

DEHYDRATION OF SYNTHETIC HYDRATED KAOLINITES: A MODEL FOR THE DEHYDRATION OF HALLOYSITE(10Å)

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Abstract—Several hydrates can be synthesized from well-crystallized kaolinites; of importance to the present work are a 10-Å hydrate (called the QS-10 hydrate), an 8.6-Å hydrate, and two kinds of partially dehydrated mixed-layer hydrates. One kind is a series of unstable materials with $d(001)$ varying continuously between 10 and 8.6 Å, and the other kind is stable with $d(001)$ approximately centered at 7.9 Å. The 10- and 7.9-Å phases have been observed in halloysites by many workers using X-ray powder diffraction, and the 8.6-Å phase has been seen by others in selected area electron diffraction photographs. Infrared spectra reveal additional similarities between the synthetic hydrates and both halloysite(10Å) and partially dehydrated halloysites. Because of these similarities, the synthetic hydrates can be used to develop a model for the dehydration of halloysite(10Å).

Previous work on the 10- and 8.6-Å hydrates identified two structural environments for the interlayer water. In one, the water is keyed into the ditrigonal holes of the silicate layer (hole water), and in the other, the water is more mobile (associated water). Both types are found in the QS-10 hydrate and halloysite(10Å), whereas only hole water occurs in the 8.6-Å hydrate. In the QS-10 hydrate, stronger hydrogen bonding between hole water and the clay makes the hole water more stable than the associated water. This difference in stability is responsible for a two-step dehydration process. The first step is the loss of associated water which results in a material with $d(001) = 8.6$ Å. This stable hydrate must be heated to temperatures near 200°C to drive off the remaining hole water. The less perfect structure of halloysite and its common curvilinear morphology reduce the difference in stability between hole and associated water molecules, so that when halloysite(10Å) dehydrates, loss of hole water and associated water overlaps, and the d -spacing goes directly to 7.2–7.9 Å.

Key Words—Dehydration, Halloysite, Hydrite, Kaolinite, Water.

INTRODUCTION

The structure of the kaolin minerals consists of a Si-tetrahedral sheet joined to an Al-octahedral sheet by sharing a plane of oxygens. MacEwan (1947) was the first to suggest that hydrated halloysites had this same layer structure and differed from kaolinite only by the presence of water in the interlayer spaces. Halloysite(10Å) is unstable under ambient conditions and rapidly dehydrates if not kept immersed in water. Even though the dehydration of halloysite(10Å) has been the subject of much research, there is no generally accepted model for the mechanism of dehydration. This lack of agreement is probably due to the variability of halloysites from different localities and to the difficulties encountered in studying this unstable material. Because of the problems in observing intermediate stages in the dehydration of natural halloysites, the present study examines the dehydration of synthetic hydrates derived from well-crystallized kaolinite. These phases are easier to work with, the experimental results are reproducible, and, to the extent that the synthetic hydrates resemble natural halloysite, the results can be used to infer the mechanism for halloysite dehydration.

The water in the interlayer spaces of halloysite(10Å) and in a synthetic 10-Å kaolinite hydrate has been found to occur in two different environments (Costanzo, 1984; Costanzo *et al.*, 1982, 1984b; Lipsicas *et al.*,

1985). One type of water (hole water) is keyed into the ditrigonal holes formed by the tetrahedral oxygens and is strongly bonded to the silicate surface; the other type (associated water) is mobile at temperatures greater than 160°K (–113°C) and is weakly bonded to the interlayer surfaces.

When the QS-10 hydrate loses interlayer water under ambient conditions, the associated water leaves first leaving the hole water behind. This loss occurs in an apparently continuous manner producing a series of partial hydrates with $d(001)$ values between 10 and 8.6 Å. The end product is a stable hydrate with $d(001) = 8.6$ Å and, except for a few remaining 10-Å layers, contains only hole water (Costanzo, 1984; Costanzo *et al.*, 1984b). Another hydrated kaolinite contains less water than the 8.6-Å hydrate and has d -spacings centered around 7.9Å.

All the spacings observed in the synthetic hydrates (10, 8.6, and 7.9 Å) have been observed in hydrated and in partially dehydrated halloysites either by X-ray or selected area electron diffraction (SAD). Study of the synthetic hydrates indicates that the fundamental hydrated phases are the 10-Å hydrate, the 8.6-Å hydrate, and the 7-Å dehydrated clay. Spacings between these values appear to result from mixed-layering of these three fundamental phases.

The present study was designed to examine in more

detail the dehydration of the synthetic kaolinite hydrates using both X-ray powder diffraction (XRD) and infrared spectroscopy (IR), and to examine the similarities and differences between the synthetic hydrates and halloysites. These similarities are shown to be sufficiently extensive that the dehydration process observed in the synthetic materials can be used to infer the mechanism for the dehydration of halloysite(10Å).

BACKGROUND

Halloysite has interested mineralogists because it is the only kaolin mineral found as a natural hydrate, and because it occurs in several very different morphologies. A large literature exists on the dehydration of halloysite(10Å), but there is little agreement about how the interlayer water begins to be lost and about the nature of the intermediate stages of dehydration.

Brindley and Goodyear (1948) studied the dehydration of halloysite(10Å) between 0 and 30% relative humidity (RH) and concluded that only two discrete phases were present in partially dehydrated halloysite. Because these phases had $d(001)$ values of 9.5 and 7.5 Å, they suggested that dehydrated halloysite was an interstratification of hydrated (10-Å) and dehydrated (7-Å) layers in various proportions. Thus, partially dehydrated halloysite could have water contents of either 1.5–2.0 (for the 9.5-Å hydrate) or 0.3–0.6 (for the 7.5-Å hydrate) water molecules per half unit cell.

In a similar study, Harrison and Greenberg (1962) observed that dehydration began at 90% RH. At about 30% RH they observed broad, poorly resolved XRD peaks at 10.1 and 7.2 Å, with continuous, weak intensity between. Below 30% RH the 7.2-Å peak became sharper and more intense with a corresponding decrease in the intensity of the 10.1-Å peak, suggesting that the broad XRD band between 7.2 and 10.1 Å was caused by an interstratification of the 10- and 7-Å layers. According to their model, the relative amounts of hydrated and dehydrated layers determined the d -spacing of the most intense XRD peak. They also concluded that during dehydration all water in any one interlayer space was lost completely.

Hughes (1966) reported substantial dehydration beginning at 80% RH, but until the humidity was reduced to 41% the main XRD peak stayed close to 9.9 Å. Below 41% RH this peak became very broad and weak with a concurrent increase in intensity of a peak at about 7.4 Å. Hughes (1966), in agreement with Brindley and Goodyear (1948), concluded that only two phases were present, one nearly or completely hydrated and the other a nearly dehydrated form of halloysite. He suggested that his samples lost water at higher RHs than reported by Brindley and Goodyear (1948) because his halloysites were from a different locality and possibly had a different drying history.

Churchman *et al.* (1972) observed that XRD profiles between 7° and $13^\circ 2\theta$ (12.6 to 6.8 Å) of partially hydrated halloysites did not match profiles calculated for mixtures of 10- and 7-Å phases or for a single phase with $d(001)$ between 10 and 7 Å. They obtained reasonable agreement by modeling a partially random interstratification of zones of 10- and 7-Å material. Their model implied that the average water content could vary continuously between 0 and 2 molecules per unit cell in contradiction to the conclusions of Brindley and Goodyear (1948). They agreed with the conclusions of Harrison and Greenberg (1962) that halloysite(10Å) dehydrated by the successive loss of all water from individual interlayer spaces.

Although the broad XRD band extending between 7.2 and 10.1 Å has been observed in many of the studies of halloysite,

it is not obvious whether the contributors to this band existed as separate phases or as some type of interstratification. Using an electron microscope equipped with an environmental cell, Kohyama *et al.* (1978) studied tubular halloysite(10Å) and the changes in morphology that resulted from the loss of the interlayer water. SAD patterns of a partially dehydrated single particle gave well-resolved reflections at 9.9, 8.6, 7.9, and 7.3 Å. Their results showed that partial dehydration occurred in a single halloysite particle, that the particle was composed of interstratified hydrated and dehydrated layers, and that the interstratification gave rise to discrete phases with different water contents.

McKee *et al.* (1973) observed an 8.1-Å basal spacing by lattice imaging of a partially dehydrated halloysite from Te Puke, New Zealand, and correlated it with the XRD band they observed between 7.44 and 8.12 Å. These authors also reported voids associated with "occasional bends" in their halloysite, but they did not identify these features as the origin of the 8.1-Å peak in the XRD pattern.

Current ideas regarding the phases which form during the dehydration of halloysite(10Å) can be summarized as follows: (1) a random interstratification of water and silicate layers (Brindley and Goodyear, 1948; Harrison and Greenberg, 1962; Hughes, 1966); (2) a partial randomness in the interlayering of zones of hydrated (10-Å) and dehydrated (7-Å) layers (Churchman *et al.*, 1972), and (3) what appears to be four well-resolved interstratifications of hydrated (10-Å) and dehydrated (7-Å) halloysite which all occur within a single particle (Kohyama *et al.*, 1978). Underlying all of these points of view is the assumption that only 10- and 7.2-Å layers exist in halloysites.

The literature also contains reports of synthetic hydrated kaolinite polytypes. Synthetic hydrates of nacrite and dickite have been reported with spacings centered about 8.4 Å (van Olphen and Deeds, 1963; Wada, 1965; Deeds *et al.*, 1966; Wada and Yamada, 1968). A 7.6-Å peak that appeared when a potassium acetate (KAc) complex of a Georgia kaolinite was washed with water was reported by Deeds *et al.* (1966). When a dickite-nacrite complex with KAc was water washed, a peak appeared at 8.4 Å along with several sharp higher-order reflections (Deeds *et al.*, 1966). These authors concluded that the 8.4-Å product was a single phase hydrate of their dickite-nacrite sample. Using both pure dickite and the dickite-nacrite samples, they concluded that the water content was about two molecules per unit cell, a value conformed by Costanzo *et al.* (1984a). Washing an halloysite-KAc complex with water gave a $d(001)$ value of 8.4 Å, along with non-integral 002 and 003 reflections at spacings between 3.5 and 3.6 Å (Churchman and Carr, 1973). Because the 8.4-Å peak was not accompanied by integral higher orders, these authors concluded that their halloysite hydrate was not analogous with the nacrite hydrate reported by Wada (1965) and Deeds *et al.* (1966).

Various synthetic kaolin hydrates (made from poorly crystallized kaolinites) and halloysites have been observed with $d(001)$ values near 7.2, 7.5, 7.9, 8.4, 9.6, and 10.1 Å (Brindley and Goodyear, 1948; Weiss *et al.*, 1963; Deeds *et al.*, 1966; Range *et al.*, 1969; Churchman and Carr, 1973; McKee *et al.*, 1973; Kohyama *et al.*, 1978; Costanzo, 1984; Costanzo *et al.*, 1980, 1982, 1984a, 1984b). All of these spacings, as well as those of the halloysite dehydration products (reported above), are clearly discernable in the synthetic hydrates of this study.

EXPERIMENTAL

The synthetic kaolinite hydrates examined were made from well-crystallized kaolinites from Cornwall (RLO1415, a china clay from St. Austell, United King-

dom) and from Georgia (KGa-1 from the Source Clay Minerals Repository of The Clay Minerals Society). The hydrates included a quasi-stable 10-Å kaolinite hydrate (referred to as the QS-10 hydrate) and two stable hydrates with $d(001) = 8.6$ and 7.9 Å (Costanzo *et al.*, 1984b). Upon dehydration of the QS-10 hydrate (by air drying), a nearly continuous series (termed "higher hydrates") of partially dehydrated materials was produced with $d(001)$ values between 10 and 8.6 Å; the end product of this series was the stable, surface-dry, single-phase 8.6-Å hydrate.

The higher hydrates were synthesized in the following manner. Briefly, 3 g of kaolinite (both of the kaolinites listed above worked well) were added to 20 ml of dimethylsulfoxide (DMSO)/8% water solution. When intercalation was complete, the sample was washed with methanol three times to remove the non-intercalated DMSO. To a suspension of the intercalated clay and methanol, 1.3 g NH_4F was added. The sample was kept well stirred at 60°C for as long as 5 hr and then water washed at least three times. If the clay was dried in a compact form, the QS-10 hydrate formed. Alternatively, if the moist clay was spread thinly on a glass slide, dehydration was rapid and the unstable higher hydrates, with $d(001)$ values between 10.0 and 8.6 Å, were obtained. The $d(001)$ depended primarily on the length of time the sample was exposed to the atmosphere; the end product of drying was the 8.6-Å hydrate.

A less hydrated material, with $d(001)$ centered around 7.9 Å (termed the "lower hydrate"), formed when the clay intercalate-methanol- NH_4F mixture either was heated for at least 8 hr at 60°C, or was left for 24 hr at room temperature before the subsequent water washings. XRD patterns of this material revealed two phases in addition to the lower hydrate; kaolinite(7Å), and an aluminum ammonium fluoride (Costanzo *et al.*, 1984a).

Prolonged exposure of kaolinite to aqueous solutions of ammonium fluoride can result in changes to the structure of the clay as indicated by XRD and IR experiments (Fijał and Tokarz, 1975). Comparison of the synthesis procedure used in this study with the experiment conditions used by Fijał and Tokarz is difficult because the DMSO solvent used in the present work is non-aqueous. Except for the choice of solvent system, the treatments used in this study are similar to experiments for which Fijał and Tokarz reported essentially no change in the integrity of the kaolinite. Any alteration of the kaolinite during the formation of the hydrates used in this study seems to have involved only the exterior surfaces and edges of the kaolinite crystallites, leaving the interiors relatively unchanged except for some F-for-OH replacement (Costanzo, 1984; Costanzo *et al.*, 1984b).

In addition to the synthetic hydrates, two halloysites

(Eureka #13 from Utah and Spruce Pine #51 from North Carolina; API Standards, Ward's Natural Science Establishment, Rochester, New York) were used for comparison.

XRD patterns were recorded with a General Electric XRD-6 diffractometer, equipped with a Cu tube. The samples were prepared as smears on glass slides. Infrared (IR) spectra were recorded on a Perkin-Elmer 237B Infrared Spectrophotometer. The samples were prepared as mulls in a fluorinated hydrocarbon supported on CaF plates.

RESULTS

If a synthetic kaolinite hydrate is to be used as a model for the study of the dehydration of halloysite(10Å), the similarities and the differences between the two must be established. This was done experimentally by examining the response of both hydrates to drying and to intercalation by ethylene glycol.

Dehydration

As mentioned above, the QS-10 hydrate is unstable and will lose water in a continuous manner. By exposing the samples of the QS-10 hydrate to ambient conditions for varying periods of time, the gradual shift of the 001 peak can be followed by XRD as the associated water is lost. Figures 1A-1H show the XRD patterns of several samples of the higher hydrates arranged in order of decreasing hydration. The most hydrated sample (Figure 1A) gave an intense 001 peak, a weak 002 peak, and a stronger 003 peak. As dehydration of this sample began, the higher order reflections were quickly lost. As the higher hydrates lost their associated water, three phases appeared; kaolinite(7Å), the 8.6-Å hydrate, and a phase with a broad, poorly resolved XRD peak centered around 7.9 Å (Figures 1F-1H). The relative proportions of the three phases that resulted from the dehydration of the QS-10 hydrate varied from sample to sample. The 001 and the 002 peaks of the 8.6-Å hydrate are identified in Figure 1H.

The XRD patterns of the lower hydrate (Figures 2C and 2D) showed broader, less well-defined peaks of kaolinite and a broad peak from a mixed-layer product centered around 7.9 Å.

The relative stability of the higher and lower hydrates under ambient conditions is seen in Figure 2 which compares the XRD patterns of the higher hydrate taken shortly after preparation (Figure 2A), and after two days of air-drying (Figure 2B). Loss of water shifted the $d(001)$ value from 9.6 to 8.6 Å. Similar treatment of a lower hydrate resulted in essentially no change in the XRD pattern (Figures 2C and 2D).

Brindley and Goodyear (1948) found it necessary to heat their halloysite(7.5 Å) to 300°C to complete the removal of interlayer water. The water in the 8.6-Å

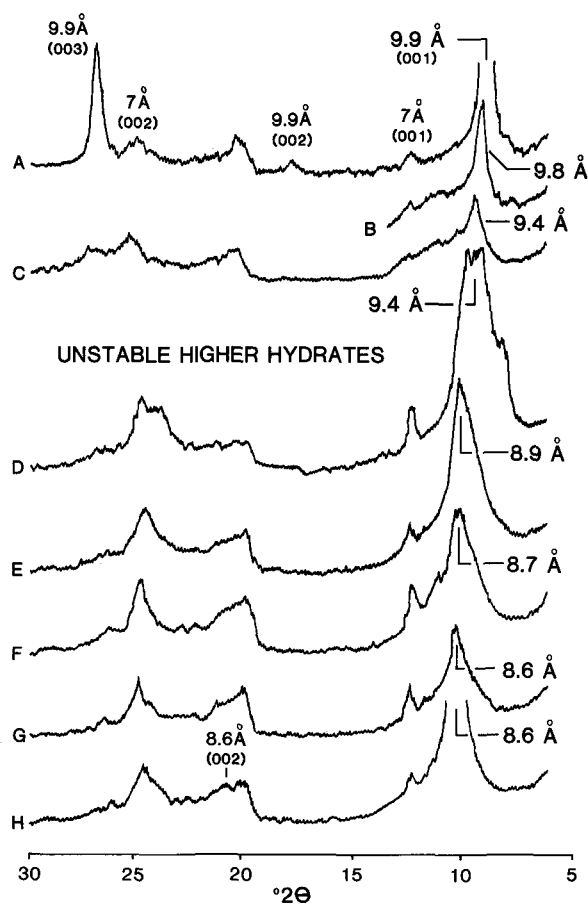


Figure 1. X-ray powder diffraction patterns ($\text{CuK}\alpha$) of several samples of higher hydrates of kaolinite arranged in order of decreasing degree of hydration. As these higher hydrates lose water, $d(001)$ decreases continuously from 9.9 to 8.6 Å. In addition to the peaks from the hydrated phase, the patterns also show the peaks from the 001 and 002 peaks and the 02,11 band of kaolinite.

hydrate (Figure 1G) only began to leave the clay at about 200°C, whereas the lower hydrate lost most of its water when heated to 200°C, as evidenced by XRD measurements before and after heating.

Glycolation

MacEwan (1946) reported that the adsorption of ethylene glycol by halloysite(10Å) produced a $d(001)$ value of 10.9 Å which was stable even when the sample was heated to 100°C for 1 hr. He also observed that halloysite(7Å), dehydrated by heating, was completely resistant to ethylene glycol treatment.

In the present study, a few drops of ethylene glycol were applied to thin films of a higher hydrate ($d(001) = 9.6$ Å), its stable dehydration product (8.6 Å), a lower hydrate (7.9 Å), and, for comparison, to Eureka halloysite(10Å) (rehydrated to 10 Å by intercalating with

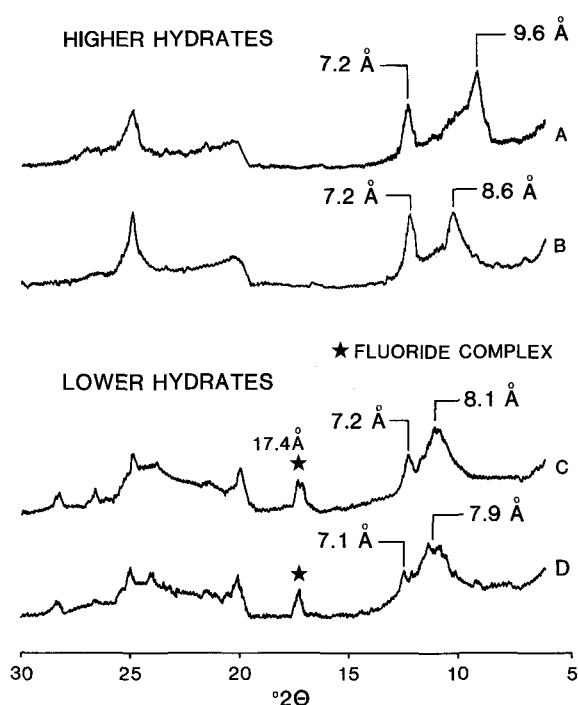


Figure 2. X-ray powder diffraction patterns ($\text{CuK}\alpha$) of (A) a higher hydrate of kaolinite, (B) the stable dehydration product produced by air-drying the higher hydrate in A for two days, (C) a lower hydrate, and (D) sample C after 3 days of air-drying.

DMSO and then water washing). These samples were then exposed overnight to ethylene glycol vapor. XRD patterns showed that a large proportion of the unstable higher hydrate (9.6 Å) and the 8.6-Å hydrate (Figures 3A and 3C) glycolated to form a 10.8-Å intercalate (Figures 3B and 3D). Although the 7.9-Å peak of the lower hydrate shifted to 10.7 Å upon glycolation (Figures 3E and 3F), the high background and poor resolution of the XRD peaks suggested that substantial mixed-layering was present after ethylene glycol treatment. The peak at 11.1 Å (Figure 3E) could possibly be due to some layers which still contained DMSO.

The glycolated lower hydrate was not stable under room-temperature conditions, and more than half of the glycolated layers collapsed when the sample was air-dried overnight. The remaining ethylene glycol was driven off by heating the sample to 50°C. The glycolated higher hydrate samples, like those in MacEwan's (1946) study, were stable even when heated to 100°C for 1 hr.

As expected, repetitive water washing of the glycolated Eureka halloysite ($d(001) = 10.7$ Å) resulted in complete conversion to a 10-Å hydrate. The same treatment applied to a glycolated higher hydrate yielded >95% 10-Å hydrate, whereas water washing the glycolated lower hydrate produced only a small amount

of interstratified material with basal spacings between 9.9 and 7.4 Å. This partially rehydrated lower hydrate was unstable under ambient conditions and collapsed to 7.4 Å after exposure to the atmosphere. The reconstituted 10-Å hydrates (the rehydrated halloysite and higher hydrate) behaved like their original counterparts; the halloysite rapidly dehydrated to 7.2 Å, and the higher hydrate went directly to an 8.6-Å spacing. In contrast to the higher hydrate, glycolation of the lower hydrate destroyed its ability to regain a 10-Å spacing.

Infrared spectroscopy

Previous IR studies of halloysite (Tarasevich and Gribina, 1972) and synthetic hydrated kaolinites (Costanzo, 1984; Costanzo *et al.*, 1984b) indicated that hole water has its ν_3 stretching band between 3572 and 3586 cm^{-1} and its ν_1 stretching band between 3522 and 3555 cm^{-1} (the exact position of the band seems to depend on the state of hydration), whereas associated water has only a broad, poorly resolved stretching band that can extend between 3200 and 3400 cm^{-1} . Both types of water have their ν_2 bending bands near 1650 cm^{-1} .

Figure 4 shows the IR spectra of the Eureka halloysite (7Å), the 8.6-Å hydrate, and the 7.9-Å hydrate. The spectrum of the Spruce Pine halloysite was essentially identical to that of Eureka and is not shown. Even though the Eureka halloysite had an XRD peak at 7.2 Å, it contained some hydrated layers. The hydrated layers were indicated by IR stretching bands at 3540 cm^{-1} (hole water) and 3436 cm^{-1} (associated water) and a bending band at 1624 cm^{-1} (Figure 4A). These bands suggest an interstratification of 10- and 8.6-Å layers. The number of 10- and 8.6-Å layers appears to be small compared to the number of dehydrated layers as shown by the 7.2-Å basal spacing. IR scans of the two synthetic hydrates (Figures 4B and 4C) indicated the presence of only a very small amount of associated water but a substantial amount of hole water. The higher hydrate (Figure 4B) contained principally 8.6-Å layers with a few randomly placed 10-Å layers as indicated by the shoulder on the low-frequency side of the stretching band (Costanzo, 1984; Costanzo *et al.*, 1984b). In addition, a few 7-Å layers are probably present, although these cannot be identified in the IR spectrum. The lower hydrate (Figure 4C) contains very few if any 10-Å layers as indicated by the narrower stretching band at 1650 cm^{-1} and by the 7.9-Å basal spacing which suggests that this material is an interstratification of 8.6- and 7-Å layers, in roughly equal proportion. These observations suggest that a 7.9-Å spacing, as observed by SAD, could form in a dehydrated halloysite by a local segregation of 8.6- and 7-Å layers. The lack of integral higher order basal spacings in the XRD patterns indicates a random interstratification of the different layers.

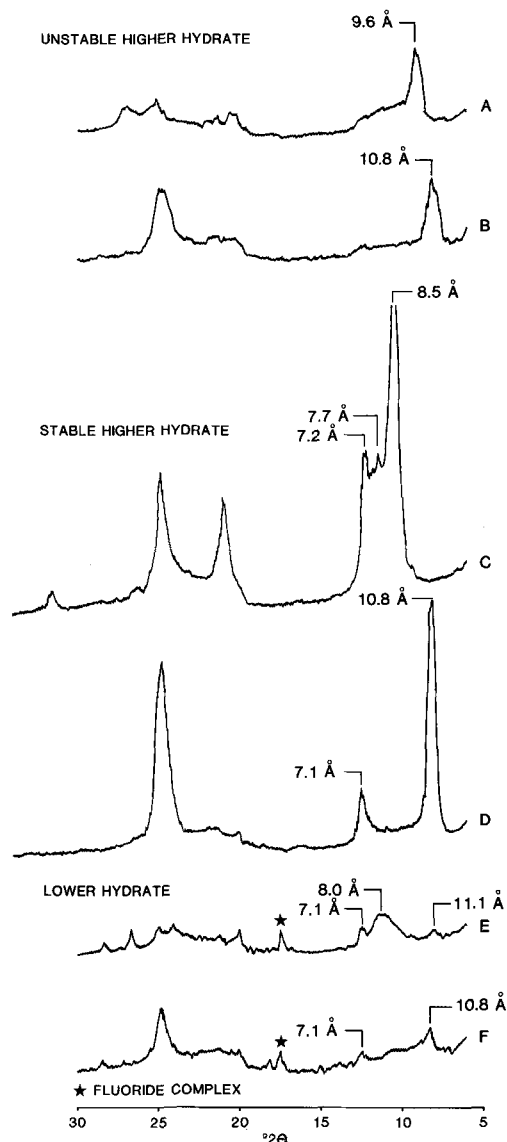


Figure 3. X-ray powder diffraction patterns ($\text{CuK}\alpha$) of (A) an almost fully hydrated higher hydrate of kaolinite, (B) sample A after glycolation, (C) a stable dehydrated higher hydrate, (D) sample C after ethylene glycol treatment, (E) a 7.9-Å lower hydrate, and (F) sample E after ethylene glycol treatment.

The higher and lower hydrates differed principally in the frequency of the ν_1 band. In the 8.6-Å hydrate this band was at 3520 cm^{-1} ; in the 7.9-Å hydrate the analogous band was found at 3530 cm^{-1} . The 10- cm^{-1} shift, while not large, suggests that the hole water in the 8.6-Å hydrate was more strongly hydrogen bonded to the clay surface than was the water in the 7.9-Å hydrate. This difference in bonding is in agreement with the previous observations of the stability of the interlayer water in these two materials to heating and

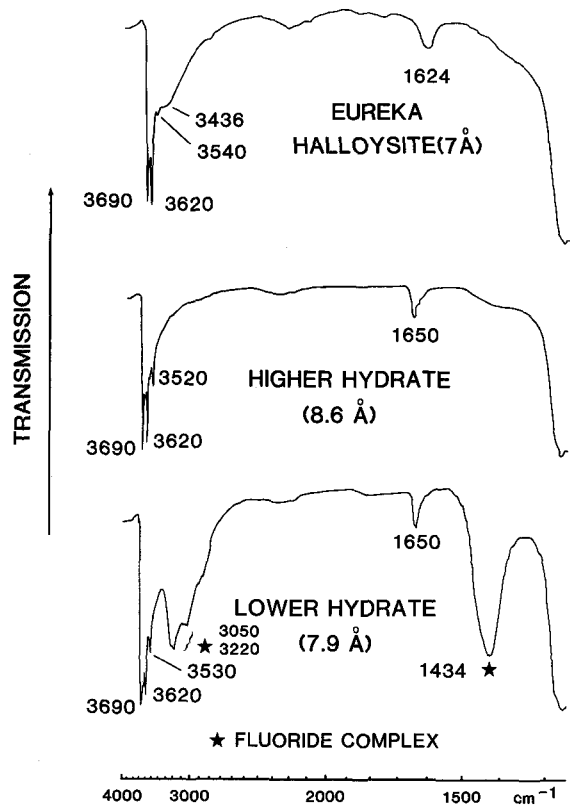


Figure 4. The infrared spectra of Eureka halloysite, a stable dehydrated higher hydrate of kaolinite (8.6 Å) and the 7.9-Å lower hydrate.

on the rehydration ability of the clay after glycolation. The 3540- cm^{-1} band in the IR spectrum of halloysite indicates even weaker hydrogen bonds than found in the 8.6- and 7.9-Å hydrates.

DISCUSSION

In many ways, the properties of the QS-10 hydrate, as examined in this study, are similar to those of halloysite(10Å); both contain hole water and associated water, both expand in the presence of ethylene glycol to give intercalates of comparable stability, and both form hydrated phases with $d(001)$ values of 8.6, 7.9, and 7.2 Å. The 8.6-Å spacing is not usually observed in XRD patterns of halloysites, but SAD reveals the existence of domains with this spacing. Presumably, the 8.6-Å coherent scattering domains are too small to be observable by XRD (Cowley, 1961).

Differences have been noted between the synthetic and naturally hydrated clays by XRD. If these differences are primarily related to the differences in the perfection of the Cornwall kaolinite and natural halloysites as opposed to a fundamental difference in crystal structure, the dehydration of the synthetic can be

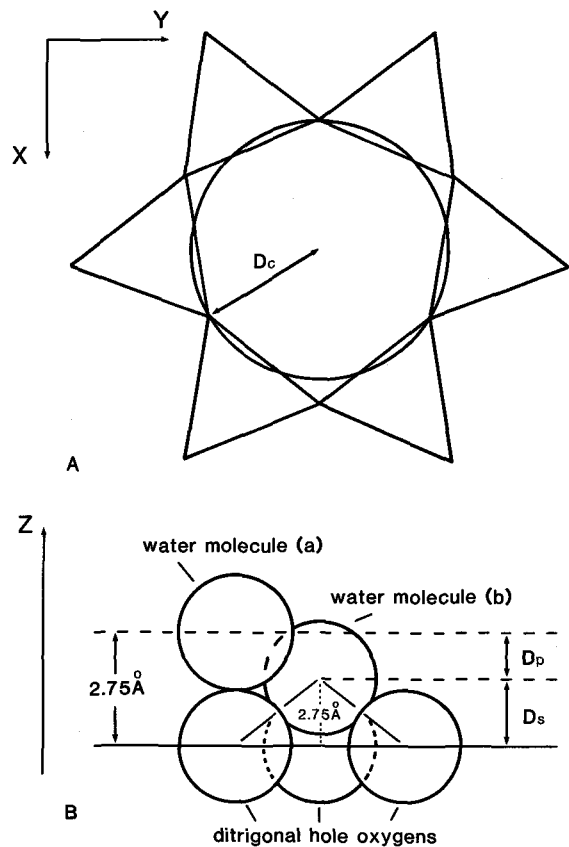


Figure 5. (A) A projection onto (001) of the basal tetrahedral oxygens of a kaolinite layer. The size of the ditrigonal hole formed by tetrahedral rotation can be estimated by the radius (D_c) of a circle which passes through the centers of the three inwardly rotated oxygens. (B) Water molecule (a) is in contact with a basal tetrahedral oxygen but does not enter the ditrigonal hole; its distance from the plane of the ditrigonal oxygens is taken to be 2.75 Å. Entry of water molecule (b) into the ditrigonal hole is limited by the three ditrigonal hole oxygens. When in contact with these, the oxygen-oxygen distances are 2.75 Å, and the distance of the water molecule from the plane of the oxygens is D_s . The water molecule enters the ditrigonal hole by a distance of ($D_p = 2.75 - D_s$).

used as an idealized model for understanding the dehydration of halloysite(10Å).

The position of the water molecules in the interlayer region is central to any discussion of the stability and dehydration properties of kaolinite and halloysite hydrates. The possible positions for the water are fewer in the 8.6-Å hydrate than in the 10-Å hydrate. The small (~ 1.5 Å) increase in $d(001)$ from the 7.1-Å spacing of untreated kaolinite to the synthetic hydrate spacing of 8.6 Å means that the water molecules must key into one or both of the bounding silicate surfaces. The common assumption is that the water molecules key into the ditrigonal holes (see, for example, Wada, 1965).

Wada (1965) reported the formation of an 8.4-Å

hydrate using nacrite, but he was unsuccessful with dickite. Deeds *et al.* (1966) repeated and confirmed these observations, and indicated that nacrite alone formed an 8.4-Å hydrate because it has a larger ditrigonal hole than either kaolinite or dickite. According to this argument, the larger hole allows a water molecule to penetrate further into the kaolin layer, thereby giving a more stable structure. No crystallographic data were presented to substantiate this view, and it is not clear on what evidence these authors based their conclusions about the relative sizes of the ditrigonal holes in the kaolin minerals.

Because there is as yet no detailed structure of either hydrated halloysite or the synthetic kaolinite hydrates, one can only examine the structures of the kaolinite polytypes and assume that, when hydrated, these structures do not distort appreciably. Tetrahedral rotation causes alternating basal oxygens to move toward or away from the center of their ideal hexagonal arrangement. As a result, the minimum dimension of the ditrigonal hole is determined by the positions of the three oxygen atoms which have rotated inward. The relative size of this opening in the kaolinite polytypes can be estimated in two ways. The first is to determine the radius of a circle which is coplanar with these three oxygens and which passes through the center of each (D_c in Figure 5A). The second is derived from the distance a water molecule can enter the ditrigonal hole (D_p in Figure 5B). This size is more difficult to calculate, but a reasonable model can be constructed knowing the center-to-center distance between two oxygens which are joined by a hydrogen bond. The crystal structure of ice indicates that this distance is approximately 2.75 Å. The maximum penetration of a water molecule occurs when it is in contact with the three inwardly rotated oxygens of the ditrigonal hole. At this point, the center of the water molecule is ideally 2.75 Å from the center of each of the three oxygens, and the distance of penetration (D_p in Figure 5B) is directly related to the distance of the water molecule from the plane of the oxygens. Geometrically, the problem is to determine the coordinates of a sphere with radius 2.75 Å which passes through three points in space.

The radius of the circle and the height of the sphere from the plane of the ditrigonal oxygens have been calculated for the crystal structures of kaolinite, dickite (Suitch and Young, 1983), and nacrite (Blount *et al.*, 1969) (Table 1). It is clear from these results that the ditrigonal hole is larger in dickite than in either kaolinite or nacrite, contrary to the proposal of Deeds *et al.* (1966). Assuming a 2.75-Å center-to-center distance for the oxygen of a water molecule hydrogen bonded to an oxygen of the kaolin layer, the water molecule penetrates a distance of 1.52 Å into the ditrigonal hole for dickite and about 1.37 Å for kaolinite and nacrite (D_p in Table 1). Because the difference in

Table 1. Minimum dimensions of the ditrigonal holes in the kaolin minerals.¹

Mineral	D_c (Å)	D_p (Å)
Kaolinite	2.382	1.367
Dickite	2.458	1.516
Nacrite	2.385	1.381

¹ These dimensions can be estimated by the radius of an inscribed circle (D_c in Figure 5A) passing through the centers of three oxygens of the ditrigonal hole, and by the penetration (D_p in Figure 5B) of a sphere (radius of 2.75 Å), passing through the centers of the three oxygens, above their mean plane.

depth of penetration is only 0.15 Å, it is difficult to see how this could determine whether or not a hydrate containing hole water would form.

Sufficient volume is available in the interlayer region of the 10-Å hydrates so that fewer geometric restraints exist on the positions of the associated water molecules. Previous study of the QS-10 hydrate (Costanzo, 1984; Costanzo *et al.*, 1984b) demonstrated that both hole and associated water are present. The data in Table 1 show that the average penetration of the hole water molecules into the ditrigonal holes of the tetrahedral sheet is 1.4 Å. Because essentially all the ditrigonal holes in the QS-10 hydrate are filled by hole water, the associated water molecules must be at a different Z level and farther from the ditrigonal hole oxygens. The different Z parameters for the two types of water molecules means that they contribute to the 001 XRD scattering differently. The present study shows that the QS-10 hydrate has a weak 002 and a strong 003 reflection (Figure 1A). These reflections disappear as dehydration begins because of the formation of an interstratified structure. It has been commonly observed that, when fully hydrated, halloysite(10Å) exhibits a 003 but not a 002 reflection (see, for example, Brindley and Brown, 1980). The absence of the 002 peak in the XRD patterns of halloysite(10Å) was taken as evidence that all the interlayer water is in the middle of the interlayer space (Churchman, 1970). Assuming that this picture is correct, hole water is distinguished from associated water in halloysite(10Å) by the bonding of the water to the clay surfaces rather than by the position of the water in the interlayer space. Because the hole water and associated water in halloysite(10Å) occupy essentially equivalent positions, during dehydration both types of water are lost at similar rates, and the halloysite(10Å) goes directly to a 7-Å material. The greater perfection of the layer in the QS-10 hydrate suggests that the distinction between hole water and associated water is greater than in halloysite(10Å). This difference is reflected in different Z parameters for the hole water and associated water in the QS-10 hydrate which might explain the appearance of the 002 peak

in the QS-10 hydrate and not in halloysite(10Å). Because of this structural difference and the stronger bonding of the hole water to the ditrigonal hole oxygens, only associated water is lost from the QS-10 hydrate under ambient conditions.

CONCLUSIONS

In previous work, it was assumed that the phases in partially dehydrated halloysites consisted of either random or partially random interstratifications of 10- and 7-Å layers. The present study shows that a third phase with a basal spacing of 8.6 Å is also possible. The proportion of 8.6-Å layers present in a partially dehydrated halloysite is probably related to imperfections of the layers and of the layer stacking; the less perfect, the fewer the number of 8.6-Å layers. The 7.9-Å spacing which is commonly seen in partially dehydrated halloysites is likely the result of mixed-layering of 7- and 8.6-Å phases.

The key to a deeper understanding of the dehydration mechanism of halloysite(10Å) lies in the properties of the hole and associated water. The greater crystallinity of the kaolinite layers in the QS-10 hydrate accentuates the difference between the two environments of the interlayer water; the hydrogen bonds between associated water and the clay surfaces are much weaker than the hydrogen bonds between the clay and the hole water molecules. This difference in bond strength results in a marked difference in the dehydration rates for hole water and associated water. Thus, dehydration of the QS-10 hydrate results in a loss of substantially all its associated water to form the stable 8.6-Å hydrate.

The situation is more complex for halloysite(10Å) where the irregular stacking combined with an imperfect structure of each layer blurs the distinction between the two types of water. The hydrogen bonding between both types of water molecules and the clay surfaces are more uniform and, during dehydration, associated water and hole water are lost simultaneously, even though the rates are not necessarily the same. Under these conditions, it is not possible to form large domains of the 8.6-Å phase, and, therefore, this spacing is not easily seen by XRD. Following this model, it is quite probable that different halloysite(10Å) samples with different types and degree of disorder will dehydrate differently. This may explain some of the divergent observations of halloysites which have appeared in the literature.

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REFERENCES

- Blount, A. M., Threadgold, I. M., and Bailey, S. W. (1969) Refinement of the crystal structure of nacrite: *Clays & Clay Minerals* **17**, 185–194.
- Brindley, G. W. and Goodyear, J. (1948) X-ray studies of halloysite and metahalloysite. Part II. The transition of halloysite to metahalloysite in relation to relative humidity: *Mineral. Mag.* **28**, 407–422.
- Churchman, G. J. (1970) Interlayer water in halloysite: Ph.D. thesis, University of Otago, Dunedin, New Zealand, 270 pp.
- Churchman, G. J., Aldridge, L. P., and Carr, R. M. (1972) The relationship between the hydrated and dehydrated states of an halloysite: *Clays & Clay Minerals* **20**, 241–246.
- Churchman, G. J. and Carr, R. M. (1973) Dehydration of the washed potassium acetate complex of halloysite: *Clays & Clay Minerals* **21**, 423–424.
- Costanzo, P. M. (1984) Synthesis and characterization of hydrated kaolinites and the chemical and physical properties of the interlayer water: Ph.D. dissertation, State University of New York at Buffalo, Buffalo, New York, 113 pp.
- Costanzo, P. M., Clemency, C. V., and Giese, R. F. (1980) Low-temperature synthesis of a 10-Å hydrate of kaolinite using dimethylsulfoxide and ammonium fluoride: *Clays & Clay Minerals* **28**, 155–156.
- Costanzo, P. M., Giese, R. F., and Clemency, C. V. (1984a) Synthesis of a 10-Å hydrated kaolinite: *Clays & Clay Minerals* **32**, 29–35.
- Costanzo, P. M., Giese, R. F., and Lipsicas, M. (1984b) Static and dynamic structure of water in hydrated kaolinites: I. The static structure: *Clays & Clay Minerals* **32**, 419–428.
- Costanzo, P. M., Giese, R. F., Lipsicas, M., and Straley, C. (1982) Synthesis of a quasi-stable kaolinite and heat capacity of interlayer water: *Nature* **296**, 549–551.
- Cowley, E. M. (1961) Diffraction intensities from bent crystals: *Acta Crystallogr.* **14**, 920–927.
- Deeds, C. T., van Olphen, H., and Bradley, W. F. (1966) Intersalation and interlayer hydration of minerals of the kaolinite group: in *Proc. Int. Clay Conf. 1966, Jerusalem*, Vol. 1, L. Heller and A. Weiss, eds., Israel Prog. Sci. Transl., Jerusalem, 183–199.
- Fijał, J. and Tokarz, M. (1975) Studies on the fluoroderivatives of silicate minerals with layered structure I. Some aspects of the reaction of kaolinite with fluoride solutions: *Mineral. Polonica* **6**, 59–69.
- Harrison, J. L. and Greenberg, S. S. (1962) Dehydration of fully hydrated halloysite from Lawrence County, Indiana: *Clay Miner.* **9**, 374–377.
- Hughes, I. R. (1966) Mineral changes of halloysite on drying: *N.Z. J. Sci.* **9**, 103–113.
- Kohyama, N., Fukushima, K., and Fukami, A. (1978) Observation of the hydrated form of tubular halloysite by an electron microscope equipped with an environmental cell: *Clays & Clay Minerals* **26**, 25–40.
- Lipsicas, M., Straley, C., Costanzo, P. M., and Giese, R. F. (1985) Static and dynamic structure of water in hydrated kaolinites: Part II. The dynamic structure: *J. Coll. Interface Sci.* (in press).
- MacEwan, D. M. C. (1946) Halloysite-organic complexes: *Nature* **157**, 159–160.
- MacEwan, D. M. C. (1947) The nomenclature of the halloysite minerals: *Mineral. Mag.* **28**, 36–44.

- McKee, T. R., Dixon, J. B., Whitehouse, U. G., and Harling, D. F. (1973) Study of Te Puke halloysite by a high resolution electron microscope: *Abstr. 31st Ann. Electron Microscopy Soc. of America Meeting, New Orleans, 1973*, 200–201.
- Range, K.-J., Range, A., and Weiss, A. (1969) Fire-clay type kaolinite or fireclay minerals? Experimental classification of kaolinite-halloysite minerals: in *Proc. Int. Clay Conf., Tokyo, 1969, Vol. 1*, L. Heller, ed., Israel Univ. Press, Jerusalem, 3–13.
- Suitch, P. R. and Young, R. A. (1983) Atom positions in highly ordered kaolinite: *Clays & Clay Minerals* **31**, 357–366.
- Tarasevich, Y. I. and Gribina, I. A. (1972) Infrared spectroscopic study of the state of water in halloysite: *Kolloidnyi Zh.* **34**, 405–411 (in Russian).
- van Olphen, H. and Deeds, C. T. (1963) Short contributions: in *Proc. Int. Clay Conf., Stockholm, 1963, Vol. 1*, I. Th. Rosenqvist and P. Graff-Petersen, eds., Pergamon Press, Oxford, 380–381.
- Wada, K. (1965) Intercalation of water in kaolin minerals: *Amer. Mineral.* **50**, 924–941.
- Wada, K. and Yamada, H. (1968) Hydrazine intercalation-intersalation for differentiation of kaolin minerals from chlorites: *Amer. Mineral.* **53**, 334–339.
- Weiss, A., Thielpape, W., Goring, G., Ritter, W., and Schafer, H. (1963) Kaolinit-Einlagerungs-Verbindungen: in *Proc. Int. Clay Conf. Stockholm, 1963, Vol. 1*, I. Th. Rosenqvist and P. Graff-Petersen, eds., Pergamon Press, Oxford, 287–305.

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