

DIFFERENCES IN THE DEHYDRATION-REHYDRATION BEHAVIOR OF HALLOYSITES: NEW EVIDENCE AND INTERPRETATIONS

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Abstract—Two reference halloysites from New Zealand (Te Puke and Opotiki) were studied by X-ray diffraction under (1) various levels of relative humidity (RH) from 95 to 0% (dehydration), and (2) various temperatures increasing from 25 to 120°C (dehydration). They were also studied by differential thermal and thermogravimetric analyses at 40 and 0.2% RH. The impact of freeze drying along with the influence of cation saturation (Ca and K) on halloysite hydration were studied. The dehydration of the two halloysite samples upon decrease in RH started below 70% RH. However, the dehydration of Opotiki was still incomplete at ~0% RH regardless of the saturation cation whereas Te Puke was completely dehydrated at ~10% RH. For each sample, the decrease in RH and the increase in temperature induce similar dehydration behavior, but the dehydration processes of the Opotiki and Te Puke samples are different. The dehydration of Te Puke proceeds with one intermediate hydration state reacting as a separate phase due to the presence of ‘hole’ water molecules. The dehydration of the fully hydrated Opotiki halloysite gives a dehydrated phase and no 8.6 Å phase. The results suggest the presence of different types of water molecule, the ‘associated’ and the ‘hole’ water, controlling the dehydration behavior of halloysites. Freeze-dried halloysite samples are essentially dehydrated and the size of their coherent scattering domains is strongly reduced. Rehydration experiments performed after dehydration either at 95% RH or by immersing the sample in water for 3 months result in their partial rehydration. Calcium saturation promotes the rehydration process. The results suggest the presence of interlayer cations in the Opotiki sample, Ca ions being associated with the strongly held ‘hole’ water. As a result of this study, we assert that the (de)hydration behavior of halloysite is highly heterogeneous and cannot be generalized *a priori*.

Key Words—Dehydration, DTA-TGA, Freeze Drying, Halloysite, Heating, Hydration, Relative Humidity, Saturating Cations, Water Status, XRD.

INTRODUCTION

Halloysite is a dioctahedral 1:1 clay mineral commonly found in both weathered rocks and soils. The chemistry and structure of halloysite are similar to those of kaolinite, the fundamental distinction being the presence of interlayer water (Churchman and Carr, 1972, 1975). For halloysite-(10 Å), the fully hydrated halloysite, two water molecules per formula unit are interlayered, leading to a d_{001} basal spacing value of 10 Å. Hendricks and Jefferson (1938) and later Brindley (1961) proposed that the interlayer water molecules in halloysite-(10 Å) form hydrogen bonds with (1) one another, (2) oxygens of the siloxane plane, and (3) hydroxyls of the (opposite) aluminol plane. Because the interlayer water is highly labile when the halloysite sample is left standing in dry air, vacuum, or heating at 35°C (Larsen and Wherry, 1917; Hofmann *et al.*, 1934; Alexander *et al.*, 1943; MacEwan, 1946; Brindley and Goodyear, 1948; Giese, 1988), halloysite-(10 Å) is very susceptible to dehydrating irreversibly,

producing the dehydrated polymorph known as halloysite-(7 Å). Consequently, it is extremely difficult (if not impossible) to handle halloysite-(10 Å) without inducing some dehydration. Churchman (1970) suggested that halloysite-(10 Å) is a metastable species, halloysite-(7 Å) being the only stable form. It was reported by several authors (*e.g.* Larsen and Wherry, 1917; Hofmann *et al.*, 1934; Alexander *et al.*, 1943; MacEwan, 1946; Brindley and Goodyear, 1948; Giese, 1988) that once the interlayer water of halloysite-(10 Å) is lost, it is not restored by treatment with water. However, rehydration can be achieved indirectly through intercalation of organic compounds such as K acetate (Wada, 1961). De Souza Santos *et al.* (1966) observed that a Brazilian platy halloysite, placed in water after dehydration in open air for a few hours, can partially rehydrate.

Since halloysite is the only kaolin mineral found as a natural hydrate, a large literature exists on the dehydration of halloysite-(10 Å). The dehydration of interlayer water in halloysite is strongly affected by the relative humidity (RH; Hughes, 1966). Harrison and Greenberg (1962) reported that a Bedford halloysite from Indiana rehydrates at RH values of <90%. When the relative humidity is held at 40%, halloysite-(10 Å) from Kusatsu (Japan) dehydrates to halloysite-(7 Å) at ~40°C (Kohyama *et al.*, 1978). Hughes (1966) suggested that

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the dehydration behavior depends on the physical-chemical characteristics of the halloysite sample and on its drying history.

The dehydration process of halloysite has been debated in the literature and many hypotheses have been reported. Brindley and Goodyear (1948) proposed that halloysite-(10 Å) gave rise to just one other form, halloysite-(7 Å). They interpreted the variations in the spacings as a physical mixture of two discrete phases attributable to the hydrated phase, on the one hand, and the dehydrated phase, on the other. Nevertheless, other authors (*e.g.* Harrison and Greenberg, 1962; Churchman *et al.*, 1972; Slansky, 1985; Jones and Malik, 1994) concluded that (1) the fully hydrated and fully dehydrated states of halloysite should be considered as the end-members of a continuous series of hydration states of the mineral, and that (2) the loss of the interlayer water takes place through an interstratification in which there is a partial segregation of the hydrated (10.1 Å) and dehydrated (7.1 Å) kaolin layers. Churchman and Carr (1972) suggested that the different hydration states of halloysite corresponding to each of the various average interlayer water contents between 0 and 2 molecules of H₂O per unit-cell may occur at similar relative humidity.

Interlayer water in halloysite occurs in two different environments, as shown by Costanzo and co-workers (Costanzo *et al.*, 1980, 1982, 1984a, 1984b; Costanzo and Giese, 1985, 1990; Lipsicas *et al.*, 1985; Raythatha and Lipsicas, 1985; Giese and Costanzo, 1986) who investigated the properties of interlayer water in synthetic 10 Å kaolinite hydrate leading to a better understanding of the status of water in halloysite. The dehydration of the 10 Å hydrate results in a loss of labile water to form a stable 8.6 Å phase. As the dehydration proceeds, mixed-layered 8.6 Å and 7 Å phases are generated leading to a 7.9–7.8 Å contribution. Costanzo and co-workers identified two structural environments for the interlayer water: (1) the 'hole' water, and (2) the 'associated' water, previously introduced by Tarasevich and Bribina (1972). The 'hole' water is located in ditrigonal cavities in the basal oxygen plane of the tetrahedral sheet, forming hydrogen bonds with the basal oxygens. Smirnov and Bougeard (1999) showed, by a molecular dynamic study of the water structure, the presence of two types of 'hole' water: (1) the first type of 'hole' water is adsorbed on the surface of the silicate sheet, and oriented with its molecular HH vector parallel to the surface, the molecular dipole being inclined; (2) the second type of 'hole' water has its HH vector perpendicular to the surface, the molecular dipole being perpendicular to the surface plane.

The 'associated' water or 'ice-like' water is located at a different level in the interlayer space and has a high degree of mobility at ambient temperatures (Costanzo *et al.*, 1982; Lipsicas *et al.*, 1985). Jemai *et al.* (1999,

2000) determined the structure of 10 Å and 8.4 Å kaolinite hydrates from comparison of experimental and calculated XRD patterns. The 10 Å hydrate is characterized by two types of water molecules located at 3 Å and 3.4 Å from the hydroxyl surface over the octahedral sheet (the water molecules' positions are determined relative to *c* axis, *e.g.* normal to the hydroxyl sheet; Jemai *et al.*, 1999). For the 8.4 Å hydrated kaolinite, the most representative XRD profile is obtained by inducing translation of two adjacent layers, and characterized by one type of water molecule at 2.4 Å from the hydroxyl surface. The water molecule is inserted between the vacant octahedral site and the ditrigonal cavity of the tetrahedral sheet due to layer translation.

The interlayer water of halloysite seems to play an important role in the physical properties of this mineral (Joussein *et al.*, 2005), its exchange properties (Grim, 1968; Norrish, 1994; Joussein *et al.*, 2005), and its reactivity when in contact with organic species (Churchman and Theng, 1984; Joussein *et al.*, 2005, 2006). It is thus very important to understand fully the hydration-dehydration behavior of halloysites for a variety of industrial or environmental applications. The aim of this paper is to compare two reference halloysites to understand better their dehydration-rehydration behavior at various RH and temperature. The role of saturation cations, along with heating and freeze-drying treatments, are also investigated.

MATERIALS AND METHODS

Two samples of the reference halloysites, Te Puke and Opotiki, from New Zealand were used. The Te Puke halloysite sample was derived from rhyolite and andesite, and formed by weathering and/or hydrothermal alteration (Hughes, 1966). The Opotiki halloysite sample was derived from rhyolite and formed by weathering (Kirkman, 1977). The morphology of the Te Puke material is dominated by small tubes with a small proportion of spheroidal particles (Hughes, 1966; Churchman and Theng, 1984), whereas the Opotiki sample is almost uniformly spheroidal in shape (Kirkman, 1977; Churchman and Theng, 1984). These halloysite samples have been studied extensively and are currently used as reference materials (Theng *et al.*, 1982, 1984; Churchman and Theng, 1984; Churchman *et al.*, 1984; Churchman, 1990; Johnson *et al.*, 1990; Soma *et al.*, 1992; Newman *et al.*, 1994; Churchman *et al.*, 1995; Theng, 1995; Joussein *et al.*, 2005). The chemical composition and the cationic exchange capacity (CEC) of the halloysite samples are reported in Table 1. The two samples are quasi-pure halloysite except for the presence of a small amount of amphibole at 8.4 Å in the Opotiki sample. The two halloysites do not have the same hydration state: Te Puke is partially hydrated, as shown by the presence of a broad 001 peak ranging from

10 to 7 Å, while Opotiki is fully hydrated, with a d spacing at ~ 10 Å (Figure 1).

The raw samples were Na saturated using 1 M NaCl and the clay fractions (<2 μm) collected by sedimentation according to Stokes law. The fine clay subfraction (<0.1 μm) was extracted by continuous flow centrifugation of the whole clay fraction (<2 μm), previously Na saturated. All samples were subsequently Ca- or K-saturated using 0.5 M CaCl_2 or 1 M KCl and washed free of Ca- or K-salts. The impacts of freeze drying and heating on the hydration behavior of halloysite were studied to identify any possible adverse effects of our sample preparation techniques. The following experimental treatments were used: Ca- and K-saturated samples were (1) heated to 100°C, or (2) freeze dried; and (3) K-saturated samples resulting from treatments (1) and (2) were then Ca saturated to favor rehydration of halloysite and kept in a waterproof container for 3 months.

To understand better the dehydration behavior of halloysites and to compare their reactions to rehydration, two different XRD experiments were performed: (1) a progressive decrease in RH at constant temperature followed by a re-equilibration under a water-saturated atmosphere; and (2) an increase in temperature under

environmental RH. For the former experiment, air-dried oriented Ca- or K-saturated samples were equilibrated for 3 h under various RH from 95 to 0%, then back to 95% RH. The chamber temperature was maintained constant at $\sim 27^\circ\text{C} \pm 1$. For the latter experiment, air-dried, oriented Ca- or K-saturated samples were equilibrated for 15 min at different temperatures from ambient 25°C (T_{25}) up to 120°C (T_{120}). The temperature fluctuation in the chamber was $\sim \pm 1^\circ\text{C}$. Samples were analyzed by XRD for each step.

The samples were examined by XRD after each treatment using oriented deposits on glass slides, scanning over the basal reflection region from 3 to $15^\circ 2\theta$ $\text{CuK}\alpha$ at a rate of $0.24^\circ/2\theta/\text{min}$ using a Philips X'pert Pro diffractometer ($\text{CuK}\alpha$, 40 kV, 40 mA) equipped with a Dew Trak RH200 humidity control device coupled to an Anton Paar THC chamber with a temperature-controller device. Peak decomposition and profile analysis were carried out using the program *Origin PFM*[®] with Gaussian algorithm after background correction. Thermogravimetric analyses were carried out on Ca-saturated samples equilibrated at 40% RH and 0.2% RH using a DuPont 951 thermogravimetric analyzer (TGA) equipped with automated RH control (e.g. Carey and Bish, 1996; Fialips *et al.*, 2005). The RH

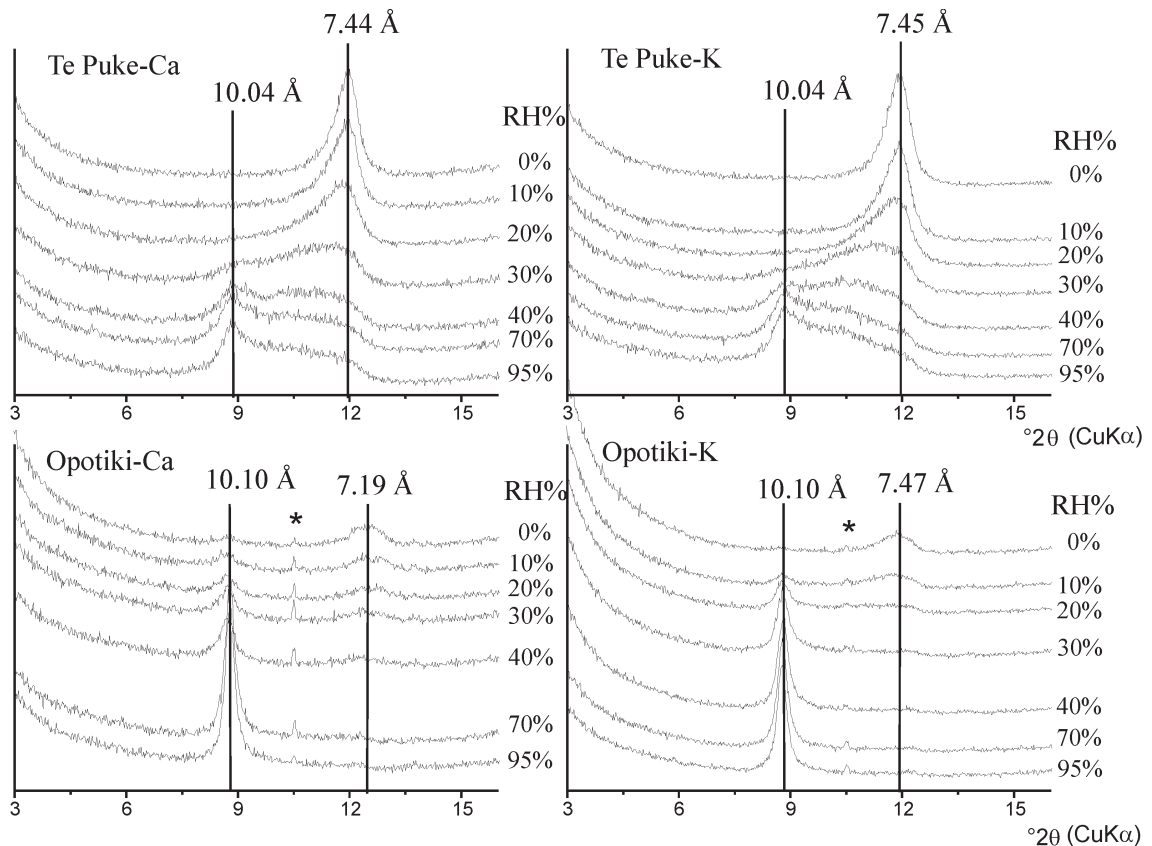


Figure 1. XRD patterns of the Ca- and K-saturated Te Puke and Opotiki halloysite samples recorded under various relative humidities (RH) decreasing from 95 to $\sim 0\%$ RH ($T = 27^\circ\text{C}$). * refers to the 8.4 Å peak due to amphibole.

was controlled by mixing water-saturated N₂ gas with dry N₂ using mass-flow controllers and the actual RH of the gas mixture was measured before entering the TGA using a calibrated Vaisala 36B humidity probe. A total mixed-gas flux of 100 cm³/min was maintained during the experiments. For each experiment, ~10–15 mg of sample were placed on the calibrated balance and first equilibrated at 23°C and the desired RH for 2 h. Weight losses were measured while heating to 900°C at 10°C/min, under constant RH.

RESULTS

Dehydration of halloysite upon decrease in relative humidity

The XRD patterns of the two halloysites acquired at 27°C under various RH decreasing from 95 to 0% are presented in Figure 1. For both halloysite samples, the XRD patterns show the decrease in intensity of the 10 Å peak relative to the 7 Å peak as RH decreases, indicating dehydration of the halloysite. However, the dehydration process is not the same for the two samples. For the Te Puke halloysite, an intermediate reflection appears between 7 and 10 Å during dehydration regardless of the exchanging cation, Ca²⁺ or K⁺. Below 30% RH, the intensity and sharpness of the 7 Å peak increase and the intensity of the broad diffraction peak between 7 and 10 Å decreases. The 10 Å peak disappears for RH <20%, indicating that the halloysites dehydration is complete. At 0% RH the XRD patterns of the Ca- and K-saturated Te Puke samples are identical.

For Opotiki halloysite, the hydrated phase seems to dehydrate without the formation of intermediates for either Ca- and K-saturated samples. The dehydration

begins at 40% RH as indicated by the presence of the 7 Å peak, which becomes dominant at RH as low as 10%. At 0% RH, a weak peak near 10 Å is still present regardless of the exchanging cation but its intensity is greater for the Ca-saturated sample than for the K-saturated sample. Moreover, the basal spacing of the dehydrated halloysite differs slightly for K- and Ca-saturated Opotiki samples, which exhibit the 7 Å peak at 7.47 and 7.19 Å, respectively. The presence of a small peak at 8.4 Å (* in Figure 1) is attributed to amphibole.

Dehydration of halloysite upon increase in temperature

The variations of the basal spacing of the Te Puke-Ca and Opotiki-Ca halloysite samples with the increase in temperature from 25 to 120°C are presented in Figure 2. These variations are similar to those obtained during the decrease in RH. With the increase in temperature, the peak at 10 Å is progressively replaced by a peak at ~7 Å for both halloysites. The dehydration of the Te Puke sample occurs *via* an intermediate peak between 7 and 10 Å, whereas the fully hydrated Opotiki sample gives rise to a dehydrated phase apparently without the formation of an intermediary phase. The 7 Å peak becomes more intense than the 10 Å peak at 40°C (T₄₀) for Te Puke and at 55°C (T₅₅) for Opotiki. The 10 Å peak of the hydrated halloysite disappears between T₄₅ and T₅₅ for Te Puke and between T₇₀ and T₉₀ for Opotiki, indicating that both halloysites fully dehydrate upon heating.

The dehydration processes observed by XRD upon increase in temperature for the fine clay fraction (<0.1 µm) of the Opotiki and Te Puke samples are similar to those observed for the bulk fractions (<2 µm) (data not shown).

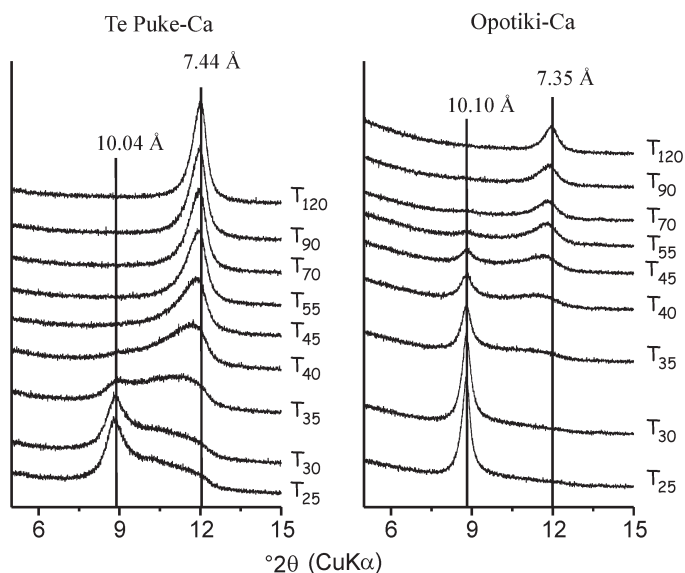


Figure 2. XRD patterns of Ca-saturated Te Puke and Opotiki halloysite samples at various temperatures increasing from 25 (T₂₅) to 120°C (T₁₂₀).

XRD peaks decomposition as a function of temperature

The results of computational fitting of the XRD profiles obtained for Te Puke at 30, 35, 40 and 50°C are presented in Figure 3. These four XRD profiles were selected as representative of the progressive decrease in intensity of the 10 Å peak upon heating along with the increase in intensity of the 7 Å peak and of the presence of an intermediate peak between 7 and 10 Å (Figure 2). At 30°C (Figure 3), three elementary curves are obtained at 10.04, 7.62 and 8.71 Å, corresponding to hydrated, dehydrated, and intermediate phases, respectively. With increasing temperature, the proportion of the three different components of the Te Puke pattern varies extensively. The 10 Å peak decreases progressively in intensity until complete disappearance at 50°C. The intermediate peak at 8.71 Å first increases in intensity at 35°C but then decreases in intensity at

40°C. At 50°C, it is replaced by a broad peak at 7.76 Å. Upon heating, the 7 Å peak increases progressively in intensity and sharpens at 50°C. Its position varies from 7.62 Å at 30°C down to 7.46 Å at 50°C. The sharp 7.46 Å peak at 50°C corresponds to a fully dehydrated halloysite.

The results of computational fitting of the XRD profiles obtained for Opotiki at 40, 45, 55, 60 and 90°C are presented in Figure 3. As discussed earlier, the dehydration of Opotiki with the increase in temperature seems to occur without the formation of intermediates (Figure 2). However, the 7 Å peak is broad, asymmetrical, and extends from 7.2 to ~8.5 Å. By computational fitting (Figure 3), a minimum of four elementary components are actually needed at 10.1, 9.8, 7.95 and 7.7 Å to fit the XRD patterns obtained for the Opotiki sample heated at 40 and 45°C. The 10.1 and 7.7 Å

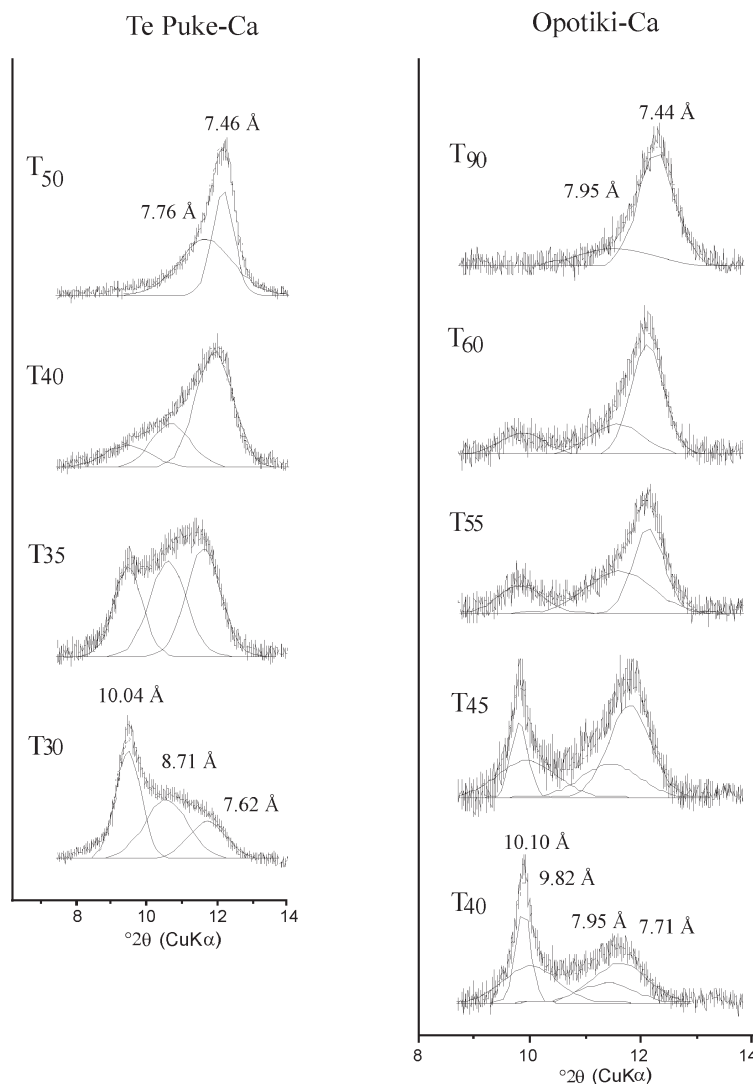


Figure 3. Computational fitting of the XRD profiles obtained for the Ca-saturated Te Puke samples heat-treated at 30, 35, 40 and 50°C, and for the Ca-saturated Opotiki samples heat-treated at 40, 45, 55, 60 and 90°C.

phases correspond to the fully hydrated and the fully dehydrated halloysite, respectively. The broad 9.8 and 7.95 Å peaks are intermediate phases. Upon heating, the intensity of the 10 Å peak decreases while the intensity of the 7 Å peak increases. At 55 and 60°C, only three components are observed at 10.0, 7.7 and 7.95 Å, corresponding to a fully hydrated, a fully dehydrated, and an intermediate phase dominated by fully hydrated and fully dehydrated halloysite layers, respectively. The position of the intermediate peak at 7.95 Å is constant with temperature but its intensity increases from 40 up to 55°C and then decreases. At 90°C, the 10 Å peak has disappeared but one component is still observed at 7.95 Å.

DTA-TGA study of the Ca-halloysite samples at 40% and 0.2% RH

The differential thermal analysis (DTA) curves obtained at 40% RH and 0.2% RH for the Te Puke and Opotiki samples previously Ca-saturated are presented in Figure 4.

At 40% RH, a first endotherm occurs at ~48°C for Te Puke and at ~52°C for Opotiki, and is attributed to the loss of adsorbed water. The corresponding weight loss (TGA curves) due to the loss of adsorbed water from 25°C to 200°C is 3.46% for Te Puke and 9.79% for Opotiki. A second endotherm occurs at ~473°C for Te Puke (14.46% weight loss from 200 to 800°C) and at ~463°C for Opotiki (11.17% weight loss from 200 to 800°C), and is attributed to the dehydroxylation of the structural OH groups.

At 0.2% RH, no adsorbed water is present on the Te Puke sample, whereas an endotherm at 82°C persists for Opotiki, indicating that the energy needed to fully

dehydrate some halloysite samples can be considerable. The temperature of halloysite dehydroxylation is greater at 40% RH than at 0.2% RH. When P(H₂O) around the material decreases, the energy needed to dehydrate the material decreases in order to stay at equilibrium.

Effect of freeze drying

The effect of freeze-drying treatment is illustrated in Figure 5. The basal spacing of Te Puke and Opotiki are shifted from ~10 Å to ~7 Å indicating that both halloysite samples are fully dehydrated upon freeze drying regardless of the saturating cation. However, the intensity of the 7 Å peak of Opotiki halloysite is dramatically weaker after the freeze-drying treatment, suggesting a decrease in the size of coherent scattering domains. As mentioned above, the 8.4 Å peak is due to the presence of amphibole. For the Te Puke halloysite, the effect of the freeze-drying treatment is more limited, whatever the saturating cation.

Rehydration behavior

The result of rehydration of the Te Puke and Opotiki Ca- or K-saturated samples at 95% RH after complete dehydration at 0% RH are presented in Figure 6. Small variations in the XRD patterns are observed for both samples after a few hours at 95% RH. The role of the saturating cation is negligible in this case. Regardless of the sample and of the exchanging cation, the 7 Å peak broadens slightly (from 0.74°2θ at 0% RH to 0.85°2θ after rehydration at 95% RH for the Te Puke halloysite whatever the saturating cation) and decreases slightly in intensity, suggesting a partial rehydration. However, no peak is observed at 10 Å for Te Puke and the weak 10 Å peak observed for Opotiki halloysite after a few hours at

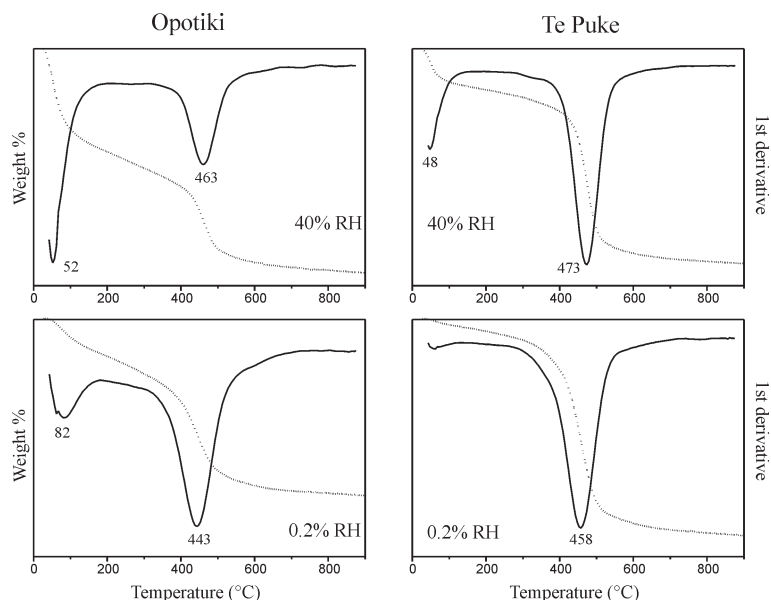


Figure 4. DTA-TGA curves for Te Puke and Opotiki samples (previously Ca saturated) at 40% and 0.2% RH. Dotted line represents the TGA.

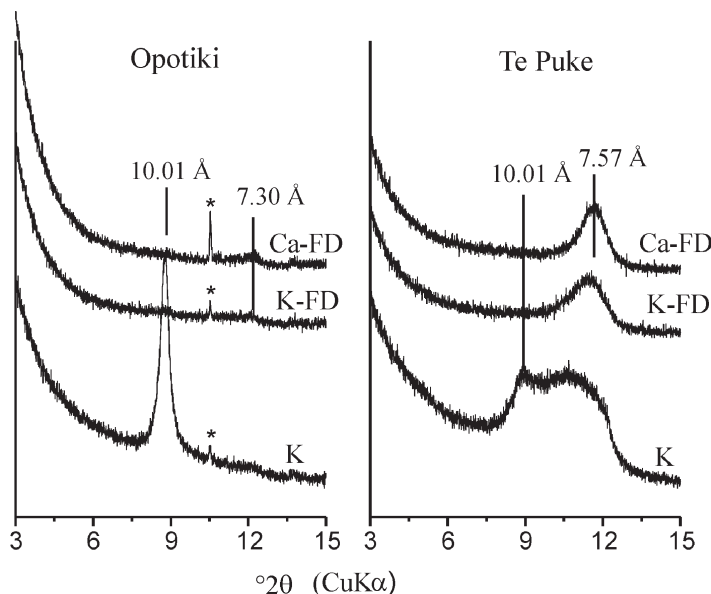


Figure 5. Effect of freeze-drying treatment on Opotiki and Te Puke samples Ca- or K-saturated. K, K-FD, and Ca-FD mean K-saturated, K-saturated and freeze-dried, and Ca-saturated and freeze-dried, respectively. * refers to the 8.4 Å peak due to amphibole.

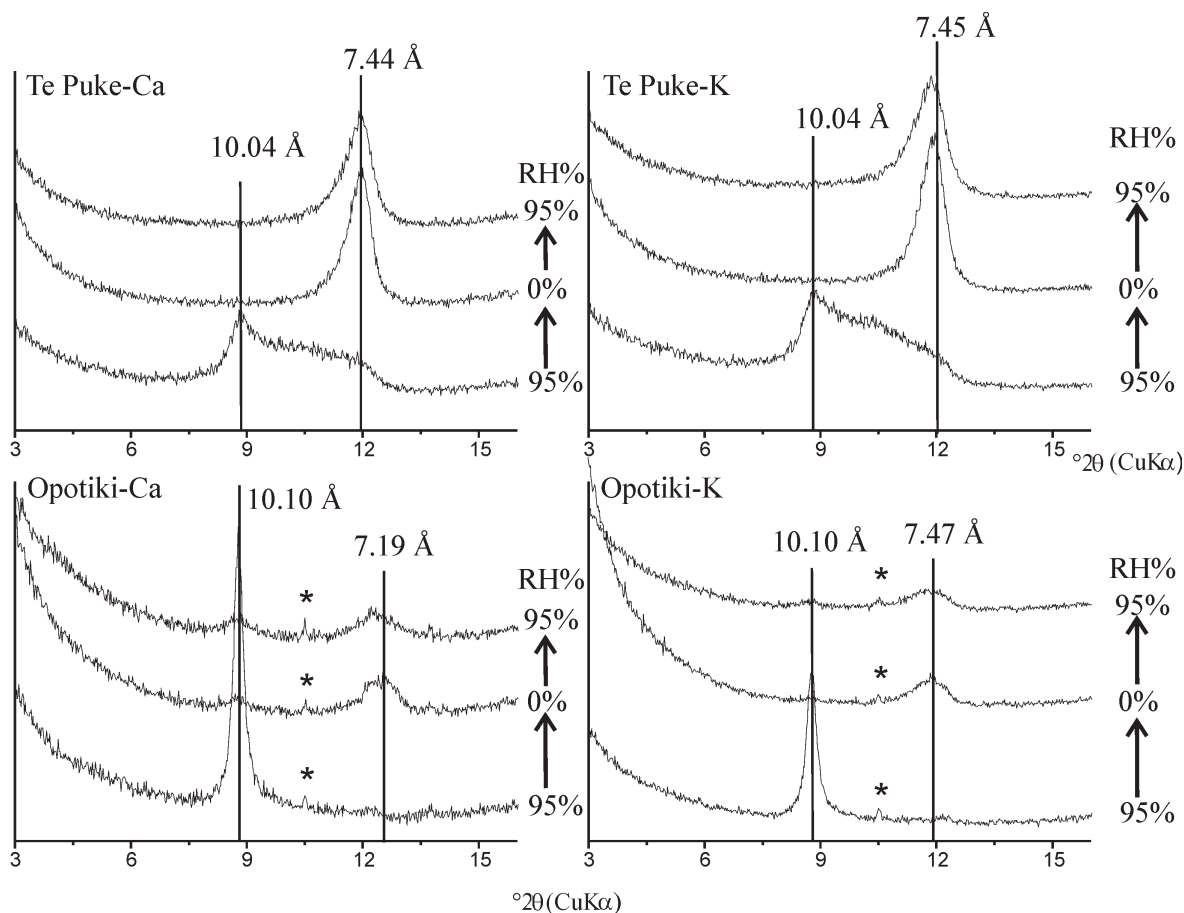


Figure 6. XRD patterns obtained after dehydration from 95% RH to 0% RH, then rehydration at 95% RH for Te Puke and Opotiki samples previously Ca- or K-saturated. * refers to the 8.4 Å peak due to amphibole.

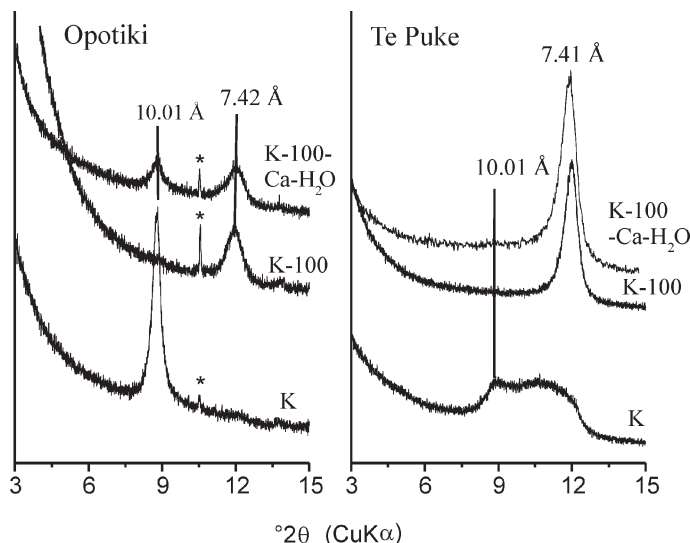


Figure 7. Effects of rehydration over a 3 month period in liquid water after heat treatment of the K-saturated Opotiki and Te Puke halloysites. K, K-100, and K-100-Ca-H₂O mean K saturated, K saturated and heat treated at 100°C for one night, and K saturated, heat treated at 100°C, Ca saturated and stored for 3 months in liquid-water, respectively. * refers to the 8.4 Å peak due to amphibole.

95% RH only barely increases in intensity compared to that obtained at 0% RH.

The effects of rehydration after 3 months in liquid water after heating or freeze-drying treatments are illustrated in Figures 7 and 8, respectively. After heating at 100°C overnight, the samples are fully dehydrated, as shown by the sharp and symmetrical peak at ~7 Å (Figure 7). The treatment of these dehydrated samples for 3 months in liquid water after Ca saturation induces a partial rehydration for the Opotiki halloysite as shown by a small peak at 10.01 Å; no rehydration takes place for the Te Puke sample as shown by the lack of constant peak breadth (Figure 7). As shown earlier, freeze-dried samples are fully dehydrated (Figures 5 and 8). After Ca saturation and storage for 3 months in liquid water, some of the clay

layers are rehydrated for both samples, as shown by the presence of a small peak at 10.01 Å. However, the 10 Å peaks are far less intense than those of the untreated samples, especially for the Opotiki halloysite.

DISCUSSION

Dehydration behavior of halloysite clay minerals

The increase in temperature and the decrease in RH both induce the progressive dehydration of the two halloysite samples, regardless of the size fraction (data not shown). Careful storage of halloysite is crucial as the dehydration of interlayer water in halloysite is strongly affected by relative humidity. However, the dehydration processes of the Te Puke and Opotiki samples are clearly different.

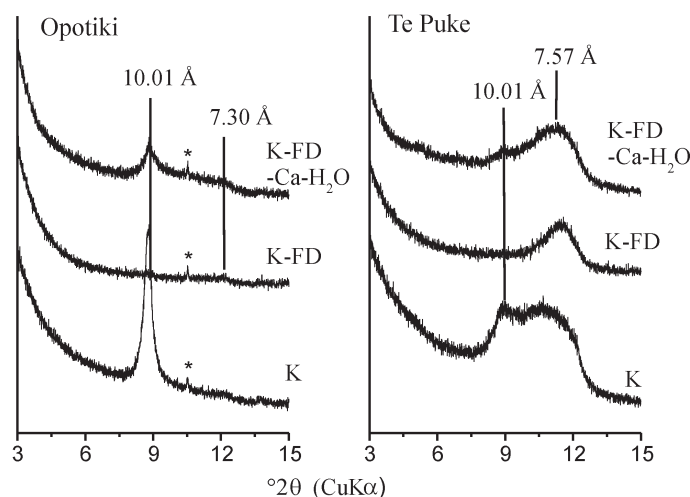


Figure 8. Effects of rehydration over a 3 month period in liquid water after freeze-drying treatment of the K-saturated Opotiki and Te Puke halloysites. K, K-FD and K-FD-Ca-H₂O mean K saturated, K saturated and freeze dried, and K saturated, freeze dried, Ca saturated and stored for 3 months in liquid water. * refers to the 8.4 Å peak due to amphibole.

At room temperature, the two halloysite samples start to dehydrate below 70% RH, dehydration increasing markedly when the RH falls to <10–20%. But, at ~0% RH, the dehydration is complete for Te Puke, whereas the Opotiki sample is not totally dehydrated, indicating that the two halloysites do not hold water similarly. Literature data also give evidence for various dehydration behaviors for halloysites under RH changes. For example, Harrison and Greenberg (1962) reported that dehydration of the Indiana halloysite sample started at 90% RH and was only complete at 0% RH, while Brindley and Goodyear (1948) showed that the dehydration of a Utah halloysite did not occur until the RH fell below 30%.

The dehydration of both the Te Puke and Opotiki halloysites upon heating starts between 30 and 35°C and increases progressively with the temperature, which is in agreement with results obtained by Kohyama *et al.* (1978) for the Kusatsu halloysite. But, Te Puke is fully dehydrated at 45°C whereas the 10 Å peak of Opotiki only disappears between 70 and 90°C, indicating once again that Opotiki holds water more strongly than Te Puke. In fact, the weight loss observed between 50 and ~450°C for the Te Puke and Opotiki samples (TGA data, Figure 5) is continuous, showing that even for Te Puke, some water molecules are held up to high temperature, in agreement with Brindley and Goodyear (1948) who found that heating up to 400°C was required for complete removal of interlayer water in Indiana halloysite.

The results of our computational analysis demonstrate that dehydration of the Te Puke halloysite proceeds *via* an intermediate hydration state giving an obvious XRD peak at ~8.7 Å. The presence of this stable intermediate component is in agreement with the work of Churchman and Carr (1972) and later Costanzo and co-workers (Costanzo *et al.*, 1980, 1982, 1984a, 1984b; Costanzo and Giese, 1985, 1990; Lipsicas *et al.*, 1985; Raythatha and Lipsicas, 1985; Giese and Costanzo, 1986) and result from the loss of associated water giving an 8.7 Å reflection. The presence of the 7.7 Å peak at 50°C in the Te Puke XRD pattern is also consistent with the work of Costanzo and co-workers and arises from the interstratification of the 8.6 and 7 Å phases.

For the Opotiki sample, the process of dehydration is different. Dehydration of the fully hydrated phase results in a dehydrated phase without the formation of intermediates at 8.7 Å. We know from the XRD data that the absence of intermediate phases during the dehydration of the Opotiki sample has nothing to do with particle size, as this has no effect (data not shown). The computational fitting shows that the dehydration results in a peak at 7.95 Å which may be interpreted as an interstratification (1) between 10 and 7 Å phases, or (2) between 8.6 and 7 Å phases. The second interpretation seems to be the more appropriate, based on infrared spectroscopy investigations by Costanzo and co-workers

on synthetic hydrated kaolinites. The 7.95 Å phase of Opotiki is still present at 90°C whereas it disappears at lower temperature for Te Puke, demonstrating once again that some water molecules are held more tenuously in Opotiki halloysite than in Te Puke, as also shown by the XRD and DTA data at ~0% RH (Figures 1 and 4). The 9.8 Å peak observed up to 45°C for Opotiki may be explained in three ways: (1) an interstratification of hydrated and dehydrated phases with a large proportion of hydrated phases (Brindley and Goodyear, 1948); (2) an interstratification of 10 Å and 8.6 Å phases with a large amount of 10 Å compound; or (3) the result of a mechanical process due to dehydration: some of the halloysite layers would start to collapse with increasing temperature even though interlayer water is present, leading to a smaller basal spacing at ~9.8 Å.

Several authors have reported that the mechanism of interstratification may operate to produce the partially hydrated forms regardless of the morphology of the halloysite particles (Harrison and Greenberg, 1962; Churchman *et al.*, 1972; Kohyama *et al.*, 1978; Okada and Osaka, 1983). Our results are in agreement with the work of Churchman *et al.* (1972) who concluded that interstratification is applicable to all the halloysites even if this process is restricted and effective only at 50°C for the Te Puke sample. However, there is no continuous series of hydration states. Halloysite dehydration is controlled by the different types of water molecules, and probably also by the layer structure due to tubular (Te Puke) or spheroidal (Opotiki) morphologies. The types of water molecules which are dominant in spheroidal halloysites interact more strongly with layers than those in tubular halloysites, possibly as the result of different layer stacking mode/order. The strong interaction between water molecules and Opotiki layers may result from (1) the significant number of structural defects which are probably more numerous in spheroidal than in tubular morphology, and (2) the position of the vacant octahedral site opposite to the ditrigonal cavity of the tetrahedral sheet due to layer translations (Jemai *et al.*, 1999). The presence of water molecules strongly held in halloysite can probably induce important differences in their physical chemical properties as well as in their response to the empirical test based on chemical reactivity (*e.g.* Joussein *et al.*, 2005).

Our study has shown that freeze-drying treatment induces full dehydration of halloysites (Figure 5) and a large decrease of their coherent scattering domain sizes, especially for Opotiki. Hillier and Ryan (2002) reported that freeze drying has no noticeable effect on the reactivity of halloysite under 'the MacEwan effect', *i.e.* reactivity of halloysite to ethylene glycol treatment. However, the MacEwan effect does not require halloysite to be hydrated. Joussein *et al.* (2005, 2006) have shown that formamide intercalation and CEC are very much affected by dehydration.

Rehydration behaviors of halloysite clay minerals

As discussed earlier, several authors have shown that the interlayer water in halloysite-(10 Å) is easily and irreversibly lost under dry air, under vacuum, or upon mild heating (*e.g.* Larsen and Wherry, 1917; Hofmann *et al.*, 11934; Alexander *et al.*, 1943; MacEwan, 1946; Brindley and Goodyear, 1948; Harrison and Greenberg, 1962; Hughes, 1966; Churchman *et al.*, 1972; Churchman and Carr, 1975; Giese, 1988). However, our results indicate that a partial rehydration may occur as suggested by the broadening and loss of intensity of the 7 Å peak after treatment of the fully dehydrated halloysites at 95% RH (Figure 6).

Moreover, the halloysites dehydrated by freeze drying or heating were partially rehydrated after Ca saturation and storage for 3 months in liquid water, except for the heat-treated Te Puke sample which did not rehydrate at all (Figures 7 and 8). However, Opotiki can rehydrate after freeze-drying treatment. De Souza Santos *et al.* (1966) observed that a platy halloysite from Brazil could partially rehydrate in water after drying in the open air for a few hours. In our case, the samples can only be rehydrated after intensive water treatment. Differences in the rehydration properties of halloysites may be due to the different types of water molecules. We have shown that Opotiki holds water strongly, even at ~0% RH. We suggest that 'hole' water is still present in halloysite after freeze drying or heating. The presence of water molecules in the freeze-dried samples would favor the penetration of other water molecules or cations in the interlayer, allowing rehydration after Ca saturation and water storage. Ca saturation proved to be very important because halloysite samples which were not Ca saturated after freeze drying or heating did not rehydrate at all after being stored in pure water for 3 months (data not shown).

Because Ca^{2+} cations have a significant hydration energy (Güven, 1992), the persistence of 'hole' water after freeze drying or heating treatments may favor the penetration of Ca ions associated with water. In this case, the presence of cations in interlayer position may also act as a reorganizer of layers (Figure 8). For Te Puke, the rehydration is effective only after the freeze-drying treatment. Heating can induce full dehydration of halloysite because water molecules are weakly bonded in the Te Puke material. After freeze drying, water molecules may still be present and favor partial rehydration.

Evidence for the presence of interlayer cations

Weiss and Russow (1963) and Bailey (1990) suggested that the presence of interlayer cations is the key to the hydration behavior of halloysite. However, even if the CEC of halloysite can reach $55 \text{ cmol}_c \text{ kg}^{-1}$ (*e.g.* Grim, 1968; Kunze and Bradley, 1964; Olivieri, 1961; Wada and Mizota, 1982; Delvaux *et al.*, 1990; Takahashi *et al.*, 2001; Joussein *et al.*, 2006), no evidence for the presence of exchangeable cations in the interlayer of halloysite has

been clearly shown. For any given RH in Figure 1, the XRD patterns of the Te Puke material are identical, regardless of the saturating cation, whereas differences are evident for the Opotiki material between the K- and Ca-saturated samples. At ~0% RH, the 001 basal peak of the dehydrated Opotiki halloysites is at 7.19 Å for the Ca-saturated sample and at 7.47 Å for the K-saturated sample (Figure 1), and the presence of the weak band at 10 Å, which is characteristic of hydrated layers, is effective for the Ca-saturated sample. These results suggest the presence of interlayer cations in the Opotiki sample and differences in the halloysite reactivity depending on (1) the size of the cation involved (ionic radii = 0.99 and 1.33 Å for Ca^{2+} and K^+ , respectively), and (2) the hydration energy of the exchanged cations ($\Delta G^{\text{hyd}} = -1515$ and -304 kJ.mol^{-1} for Ca^{2+} and K^+ respectively; Güven, 1992). It is well known that the hydration state of clay minerals is governed by the affinity of the cation for water (*e.g.* Sato *et al.*, 1992). At 0% RH, cations are devoid of water molecules and sometimes located in the hexagonal cavity, as described by Wada (1959) for K^+ . The difference in the basal spacing observed between K- and Ca-Opotiki at ~0% RH (7.47 Å vs. 7.19 Å) may be explained by the presence of K in the interlayer position and in relation to the size of the hexagonal cavity in the oxygen network of the silicate layer, because K^+ is assumed to fit into this cavity (Wada, 1959). Moreover, since the affinity of water for Ca^{2+} is greater than for K^+ (*cf.* before), the clearance 10.10 Å space observed for the Ca-saturated sample under 0% RH is related to the presence of Ca^{2+} ions in interlayer positions associated with strongly held water molecules, probably the 'hole' water. Nevertheless, the presence of interlayer cations in Opotiki material, whereas none would be present for the Te Puke material, cannot be justified by the low CEC or the chemical composition of the samples, as both samples show similar values (Table 1). The contrasting interlayer cation contents may be related to the different morphologies of halloysite (tubular vs. spheroidal).

CONCLUSIONS

This study has demonstrated that comparing the properties of various halloysites is made difficult by the lack of uniformity in the (de)hydration behavior of halloysite samples and cannot be generalized. From this work, several points are emphasized:

(1) Careful storage of halloysite is crucial since the dehydration of interlayer water in halloysite is strongly affected by atmospheric relative humidity. Halloysite begins to dehydrate below 70% RH. Freeze-drying treatment induces dehydration, whatever the saturating cation, and may reduce strongly the size of coherent scattering domains.

(2) Two different dehydration behaviors were shown. The dehydration for the Te Puke halloysite proceeds with only one intermediate hydration state reacting as a

Table 1. Chemical compositions (wt.%) adapted from Theng *et al.* (1982) and Churchman and Theng (1984) and CEC values from Joussein *et al.* (2005) for the reference halloysite samples studied.

Samples	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	MnO	LOI*	CEC cmol _c kg ⁻¹
Te Puke	44.82	36.70	3.40	<0.01	<0.01	0.01	0.05	0.37	0.01	15.80	5.2
Opotiki	44.84	36.10	4.18	<0.01	<0.01	0.01	0.03	0.28	0.01	15.60	7.0

* Loss on ignition at 1000°C.

separate phase, whereas the fully hydrated phase gives the dehydrated phase with the presence of a sequence of mixed layers for the Opotiki sample. The different types of water molecule in both Te Puke and Opotiki control the dehydration behavior of the halloysite. However, the two halloysites do not hold water in the same way. The Opotiki material holds water more tenuously than that of Te Puke. The presence or not of different types of 'hole' water in the halloysite interlayers may explain the differences in their physical chemical properties as well as in their response to the empirical test based on chemical reactivity.

(3) Some halloysites can intercalate cations which play a significant role in rehydration properties. A partial rehydration of halloysite after freeze drying or heating was only obtained when the halloysite was Ca saturated and stored in water. Cations with large hydration energies are associated with the strongly held 'hole' water.

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