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STATIC AND DYNAMIC STRUCTURE OF WATER IN HYDRATED KAOLINITES. I. THE STATIC STRUCTURE

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Abstract—Four hydrates with d(001) = 8.4, 8.6, and 10 Å (two types) were synthesized by intercalating kaolinite with dimethylsulfoxide and treating the intercalated clay with fluoride ions. X-ray powder diffraction, infrared spectroscopy, differential scanning calorimetry, thermal gravimetric analysis, and kinetics of dehydration experiments have led to the identification of two types of interlayer water. One type of water (hole water) is situated in the ditrigonal holes of the silica tetrahedral surface; the second type (associated water) forms a discontinuous layer of mobile water. The 8.4-Å and 8.6-Å hydrates have only hole water, whereas the two synthetic 10-Å hydrates and halloysite(10Å) contain both hole and associated water. The hole water is probably hydrogen bonded to the basal oxygens of the silica tetrahedra or, in the 8-Å hydrates when fluorine exchanges for inner-surface hydroxyls, the water molecules may reorient and form stronger hydrogen bonds to the fluorine. Associated water forms water-water hydrogen bonds approximately equal in strength to liquid water but is less strongly bonded to the clay surfaces than hole water. At room temperature the hole and associated water in the 10-Å hydrates do not form an ice-like structure.

Key Words—Dimethylsulfoxide, Halloysite, Hydroxyl, Infrared spectroscopy, Kaolinite, Water.

INTRODUCTION

The extent to which a silicate surface perturbs neighboring water molecules is a point of contention. One view is that the perturbation extends to distances of tens of Ångstrom units (Low, 1979; Tarasevich, 1980). Others maintain that the clay surface influences only a few monolayers of water (Prost, 1982; Sposito and Prost, 1982; Fripiat *et al.*, 1982). In either case it is the first few water layers in contact with the silicate surface that are the most important and the most difficult to study.

Most studies of water–silicate surface interactions have been made with smectites because of their large surface area. The smectite layer charge is balanced by exchangeable interlayer cations, but these interact with the interlayer water molecules such that the water behaves more like an aqueous solution (Sposito and Prost, 1982). This behavior makes it difficult to determine the influence of the silicate surface on pure adsorbed water.

The interlayer water in halloysite(10Å) is essentially free of cations; its interactions with silicate surfaces thus could serve as a baseline for comparison with water-smectite studies. Halloysites, however, are not very suitable materials because they dehydrate readily if not kept wet and their poor crystallinity, variable morphology, and widely differing environments of formation complicate experimental interpretation. Some of these difficulties can be avoided by working with a hydrated clay formed from a well-crystallized kaolinite. Recently, Costanzo *et al.* (1980, 1984) reported the synthesis of an unstable 10-Å halloysite-like hydrate using a Cornwall kaolinite. Since then, Costanzo *et al.* (1982) reported the synthesis of a 10-Å hydrate which is stable under certain conditions in the absence of liquid water. When fully expanded, these hydrates have a surface area of ~1000 m^2/g. This communication discusses the synthesis of four related hydrates and the structure of the interlayer water in each as derived from infrared, X-ray powder diffraction, heat capacity, and desorption experiments. A related communication (Lipsicas *et al.*, 1984) deals with the dynamic properties of the interlayer water in these hydrates as shown by nuclear magnetic resonance spectroscopy. These two studies give a detailed picture of the static and dynamic properties of water, with a low concentration of ions, in contact with a silicate surface.

BACKGROUND

Infrared spectroscopy (IR) has been the principal means of studying water intercalated in clay minerals. The kaolin minerals have OH-stretching bands between 3695 and 3620 cm^{-1}. In halloysite(10Å) the intensity of the 3695-cm^{-1} band is reduced compared to the dehydrated clay (Farmer, 1974); similar results were observed for kaolinite intercalated with salts and small organic molecules (Ledoux and White, 1966; Olejnik *et al.*, 1968, 1971). This reduction in intensity accompanied by the appearance of new bands at lower frequencies has been ascribed to the formation of stronger hydrogen bonds between the inner-surface hydroxyls and the intercalated molecules. Inasmuch as the 3695-cm^{-1} band does not completely disappear upon intercalation, some inner-surface hydroxyls apparently are not perturbed by the guest molecules.

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Yariv and Shoval (1975) compared the IR spectra of kaolinite and a partially dehydrated Te Puke (New Zealand) halloysite. The existence of a 3700 cm^{-1} band in both led them to conclude that no hydrogen bonds exist between clay hydroxyls and water molecules. Cruz *et al.* (1978) also observed no shift in the inner-surface OH-stretching frequencies of an halloysite(10Å) compared to kaolinite and concluded that the hydrogen bonding from the inner-surface hydroxyls to the water molecules is weak.

In the IR spectra of hydrated and partially dehydrated halloysites, Tarasevich and Gribina (1972) observed a split in the water deformation band centered at 1640 cm^{-1}. This led them to suggest that there are two types of water in halloysite(10Å); one consisting of isolated water molecules bonded to the ditrigonal holes of the tetrahedral sheet ("hole" water) and the other being more mobile interlayer water ("associated" water). As in the studies of Yariv and Shoval (1975) and Cruz *et al.* (1978), they observed a negligible shift in the 3695-cm^{-1} band of halloysite(10Å) during dehydration and concluded that the interlayer hydrogen bonds in kaolinite have the same strength as the bonds between inner-surface hydroxyls and adjacent water molecules in halloysite(10Å).

In summary, the IR data presented in these papers suggest that the inner-surface OH-stretching vibrations of kaolinite and halloysite (both hydrated and dehydrated) are similar. This similarity has been taken as evidence that no hydrogen bonds are present (Yariv and Shoval, 1975), that the surface hydroxyls participate in weak hydrogen bonds (Cruz *et al.*, 1978), or that an equally strong bond forms from the inner-surface OH groups to water (in the hydrated state) or silicate oxygens (in the dehydrated state) (Tarasevich and Gribina, 1972).

There is also little agreement in the literature on the nature of the hydrogen bonding of the water molecules to the oxygens of the silicate surface and to other water molecules. This lack of agreement is not surprising because intercalated water gives broad, ill-defined IR bands and non-intercalated (pore) water adsorbs strongly in the same frequency region.

SYNTHESIS

The synthetic hydrates were prepared from well-crystallized kaolinite from Cornwall (RLO1415, English China Clays, St. Austell) and Georgia (KGa-1, Source Clays Repository of The Clay Minerals Society). Both kaolinites yielded hydrates which were indistinguishable. The four hydrates had the general formula $Al_2Si_2O_5(OH)_4 \cdot nH_2O$ with n = 1 (monohydrate) or 2 (dihydrate). These are: an 8.4-Å crystalline monohydrate (Giese and Costanzo, 1979), an 8.6-Å noncrystalline monohydrate, a 10-Å unstable dihydrate (Costanzo *et al.*, 1984), and a 10-Å quasi-stable dihydrate (herein referred to as the QS-10 hydrate) (Costanzo *et al.*, 1982). The two monohydrates contained no pore water and were stable under ambient conditions for very long periods of time. To remain fully intercalated the unstable 10-Å hydrate had to be kept in contact with liquid water which made the material unsuitable for the experimental techniques used in the present investigation. The dynamic properties of the interlayer water in this hydrate are discussed elsewhere (Lipsicas *et al.*, 1984). In contrast, the QS-10 hydrate could be kept fully hydrated for several months in the absence of liquid water if the sample was stored in a closed container and refrigerated.

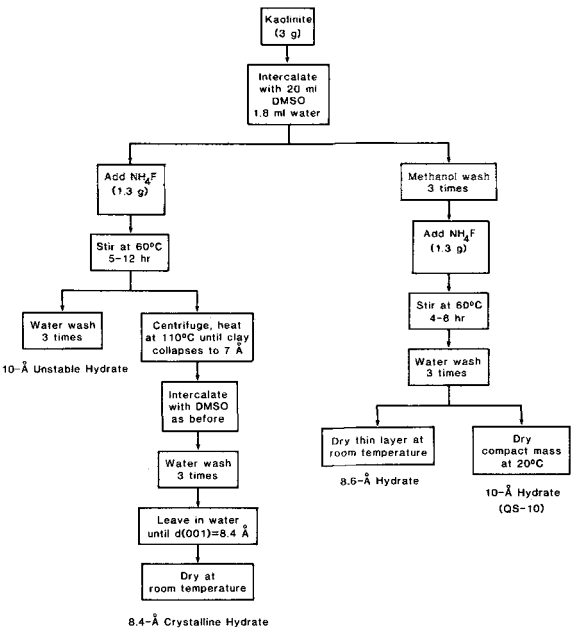


Figure 1. Flow chart showing the steps in the synthesis of four hydrated kaolinites.

Figure 1 shows the steps necessary to synthesize the four hydrates. Each sequence of treatments changed the physical and chemical properties of the kaolinite inner-surfaces to different degrees. These changes were due in part to the replacement of hydroxyl by fluorine and in part to an increase in layer stacking disorder (Costanzo *et al.*, 1984).

A major difference between the synthesis of the 8.4-Å and 8.6-Å hydrates lay in the fluoride treatment. During the synthesis of the 8.6-Å hydrate, water washings removed ammonium fluoride and dimethylsulfoxide (DMSO); at no time during the fluoride treatment was the sample completely dried or heated above 60°C. In contrast, during the synthesis of the 8.4-Å hydrate, the DMSO and volatile fluoride were removed by drying the clay at 110°C. During this heating, the clay collapsed to 7.2 Å and more F-for-OH substitution took place. Chemical analysis of the 8.4-Å hydrate showed fluoride contents of 3–5 wt. %, whereas the 8.6-Å hydrate contained less than 2 wt. %. The 8.4-Å hydrate showed (*hkl*) X-ray powder diffraction (XRD) reflections indicating a reasonably well-ordered crystal structure (Giese and Costanzo, 1979).

The synthesis of the QS-10 hydrate differed from that for the 8.6-Å hydrate only in the final drying step. The QS-10 hydrate formed when the wet clay was dried slowly by placing the moist clay at the bottom of a centrifuge tube or in the corner of a tilted beaker keeping the container loosely capped. The exposed surface of the clay was thereby reduced, and the clay lost pore water slowly over a period of several days to form a compact, mechanically hard lump of QS-10 hydrate.

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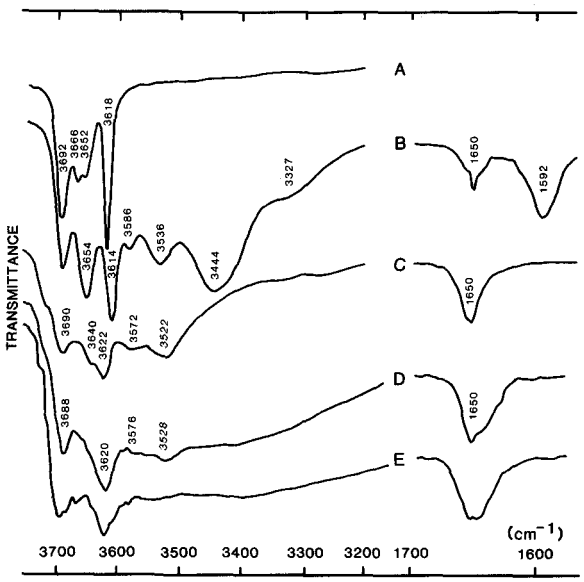


Figure 2. Infrared absorption spectra of (A) Cornwall kaolinite, (B) 8.4-Å crystalline hydrate, (C) 8.6-Å noncrystalline hydrate, (D) quasi-stable hydrate (QS-10), and (E) halloysite(10Å) from Utah.

If the moist clay was spread thinly for drying, it lost both pore and some interlayer water to yield the noncrystalline 8.6-Å hydrate. The 8.6-Å hydrate, the QS-10 hydrate, and the halloysite(10Å) gave only (00*l*) reflections.

The QS-10 hydrate could be kept fully hydrated for several months by reducing the kinetics of the dehydration. This was accomplished by keeping the sample refrigerated and in a massive form to reduce the rate of diffusion of the water out of the sample. For XRD experiments where a powder was needed and pore water was not a problem, the samples were moistened with a few drops of water and crushed just prior to the scan. Under these conditions, the clay remained hydrated long enough to scan the (001) peak. Samples for IR were prepared as mulls in a fluorinated organic which retarded dehydration long enough to record the spectrum. Heat capacity samples were sealed hermetically in capsules and kept cold prior to the runs.

EXPERIMENTAL TECHNIQUES

All chemicals were Fisher Certified Reagent grade. XRD scans were made of oriented smears on glass microscope slides with a General Electric XRD-6 diffractometer and CuKα radiation.

Most of the IR spectra were recorded with a Pye-UNICAM 3-300 double beam spectrometer. Samples were supported on 1-mm thick polycrystalline silicon discs, and the clays were prepared as mulls using a fluorinated hydrocarbon. One sample was examined with a Nicolet Fourier Transform IR spectrometer, Model SX60. This sample was dispersed in KBr and was run in the diffuse reflection mode.

Heat capacity (Cp) measurements were made with a Perkin-Elmer DSC-2, differential scanning calorimeter (DSC) equipped for low temperature operation. A glove box purged with dry nitrogen surrounded the sample and reference assembly to prevent frost accumulation during measurements. The sample and reference heaters were surrounded by flowing helium; the heat sink was a container of liquid nitrogen. With this arrangement a minimum temperature of 100°K (−163°C) was reached easily; the maximum temperature of 300°K (27°C) was set by the slope of the baseline.

In this study the power (dH/dt) necessary to heat a sample at a specified rate was compared with that of a standard material of known Cp. Benzoic acid (Fisher Certified Primary Standard for Calorimetry) was used as the standard; Cp values were taken from the work of Ginnings and Furukawa (1953). The temperature calibration was based on the solid phase transition of high purity cyclohexane, 186.1°K (−86.9°C) and its melting point, 279.7°K (6.7°C). Between these values the DSC was accurate to within 1°; at temperatures below 186.1°K (−86.9°C) the error may have been as much as 3°.

A 5–10-mg sample was sealed in an aluminum pan. During heating, the power needed to keep the sample and reference at the same temperature was measured and the difference was plotted on a strip chart. All scans were made at a heating rate of 5°/min over a 50–100°C range. For each scan a straight background line was drawn between the starting and ending isothermal, and the pan displacement at specific temperatures (in increments of 10° or 20°) was determined with respect to this line. A similar scan was made with an empty pan. The sum of the ordinate displacement for the sample and the empty pan is proportional to Cp (Daniels, 1973); this proportionality was determined by repeating the procedure with benzoic acid. Several replicate measurements were made on a sample at each temperature and the resulting Cp's were averaged. The instrument is capable of 1% accuracy on a single measurement, but because the Cp of the intercalated water was calculated from multiple measurements (for example, clay, intercalated clay, standard, and empty pan) the aggregate error is ~5–10%.

Thermogravimetry (TGA) was run using a Perkin-Elmer TGS-2 instrument. The sample was heated linearly at 20°C/min in a dry nitrogen atmosphere.

INFRARED RESULTS

The IR spectra of the Cornwall kaolinite, the 8.4-Å, 8.6-Å, and QS-10 hydrates, and a halloysite(10Å) from Utah are shown in Figure 2. The top scan is the Cornwall kaolinite, the starting material for the 8.4-Å crystalline hydrate (Figure 2A). Although the 8.6-Å and

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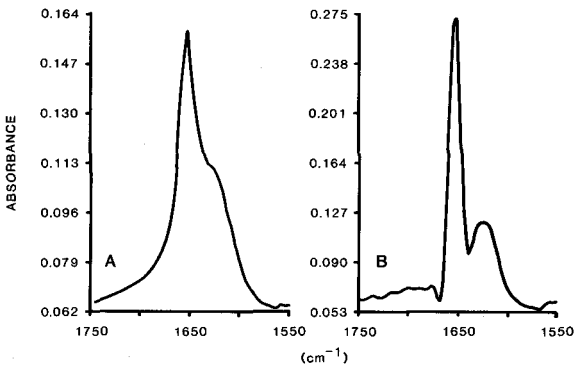


Figure 3. (A) Fourier transform infrared spectra of the 1650-cm^{-1} bending band of hole water in the 8.6-Å hydrate; (B) the spectrum in (A) but deconvoluted to show the two contributing bands.

the QS-10 hydrates described here were made from Georgia well-crystallized kaolinite, the spectra of the Cornwall and Georgia kaolinites are similar and only the former is shown.

8.4-Å and 8.6-Å hydrates

In the present investigation, the band due to the inner-surface hydroxyls, which typically appears at 3620 cm^{-1}, was sharp and at nearly the same frequency in kaolinite and the two 8-Å hydrates (Figures 2A, 2B, and 2C), indicating that little change took place in the orientation and environment of the inner-surface hydroxyl as the result of the presence of hole water.

The intensity of the high-frequency stretching band, most often seen at 3695 cm^{-1}, was weaker in the 8-Å hydrates than in the kaolinite. The 3666- and 3652-cm^{-1} vibrations of kaolinite were replaced by a single, strong and well-resolved band at 3654 cm^{-1} in the 8.4-Å hydrate (Figure 2B) and a weaker band at 3640 cm^{-1} in the 8.6-Å hydrate (Figure 2C).

The bands at 3695, 3654, and 3614 cm^{-1} of the 8.4-Å hydrate were similar to the spectrum observed in dickite (Farmer, 1974), for kaolinite intercalated with DMSO (Olejnik *et al.*, 1968), and for strongly disordered kaolinite (Cruz-Cumplido *et al.*, 1982). It is not clear what features in these three very different materials were responsible for the similarity of the OH-stretching bands.

The IR spectrum of the 8.4-Å hydrate had bands at 3586 and 3536 cm^{-1} with the same relative intensities as the 3572- and 3522-cm^{-1} bands of the 8.6-Å hydrate. Bands equivalent to these were observed by Tarasevich and Gribina (1972) at 3600 and 3555 cm^{-1} in hydrated and partially dehydrated halloysites. Their deuteration experiments indicated that these vibrations are due to intercalated water. The fact that they observed these bands in partially dehydrated halloysites (d(001) ≃ 7.2 Å) indicates that this water was keyed into the ditrigonal holes of the silica tetrahedra (hole water).

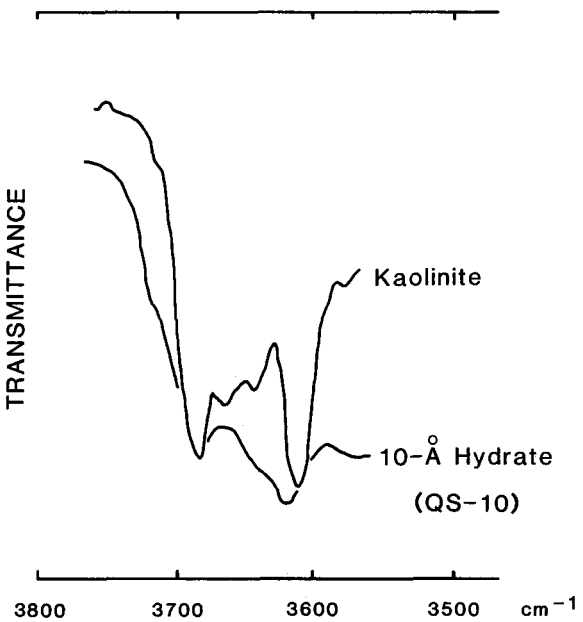


Figure 4. The infrared spectrum of the OH-stretching regions of the Cornwall kaolinite and the QS-10 hydrate. The bands of the QS-10 hydrate are broader than kaolinite and a shoulder at 3720 cm^{-1} is present in the QS-10 hydrate.

In the 8.4-Å hydrate, ~13–23% of the inner-surface hydroxyls were replaced by fluorine which can accept hydrogen bonds from nearby water molecules. Water which is hydrogen bonded to halides typically has its ν_1 and ν_3 bands shifted to lower frequencies (Farmer, 1974). Thus, in the 8.4-Å hydrate a strong band that appeared at 3444 cm^{-1} and a weaker band at 3327 cm^{-1} were probably due to a second population of ditrigonal hole water which was more strongly hydrogen bonded than the first group. The presence of two types of hole water was also indicated by the two ν_2 bands at 1650 and 1592 cm^{-1} (Figure 2B). The width of the 3444-cm^{-1} band suggested that some water molecules were bonded to the fluorine in a disordered fashion. This disorder may explain the fact that the ν_1 and ν_3 are not resolved in the 3444-cm^{-1} band. The weak absorption at 3327 cm^{-1} is probably the first overtone of the ν_2 vibration. The bending band of the water molecules forming hydrogen bonds to fluorine had a rather low frequency (1592 cm^{-1}), but similar values have been reported for water in $AlF_3 \cdot 3H_2O$ (Nyquist and Kagel, 1971).

The 8.6-Å hydrate showed three bands below 3622 cm^{-1}, a weak band at 3572 cm^{-1}, a stronger band at 3522 cm^{-1}, and a band at 1650 cm^{-1}. The 1650-cm^{-1} band was fairly broad and looked like a multiplet. There was no indication of a second bending band near 1592 cm^{-1} as was found in the 8.4-Å hydrate. This is not surprising because the fluorine content of the 8.6-Å hydrate corresponds to about 10% F replacement of

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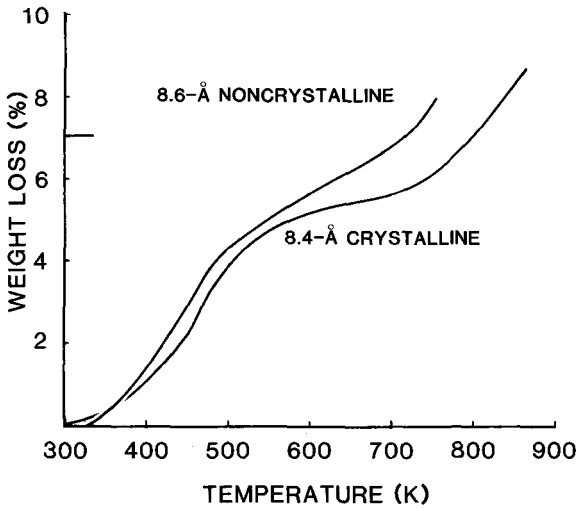


Figure 5. Weight loss curves for 8.4-Å and 8.6-Å hydrates. The heating rate was 20°C/min; the sample was heated in a dry nitrogen atmosphere. Horizontal line on vertical axis = theoretical weight loss for complete loss of intercalated water.

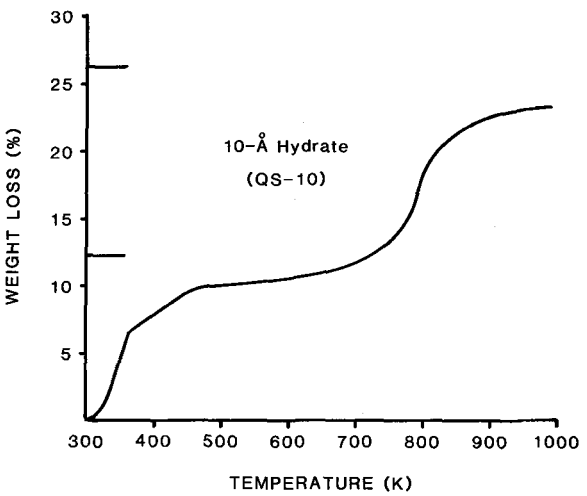


Figure 6. Weight-loss curve for the QS-10 hydrate run under the same conditions as the samples in Figure 5. Horizontal lines = theoretical weight loss for interlayer water (lower) and dehydroxylation (upper).

inner-surface OH much of which is probably near the edges of the crystals (Costanzo *et al.*, 1984). Furthermore, there is little indication of the 3444-cm^{-1} band of the 8.4-Å hydrate. To resolve, if possible, the contributors to the 1650-cm^{-1} band of the 8.6-Å hydrate, the IR spectrum was recorded with a Fourier transform infrared spectrometer (FTIR). This spectrum (Figure 3A) showed a narrow band at 1650 cm^{-1} with a shoulder at ~1625 cm^{-1}. To resolve the components of the band, the FTIR scan was deconvoluted (Kauppinen *et al.*, 1981) as shown in Figure 3B. This spectrum consisted of a band at 1650 cm^{-1} with a width at half height of 15 cm^{-1} and a much weaker band at 1625 cm^{-1} with a half-height width of 30 cm^{-1}. The narrowness of the 1650-cm^{-1} band indicates water in a single, well-defined environment, i.e., hole water. The 1625-cm^{-1} peak in the deconvoluted FTIR is probably due to associated water from a small amount of 10-Å hydrate present as a separate phase or as interstratified layers.

Quasi-stable 10-Å hydrate (QS-10) and halloysite(10Å)

The IR spectra of the 10-Å hydrates (Figures 2D, 2E) showed a 3620-cm^{-1} band which was broader and weaker than in kaolinite. The broadness of this band in halloysite(10Å) is likely due to the poorer crystallinity of the halloysite layers. This argument does not apply to the QS-10 hydrate because the parent clay (Georgia kaolinite) is well crystallized, and it is difficult to understand how stacking disorder resulting from expansion and hydration of the kaolinite could have significantly perturbed the inner-surface hydroxyls. Relative to kaolinite, the 3688-cm^{-1} band was weak and broader in the QS-10 hydrate (Figure 2D), and in the halloysite(10Å) (Figure 2E). A high-frequency shoulder centered at 3720 cm^{-1} in the QS-10 hydrate is clearly indicated in Figure 4.

Both 10-Å hydrates displayed a very broad absorption centered at ~3400 cm^{-1}. Tarasevich and Gribina (1972) assigned this region to hydrogen bonding from the associated water molecules. In the QS-10 hydrate, a poorly resolved band was noted at 3528 cm^{-1}, and in some samples a very weak band was present at about 3576 cm^{-1}. These bands are more difficult to detect in the hydrated halloysite, but both were found by Tarasevich and Gribina (1972) at 3555 and 3600 cm^{-1} in every sample they studied. In the synthetic 10-Å hydrates, these bands are likely due to hole water because of their similarity to bands present in the 8.4-Å and 8.6-Å hydrates.

THERMOGRAVIMETRY

8.4- and 8.6-Å hydrates

Beginning at about 300°K (27°C) for the 8.4-Å crystalline hydrate and at slightly higher temperatures for the 8.6-Å noncrystalline hydrate, both hydrates lost water smoothly (Figure 5). Above 350°K (77°C) the quantity of water lost from the 8.6-Å hydrate was greater than from the 8.4-Å hydrate.

At approximately 500°K (227°C) for the 8.6-Å hydrate and 550°K (277°C) for the 8.4-Å hydrate, the weight-loss curves flattened. At these temperatures the majority of clay layers had collapsed trapping pockets of water in the interior of the crystallites. As a result, the apparent weight loss (Figure 5) was slightly less than theoretical. Dehydroxylation began at about 720°K (347°C) for both hydrates.

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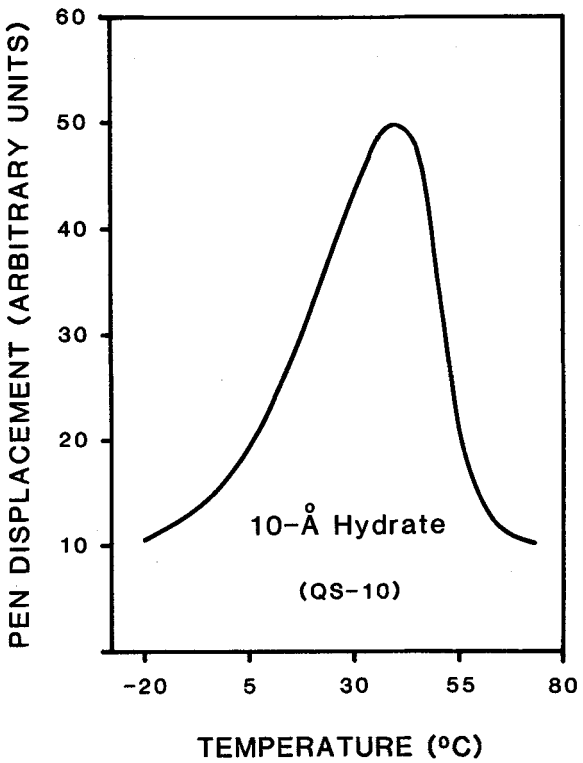


Figure 7. Differential scanning calorimeter scan for the dehydration of the QS-10 hydrate.

Quasi-stable 10-Å hydrate

The weight-loss curve of the QS-10 hydrate is shown in Figure 6. The experimental conditions were identical to those described in the previous section. The lack of a well-defined, separate weight loss below 350°K (77°C), and the reasonable agreement between the observed and theoretical weight loss indicate that little if any pore water was present in the sample.

Two stages in the low-temperature part of the weight-loss curve were apparent. The first ended with approximately a 7% loss (375°K, 102°C) and the second, at about a 10% loss (460°K, 187°C). At temperatures above 500°K (227°C), a continuous, slow loss of trapped interlayer water was recorded up to the beginning of dehydroxylation.

KINETICS OF DEHYDRATION

The loss of an adsorbed species during heating is an endothermic process. The variation of dH/dt vs. T (H = enthalpy; T = temperature; t = time) was recorded with the DSC. The DSC scans were used to determine the kinetics, the activation energy of desorption (Adams, 1978), and ΔH for the reaction.

The kinetics of desorption of small molecules intercalated in kaolinites often can be described by the relation of Avrami-Erofeev:

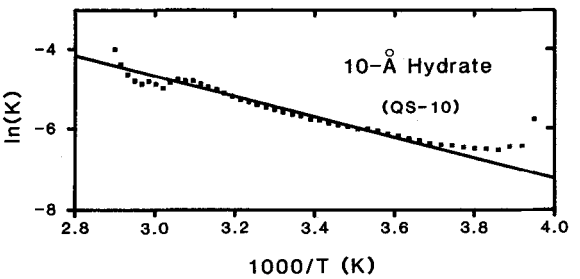


Figure 8. Arrhenius plot from the differential scanning calorimeter curve in Figure 7. The activation energy is 21.3 kJ/mole.

$$-\ln(1 - \alpha) = (kt)^2,$$

where α = the fraction of sample reacted, k = the rate constant, and t = time (Guarini and Spinicci, 1972; Adams, 1978).

The DSC curve for the loss of associated water from the QS-10 hydrate (Figure 7) gave ΔH = 44.5 kJ/mole. This value compares with the enthalpy of vaporization of water (43.2 kJ/mole) and the enthalpy of sublimation of ice (51.0 kJ/mole). Because the ΔH value for the loss of intercalated water from the QS-10 hydrate is between these two values, the interlayer water must have properties intermediate between those of liquid water and ice.

The Arrhenius plot (Figure 8) derived from the DSC curve, using the relation of Avrami-Erofeev, yielded an activation energy of 21.3 kJ/mole. This energy refers to the low T (approximately 7 wt. %) loss of the associated water which occurs below the first break in slope in Figure 6. Inasmuch as this initial weight loss was not very reproducible, ΔH, which is a function of the weight of the water lost, varied. The activation energy, which does not depend on the total amount of water desorbed, varied much less, and an average value of 20.6 ± 1.0 kJ/mole was obtained. The energy of a single hydrogen bond is about 21 kJ/mole or 42 kJ/mole of water, suggesting that, on average, only one hydrogen bond per associated water molecule was broken during desorption.

The excellent fit of the experimental data to a single straight line in the Arrhenius plot indicates that the desorption of the associated water involved a single process. If pore water had been present in the sample, the desorption would have taken place in two stages, yielding two activation energies.

HEAT CAPACITY

Cruz *et al.* (1978) showed that the Cp of an intercalated phase can be derived from the Cp of the clay and the Cp of the intercalated clay using the relation;

$$Cp(int) = (1 - x)Cp(clay) + xCp(guest).$$

Sposito and Prost (1982) pointed out that this proce-

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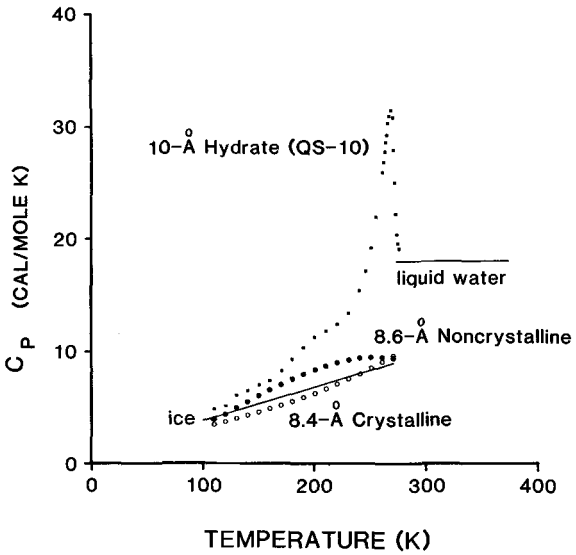


Figure 9. Heat capacity of the intercalated water in the 8.4-Å, 8.6-Å, and QS-10 hydrates compared to ice and liquid water.

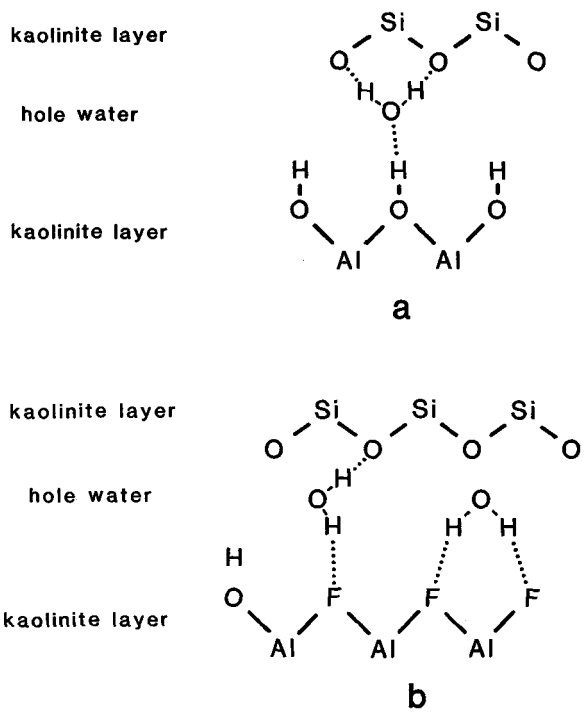


Figure 10. (a) Schematic view of the water molecule orientations in the 8.4-Å crystalline hydrate. In the absence of fluorine, the C_2 axis of the water molecule is perpendicular to (001). (b) The presence of fluorine can lead to a reorientation of the C_2 axis to allow hydrogen bonds to form between the water molecule and one or more fluorine atoms.

dure is not strictly correct because the Cp of the expanded clay layers [(1 − x)Cp(clay) in the relation] is not necessarily the same as the Cp of the bulk clay as assumed in the calculation. In spite of this, the calculated Cp for the intercalated phase can be used to identify heat capacity anomalies and to compare relative values. The value of x, the weight fraction of the intercalated molecule, for each sample used for the Cp measurements was determined by weight loss upon heating. XRD of the intercalated sample provided an independent although less accurate estimate of x.

The Cp values for the QS-10 hydrate, the 8.4-Å, and the 8.6-Å hydrates are shown in Figure 9. As reported earlier (Costanzo *et al.*, 1982), at low temperatures the Cp values for water in the QS-10 hydrate are similar to those of ice. The present study shows that the Cp values for the water in the 8-Å hydrates are also similar to those of ice. At about 160°K (−113°C), the Cp of water in the QS-10 hydrate increased with temperature at a faster rate than did the Cp of water in the 8-Å hydrates and ice; above 240°K (−33°C) the Cp of the water in the QS-10 hydrate rose rapidly with temperature resulting in a heat capacity anomaly which peaked at about 269°K (−4°C). This anomaly was probably related to a temperature-dependent exchange between the hole water and associated water (Lipsicas *et al.*, 1984). The Cp values suggest that the associated water in the QS-10 hydrate is more mobile than the hole water in the 8-Å hydrates. A similar divergence of Cp values from those of ice was observed by Eger *et al.* (1979) to take place at 200°K (−73°C) for water in a Ge CaX zeolite and at 140°K (−133°C) for water in Li-hectorite.

DISCUSSION

The d(001) values taken together with the weight loss due to dehydration indicate that the 8.4-Å and 8.6-Å hydrates ideally have one water molecule (hole water) keyed into each ditrigonal hole. Where no fluorine replaces OH, the water molecules in the 8-Å hydrates lie between a plane of oxygens and a plane of

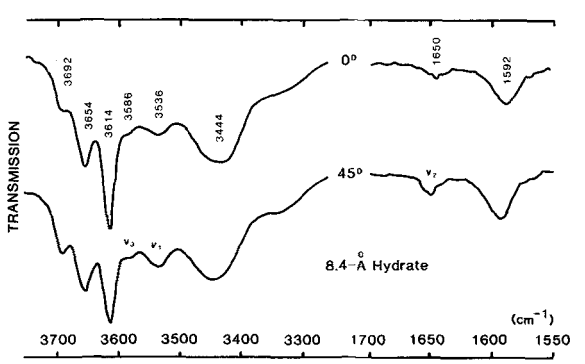


Figure 11. The infrared absorption spectrum of the crystalline 8.4-Å hydrate run at 0 and 45° orientation to show the pleochroism of the ν_1 water stretching band at 3536 cm^{-1} and the ν_2 band at 1650 cm^{-1}.

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hydroxyls. This dipolar environment likely orients the C_2 axis of the water molecule nearly perpendicular to the (001) plane, with the positive end (the water hydrogens) pointing toward the basal oxygens (Figure 10a). In this orientation, the hole water hydrogens are able to bond to the basal oxygens and the lone pair electrons of the water oxygen can accept hydrogen bonds from the hydroxyls of the opposite surface.

Because the hole-water hydrogens are not directed into the interlayer space, their OH-stretching vibrations should be insensitive to the degree of hydration of the clay, as was observed by Tarasevich and Gribina (1972) during dehydration of an halloysite(10Å).

As shown by the extra IR bands at 3444 cm^{-1} and 3327 cm^{-1} in the 8.4-Å hydrate, the electronegative fluorine, where present, can reorient a water molecule to form a hydrogen bond of the type O(H)---F. Water which has its C_2 axis normal to the layer should have pleochroic ν_1 and ν_2 bands, whereas water tilted to form hydrogen bonds to fluorine of the adjacent layer (Figure 10b) should show little or no pleochroism of its bands. Because the 8.4-Å hydrate has ~20% of its surface OH groups replaced by fluorine, it should contain hole water with two different orientations; normal and inclined to (001). Figure 11 shows the IR spectra of the 8.4-Å hydrate with the beam normal to the oriented sample and when tilted at 45°. There was relatively little change in transmission of the 3444 cm^{-1} and the 1592 cm^{-1} bands (assigned to water molecules whose C_2 is inclined to (001)) when the sample was rotated from 0° to 45°. In contrast, the hole water which has its C_2 nearly normal to the clay layer does show a pleochroic effect in the ν_1 (3536 cm^{-1}) and ν_2 (1650 cm^{-1}) bands but not the ν_3 (3586 cm^{-1}) band. These observations are in agreement with the proposed orientations for the two types of hole water.

Some water molecules may have more than one fluorine in their coordination sphere to which they can form bonds with both hydrogens (Figure 10b). The IR spectrum of the 8.4-Å hydrate shows two bending-mode bands (Figure 2B), one at 1650 cm^{-1} which is where water forming H---O bonds is expected and the other at 1592 cm^{-1}. The latter band is considerably shifted and may be due to water molecules forming H---F bonds with both hydrogens. In the 8.4-Å hydrate the bonding across the interlayer space is fundamentally different from that in the 8.6-Å hydrate. The stronger interlayer bonding of the 8.4-Å hydrate results in a well-ordered layer stacking.

The intercalated water of the 8-Å hydrates had Cp values which were not substantially different from ice Ih in the temperature range of 100°K (−173°C) to 300°K (27°C); however, this does not mean that the water is "frozen." In the 8-Å hydrates the water molecules key into ditrigonal holes. As such, they are approximately 5 Å apart, and therefore a hydrogen bonded ice-like structure is not possible. The Cp values indicate only that the water molecules are not capable of translational motion; NMR experiments indicate that the molecules rotate (Lipsicas *et al.*, 1984).

The layer spacing and water weight loss indicate that the QS-10 hydrate has twice as much interlayer water as the 8-Å hydrates. Ideally half of this water is keyed into the ditrigonal holes, as in the 8-Å hydrates, and the other half is the mobile associated water. The IR stretching bands of the associated water are at lower frequency than the bands of the hole water which, in turn, are at lower frequency than the inner-surface hydroxyl bands. Thus, at least three kinds of hydrogen bonds are present in the 10-Å hydrate and in halloysite(10Å). The strongest are the intermolecular bonds involving associated water, the next strongest are from hole water to the silicate surface, and the weakest are from the inner-surface hydroxyls to the water molecules.

Above 160°K (−113°C) the associated water in the QS-10 hydrate is no longer rigidly fixed to specific sites in the interlayer space resulting in a variation in the strength of the hydrogen bonds. For example, the shoulder on the high-frequency side of the 3695-cm^{-1} band (Figure 4) is due to a weaker hydroxyl hydrogen bond than is found in the parent kaolinite. The IR spectrum of the QS-10 hydrate and halloysite(10Å) is composed of the bands of unperturbed inner-surface hydroxyls (ideally, 3695, 3670, and 3650 cm^{-1}) plus bands shifted to higher and lower frequency by variable amounts according to the strength of the hydrogen bond of each contributor. The sum of all these is a broad band which begins at ~3700 cm^{-1} and extends to, and perhaps beyond, the 3620-cm^{-1} inner-surface hydroxyl band. This smearing out process is likely responsible for the lack of definition in the IR spectra of the QS-10 hydrate and the hydrated halloysite.

CONCLUSION

The picture of the intercalated water which emerges from this study is that of two distinctly different types of water molecules, each with its own structural position, its own mode of bonding to the clay surfaces and to each other, and its own motional freedom in the interlayer volume. This picture is very different from the uniform, rigid ice structure originally suggested by Hendricks and Jefferson (1938). The Hendricks and Jefferson model should be looked upon as a first attempt, one based largely on geometric arguments. The structure described here is more complex and subtler being based on more data and, especially, on data which are partially derived from the dynamic properties of the intercalated water.

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REFERENCES

Adams, J. M. (1978) Differential scanning calorimetric study of kaolinite:N-methylformamide intercalate: *Clays & Clay Minerals* **26,** 169–172.

Costanzo, P. M., Clemency, C. V., and Giese, R. F., Jr. (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. (1984) Synthesis of a 10-Å hydrated kaolinite: *Clays & Clay Minerals* **32,** 29–35.

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.

Cruz, M. I., Letellier, M., and Fripiat, J. J. (1978) NMR study of adsorbed water. II. Molecular motions in the monolayer hydrate of halloysite: *J. Chem. Phys.* **69,** 2018–2027.

Cruz-Cumplido, M., Sow, C., and Fripiat, J. J. (1982) Hydroxyl infrared spectrum, crystallinity and cohesion energy in kaolin: *Bull. Mineral.* **105,** 493–498.

Daniels, T. (1973) *Thermal Analysis:* Wiley, New York, 272 pp.

Eger, I., Cruz-Cumplido, M. I., and Fripiat, J. J. (1979) Quelques données sur la capacité calorifique et les propriétés de l'eau dans divers systèmes poreaux: *Clay Miner.* **14,** 161–172.

Farmer, V. C. (1974) The layer silicates: in *The Infrared Spectra of Minerals,* V. C. Farmer, ed., Mineralogical Society, London, 331–364.

Fripiat, J., Cases, J., Francois, M., and Letellier, M. (1982) Thermodynamic and microdynamic behavior of water in clay suspensions and gels: *J. Colloid Interface Sci.* **89,** 378–340.

Giese, R. F. and Costanzo, P. M. (1979) Synthesis of a monohydrate of kaolinite with d_{001} = 8.4 Å: *Geol. Soc. Amer. Abstr.* **11,** p. 432 (abstract).

Ginnings, D. C. and Furukawa, G. (1953) Heat capacity standards for the range 14–1200°K: *Amer. Chem. Soc.* **75,** 522–527.

Guarini, G. G. L. and Spinicci, R. (1972) DSC study of the kinetics of thermal dehydration of $BaCl_2xH_2O$: *J. Therm. Anal.* **4,** 435–450.

Hendricks, S. B. and Jefferson, M. E. (1938) Structures of kaolin and talc-pyrophyllite hydrates and their bearing on water sorption of the clays: *Amer. Mineral.* **23,** 863–875.

Kauppinen, J. K., Moffatt, J. D., Mantsch, H. H., and Cameron, D. G. (1981) Fourier transforms in the computation of self-deconvoluted and first-order derivation spectra of overlapped band contours: *Anal. Chem.* **53,** 1454–1457.

Ledoux, R. L. and White, J. L. (1966) Infrared studies of hydrogen bonding of organic compounds on oxygen and hydroxyl surfaces of layer lattice silicates: in *Proc. Int. Clay Conf., Jerusalem, 1966,* **1,** L. Heller and A. Weiss, eds., Israel Prog. Sci. Transl., Jerusalem, 361–374.

Lipsicas, M., Straley, C., Giese, R. F., and Costanzo, P. M. (1984) Static and dynamic structure water in hydrated kaolinite: Part II. The dynamic structure. *J. Colloid Interface Sci.,* submitted.

Low, P. F. (1979) Nature and properties of water in montmorillonite-water systems: *Soil Sci. Soc. Amer. J.* **43,** 651–658.

Nyquist, R. A. and Kagel, R. O. (1971) *Infrared Spectra of Inorganic Compounds:* Academic Press, New York, Spectrum 605.

Olejnik, S., Aylmore, L. A. G., Posner, A. M., and Quirk, J. P. (1968) Infrared spectra of kaolin mineral-dimethyl sulfoxide complexes: *J. Phys. Chem.* **72,** 241–249.

Olejnik, S., Posner, A. M., and Quirk, J. P. (1971) The infrared spectra of interlamellar kaolinite-amide complexes. II. Acetamide, N-methylacetamide and dimethylacetamide: *J. Colloid Interface Sci.* **37,** 536–547.

Prost, R. (1982) Near infrared properties of water in Na-hectorite pastes: in *Proc. Int. Clay Conf., Bologna, Pavia, 1981,* H. van Olphen and F. Veniale, eds., Elsevier, Amsterdam, 187–195.

Sposito, G. and Prost, R. (1982) Structure of water adsorbed on smectites: *Chem. Reviews* **82,** 554–572.

Tarasevich, Y. I. (1980) The state of bound water in mineral suspensions: *Chem. Tech. Water* **2,** 99–108 (in Russian).

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).

Yariv, S. and Shoval, S. (1975) The nature of the interaction between water molecules and kaolin-like layers in hydrated halloysite: *Clays & Clay Minerals* **23,** 473–474.

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Резюме—Четыре гидрата с d(001) = 8,4, 8,6, и 10 Å (два типы) синтезировались путем прослаивания каолинита диметилсулфоокисью и обработкой прослойки фтористыми ионами. Два типа межслойной воды идентифицировались при помощи ренигеновской порошковой дифракции, инфракрасной спектроскопии, дифференциальной развертывающей калориметрии, термо-гравиметрического анализа и экспериментов по кинетике дегидратации. Один тип воды (пустотная вода) находится в дитригональных местах кремниевой тетраэдрической поверхности; второй тип (ассоциированная вода) образовывает неравномерный слой подвижной воды. 8,4 Å и 8,6 Å гидраты имеют только пустотную воду, тогда как два синтетических 10 Å гидрата и галлуазит (10 Å) содержат оба типа, пустотную и ассоциированную воду. Пустотная вода является, вероятно, связанной водородной связью с основными атомами кислорода тетраэдров окиси кремния или, молекулы воды могут изменять ориентацию и образовывать более сильную водородную связь с фтором в 8 Å гидратах, если фтор обменивает гидроксиловые группы внутренних поверхностей. Ассоциированная вода образовывает водородные связи вода-вода с прочностью приблизительно такой, как вода в жидком состоянии, но она легче связана с глинистой поверхностью, чем пустотная вода. В комнатной температуре ни пустотная ни ассоциированная вода не формируют структуры типа льда в 10 Å гидратах. [E.G.]

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Resümee—Vier Hydrate mit d(001) = 8,4, 8,6, und 10 Å (zwei Arten) wurden synthetisiert, indem Kaolinit mit Dimethylsulfoxid wechselgelagert und der wechselgelagerte Ton mit Fluoridionen behandelt wurde. Röntgenpulverdiffraktometrie, Infrarotspektroskopie, Differentialrasterkalorimetrie, und Thermogravimetrie sowie die Kinetik von Dehydratationsexperimenten haben zur Bestimmung von zwei Arten von Zwischenschichtwasser geführt. Eine Art Wasser (sog. Hohlraumwasser) befindet sich in den ditrigonalen Hohlräumen der Siliziumtetraederoberfläche; die zweite Art (sog. assoziiertes Wasser) bildet eine diskontinuierliche Lage von mobilem Wasser. Die 8,4 Å- und 8,6 Å-Hydrate haben nur sog. Hohlraumwasser, während die zwei synthetischen 10 Å-Hydrate und Halloysit(10 Å) sowohl Hohlraumals auch assoziiertes Wasser enthalten. Das Hohlraumwasser ist wahrscheinlich durch Wasserstoffbrücken an die Basissauerstoffe der SiO_4-Tetraeder gebunden oder—in den 8 Å-Hydraten, wenn das Fluorid anstelle des Hydroxyls der inneren Oberfläche tritt—die Wassermoleküle können auch reorientiert sein und festere Wasserstoffbindungen zu den Fluoridionen bilden. Das assoziierte Wasser bildet Wasser-Wasser Wasserstoffbindungen, die etwa gleich fest sind wie im flüssigen Wasser, aber weniger fest an die Tonoberfläche gebunden sind als das Hohlraumwasser. Bei Raumtemperatur bilden das Hohlraum- und das assoziierte Wasser in den 10 Å-Hydraten keine Eis-ähnliche Struktur. [U.W.]

Résumé—Quatre hydrates avec d(001) = 8,4, 8,6, et 10 Å (deux types) ont été synthetisés en intercalant la kaolinite avec la diméthylsulfoxide et en traitant l'argile intercalé avec des ions fluorides. La diffraction des rayons-X, la spectroscopie infrarouge, la calorimétrie différentielle balayante, l'analyse gravimétrique thermale, et des expériences de kinétique de déshydration ont mené à l'identification de deux types d'eau intercouche. Un type d'eau (eau de trou) est situé dans les trous ditrigonaux de la surface tétraèdrale de la silice; le second type (eau associée) forme une couche discontinue d'eau mobile. Les hydrates de 8,4 Å et de 8,6 Å ont seulement de l'eau de trou, alors que les deux hydrates synthétiques de 10 Å et l'halloysite(10Å) contiennent à la fois l'eau de trou et associée. L'eau de trou est probablement liée par l'hydrogène aux oxygènes de base des tétraèdres de la silice ou, dans les hydrates de 8-Å lorsque la fluorine est échangée pour les hydroxyles de la surface intérieure, les molécules d'eau peuvent se réorienter et former des liens hydrogènes plus forts avec la fluorine. L'eau associée forme des liens hydrogènes eau-eau à peu près aussi forts que l'eau liquide, mais est moins fort liée aux surfaces argiles que l'eau de trou. A température ambiante, l'eau de trou et associée dans les hydrates de 10 Å ne forme pas une structure semblable à de la glace. [D.J.]

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