of the OH groups reformed within the same sheet, the bonds between the octahedral cation and the hydroxyl oxygen should be stronger than in the untreated sample. As a result, the bonding between O and H within the reformed OH group is weaker, and the ν (OH) from the rehydroxylated R-OH-R environment would then be shifted toward lower frequencies compared to the ν (OH) from same cations-OH pair in the untreated sample (Guggenheim, 1990, Evans and Guggenheim, 1988). While the lower IR frequency was observed from nontronite experiments, they have not been recognized in any other samples. In contrast, other 2:1 layer structures all show an opposite relationship in ν (OH) with dehydroxylation and rehydroxylation. For example, the FTIR spectrum from a partially rehydroxylated pyrophyllite specimen is distinctive. Even though the rehydroxylated Al-OH-Al arrangements are surrounded by Al-O_r-Al there is no noticeable shift in the main OH band (3675 cm⁻¹) to a lower frequency and new ν (OH) bands appear only with higher frequencies. This observation shows that the influence of Al-O_r-Al bonds on the OH vibration frequency is negligible. The origin of the additional ν (OH) bands in the rehydroxylated pyrophyllite from this study, from Perez-Rodriguez et al. (2010), and Wang et al. (2002) is not known at the present time.

Octahedral vacancy in partially rehydroxylated nontronite

During dehydroxylation of nontronite, glauconite, and celadonite, the migration of Fe from a *cis*-site to the vacant *trans*-site results from lengthening the Fe-O_r-Fe distance in the former *tv* Fe³⁺-OH-Fe arrangement beyond the acceptable limit of the *b* unit cell dimension (Muller et al., 2000b, c; Kogure and Drits, 2010). Therefore, the migration of octahedral cations during dehydroxylation of Fe-rich dioctahedral 2:1 layer clays must be accompanied by a positioning of the O_r atom in one of the former OH locations.

In the present study the rehydroxylated nontronite is interpreted to be a *cv* structure although the temperature of dehydroxylation in the MDTG interval is the same as that of rehydroxylated Al- and Al,Mg-rich 2:1 layer clay structures that are exclusively *trans*-vacant regardless of their initial octahedral vacancy (Drits et al., 1998, Drits, 2003). Although dehydroxylation of *cv* structures usually occurs above 600°C, this elevated temperature is probably only required to provide the energy for the migration of the octahedral cations, which results in the formation of a *pseudo-tv* structure (Drits, 2003, Drits et al. 2011a, b). However, if a *cv* structure is thermally stable and the octahedral cations migration is not required during dehydroxylation, the dehydroxylation temperature of *cv* structures may be as low as that in Al- and Al,Mg-rich *tv* structures (< 600°C).

During cooling and rehydroxylation of dehydroxylated nontronite, there is not an energetic or crystal-chemical advantage for the reverse migration of Fe atoms from the occupied former *trans*-sites to the nearest vacant *cis*-sites. In the rehydroxylated nontronite structure, all the O and OH anions in the octahedral configuration are equally saturated by the trivalent cations that dominate the sheet composition. During rehydroxylation of the *pseudo-cv* nontronite dehydroxylate structure, the O_r atom protonates and becomes an OH anion without a significant

change in position and the structure remains *cv*. This mechanism is in agreement with Muller et al. (2000a, b, c) who found that the structure of dehydroxylated and subsequently rehydroxylated celadonite and glauconite has a significant amount of *cv* layers in addition to a *tv* layer portion resulting from the reverse cations migration. There are no rehydroxylated Al-rich 2:1 layer clay structures that have been shown to have a *cv* layer component.

Short cooling times, low rehydroxylation temperatures, and incomplete water saturation such as in the heating-cooling experiments and in rehydration under ambient humidity provided less opportunity and energy for the reverse migration than in the studies as by Muller et al. (2000a, b). The persistence of the *cv* structure in rehydroxylated nontronite is consistent with the shift of $\text{Fe}^{3+}\text{-OH-Fe}^{3+}$ ν (OH) frequency to the lower values.

Quantum mechanical calculations of the ν (OH) frequency in experimental studies

The predicted IR ν (OH) frequencies of dioctahedral 2:1 layer clays based on quantum mechanical calculations are difficult to apply to a detailed interpretation of the IR ν (OH) frequencies observed in natural samples. The predicted and measured ν (OH) frequencies are usually not fully consistent, which indicates that model ν (OH) frequencies are not directly applicable to the interpretation of ν (OH) frequencies from natural samples. The most significant example is pyrophyllite, which is the simplest and most homogenous 2:1 layer clay structure. Natural pyrophyllite produces a distinct FTIR band, which should correspond to the theoretically calculated ν (OH) frequency if the calculations are correct. Most theoretical ν (OH) frequency calculations published for pyrophyllite (e.g. Sainz-Díaz et al., 2004; Larentzos et al., 2007; Molina-Montes et al., 2008c) are far from the 3675 cm^{-1} value measured many times on natural *tv*-pyrophyllite samples (e.g. Besson and Drits, 1997a; Zviagina et al., 2004; Wang et al., 2002; Lantenois et al., 2007; Drits et al., 2011b). Only Botella et al. (2004) calculated a ν (OH) frequency for pyrophyllite that is consistent with the abundant experimental results. The discrepancy between the theoretical calculations and the experimental data is too great to consider the calculated values in interpretations about reaction mechanisms, where the resolution of several cm^{-1} matters significantly (e.g., Lantenois et al., 2007; Drits et al., 2011b; this study). From this standpoint, the ν (OH) frequencies predicted for an intermediate semi-dehydroxylated phase are even more questionable since there is no experimental data to verify the quantum mechanical calculations.

Influence of tetrahedral Al substitution on hydrogen bonding and the ν (OH) frequency.

The relationships between ν (OH) frequency and the nature of the octahedral cations bonded directly to the OH group, and tetrahedral and interlayer cations forming the nearest local environment around the OH group were considered in detail by Besson and Drits (1997b). These authors also linked the orientation of the OH vector (ρ) to the strength of the bonding between the hydroxyl proton and the nearest structural oxygen atoms ($\text{O-H}\cdots\text{O}$). For a given pair of octahedral cations coordinating OH group (R), the most significant factor affecting the ν (OH) frequency is the bond strength within the hydroxyl group, which is controlled by the strength and distribution of the hydrogen bonds between hydroxyl the proton and basal and apical oxygen atoms such as $\text{O-H}\cdots\text{O}_{\text{apical}}$, or the combination of $\text{O-H}\cdots\text{O}_{\text{apical}}$ and $\text{O-H}\cdots\text{O}_{\text{basal}}$. Comparison of the ν (OH) frequency and the inclining angle of the OH vector (ρ) for pyrophyllite (3675 cm^{-1}

and 26°), kaolinite and dickite (3620 cm^{-1} and 1°) that all have identical local OH environments, shows that lower $\nu(\text{OH})$ frequencies correspond to lower ρ angles. In kaolinite and dickite the distances between the hydroxyl proton and the nearest apical oxygen atoms are very short. Therefore the hydrogen bonding is proportionally stronger, which increases the interaction between the octahedral cation and hydroxyl oxygen, which decreases the $\nu(\text{OH})$ frequency to 3620 cm^{-1} . In contrast, pyrophyllite has a high ρ angle which increases the distance between the hydroxyl proton and the nearest apical and basal oxygen atoms. This longer distance results in with weaker $\text{O-H}\cdots\text{O}_{\text{apical}}$ and $\text{O-H}\cdots\text{O}_{\text{basal}}$ bonding that produces the higher $\nu(\text{OH})$ frequency in pyrophyllite than is observed in kaolinite.

A similar relationship is observed in aluminoceladonite and illite. In the aluminoceladonite, the most intense $\nu(\text{OH})$ frequency from Al-OH-Al is $\sim 3620\text{ cm}^{-1}$, which is much lower than the $\nu(\text{OH})$ frequencies from a Fe- and Mg-free illite or a muscovite. The reason for the low $\nu(\text{OH})$ frequency in aluminoceladonite is that almost all tetrahedral sites are occupied by Si, which like kaolinite produces the minimum possible ρ angle of the OH vector resulting in short bond distances between the hydroxyl proton and the nearest apical oxygen atoms. As a result, the lowest frequency of the $\nu(\text{OH})$ from the Al-OH-Al environment is observed in the FTIR spectrum of the aluminoceladonite samples (Besson and Drits 1997b). In contrast, Fe- and Mg-free muscovite has characteristically broad and poorly resolved maxima in the OH stretching vibration region where $\nu(\text{OH})$ frequencies are all higher than $\sim 3620\text{ cm}^{-1}$ despite a homogeneous octahedral composition formed exclusively by Al-OH-Al groups. The high degree of Al for Si substitution in muscovite significantly increases the ρ angle of the OH vector and thus increases the distances between the hydroxyl proton and apical oxygen atoms. The hydroxyl proton is then positioned closer to the depressed basal oxygen atom, which results in the formation of three hydrogen bonds including $\text{O-H}\cdots\text{O}_{\text{apical1}}$, $\text{O-H}\cdots\text{O}_{\text{apical2}}$, and $\text{O-H}\cdots\text{O}_{\text{basal}}$ (Gatta et al., 2011). This configuration results in weaker hydrogen bonding with the non hydroxyl oxygen atoms and is accompanied by an increase in the $\nu(\text{OH})$ frequency from Al-OH-Al environments. A $2M_1$ muscovite studied by Zhang et al., (2005) produced $\nu(\text{OH})$ frequencies of 3630 , 3645 , 3660 cm^{-1} , which is similar to those recorded by Liang et al. (1998).

Bands of similar $\nu(\text{OH})$ frequencies from Al-OH-Al environments with a variable quantity of neighboring tetrahedral Al occur also in illite. The illite structure has lower degree of Al for Si substitution, with the most probable substitution of one Al in a tetrahedral ring of six tetrahedral cations, compared to muscovite, which has roughly an equal statistical probability of one and two Al atoms per tetrahedral ring. Therefore, a greater contribution to the band with a $\nu(\text{OH})$ frequency at $\sim 3620\text{ cm}^{-1}$ from the six Si atoms in the neighboring tetrahedral ring can be expected in illite than in muscovite. Indeed, the decomposition of the FTIR spectrum from the RM30 illite sample revealed three $\nu(\text{OH})$ frequencies from Al-OH-Al arrangements at 3625 , 3640 , and 3658 cm^{-1} , with the following optical densities, 26.1, 30.06, and 25.5 %, respectively (Besson and Drits, 1997b). In the present model this sequence of $\nu(\text{OH})$ frequencies in illite reflects a progressive increase in the ρ angle of the OH vector and decreasing distances between the hydroxyl proton and the nearest apical oxygen atoms.

The validity of this model is supported by the comparison of the $\nu(\text{OH})$ frequencies from illite and beidellite. The tetrahedral Al content in beidellite is significantly lower than that in illite in which produces the highest probability of having only zero or one Al per tetrahedral ring of beidellite. The two main bands near 3620 cm^{-1} and 3670 cm^{-1} in the IR spectrum of the beidellite sample from this study correspond to the two main local Al-OH-Al environments around the OH groups, wherein one of them there is no interlayer cations and little or no

tetrahedral Al substitution which is a pyrophyllite-like environment ($\nu(\text{OH})$ at 3670 cm^{-1}). In the other local environment a single tetrahedral Al substitution occurs and the tetrahedral cavity is occupied by an interlayer cation, which satisfies the local charge imbalance. In the latter case, the ρ angle of the OH vector is low enough to provide strong hydrogen bonding in the $\text{O-H}\cdots\text{O}_{\text{apical}}$ arrangement, and results in a decrease in the $\nu(\text{OH})$ frequency to 3620 cm^{-1} . However, a comprehensive interpretation of the distribution of $\nu(\text{OH})$ frequencies related to the Al-OH-Al environment in beidellite requires a more detailed investigation due to unknown influence of interlayer water.

Experiment-based interpretations have been confirmed by studies applying molecular modeling. Using the functional density theory, Botella et al. (2004) proved the intuitive relationships that, for the same structure and composition, local tetrahedral Al substitution significantly increases the $\rho(\text{OH})$ angle, due to the hydrogen attraction to the tetrahedral sheet, while the presence of interlayer cations decreases the $\rho(\text{OH})$ angle due to mutual repulsion between the hydroxyl hydrogen and the interlayer cation. These relationships are valid for all octahedral compositions. Although Botella et al. (2004) support the correlation between the $\nu(\text{OH})$ frequency and the length of the O–H bond, rather than the $\rho(\text{OH})$ angle, their calculated $\rho(\text{OH})$ angles match perfectly the experimental relationships determined by the earlier papers.

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