

SYNTHESIS OF A 10-Å HYDRATED KAOLINITE

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Abstract—Hydrated kaolinite ($d(001) = 10 \text{ \AA}$) can be synthesized by mild heating of a kaolinite-organic suspension, allowing time for the clay to be intercalated by the organic solvent, and then dissolving a fluoride salt in the liquid. After mild heating of the suspension, the salt and organic solvent are removed by repeated water washings. The kaolinite retains interlayer water in the form of a 10-Å kaolinite hydrate. The influence of the intercalating agent, type of salt, concentration of salt, and the time of treatment on the synthesis of 10-Å hydrate was examined for several kaolinites. The most effective salt is NH_4F ; much smaller yields were obtained using KF and RbF. Not all organic molecules gave high yields of the hydrate; dimethyl sulfoxide, formamide, and hydrazine worked well but N-methyl formamide did not. The reaction between clay and salt resulted in the replacement of some hydroxyls by fluoride. This replacement was rapid; after 1 min of fluoride treatment a substantial yield of hydrate was obtained. The intercalation step separated the layers and also disordered the kaolinite, facilitating the F for OH replacement at or near crystallite edges. This replacement weakens the interlayer bonding at the edges and thereby reduces the possibility of layer collapse and attendant dehydration.

Key Words—Dimethyl sulfoxide, Fluoride, Formamide, Halloysite, Hydrazine, Hydroxyl, Intercalation, Kaolinite.

INTRODUCTION

Halloysite (10\AA), the only naturally hydrated 1:1 phyllosilicate, has a formula of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$. The aluminosilicate layer is assumed to be the same as found in kaolinite, but layer stacking in halloysite is highly disordered with random shifts in both the *a* and *b* directions (Brindley and Robinson, 1946). The 1:1 layers are polar with hydroxyls on one surface and oxygens on the other, so it is not surprising that the interlayer bonding of the kaolinites is due to long hydrogen bonds (Hendricks, 1939; Cruz *et al.*, 1972; Giese, 1978). The interlayer bonding in halloysite (10\AA) consists of hydrogen bonds from the hydroxyl surface to interlayer water molecules which in turn form hydrogen bonds to adjacent water molecules and to oxygens of the adjacent surface. The arrangement of the interlayer water molecules, as proposed by Hendricks and Jefferson (1938), resembles that found in ice Ih. This model of the structure of water in halloysite (10\AA) is widely referenced in the literature but it is probably much too simple. The study of interlayer water in hydrated halloysites is difficult because of their great morphological variability, poor crystallinity, and the presence of pore water. The study of synthetic hydrated kaolinites should provide a better understanding of the role of water in halloysites.

The experimental approach used here is based on the calculations of Wolfe and Giese (1978) which showed that the substitution of fluoride for hydroxyl groups dramatically alters the nature of, and weakens the interlayer bonding of kaolinite. Recently, Costanzo *et al.* (1980) showed that intercalating a Cornwall kaolinite with dimethyl sulfoxide (DMSO), treating it

with ammonium fluoride dissolved in the clay/organic solution, and subsequently removing the DMSO and salt by repeated water washings creates substantial yields of a 10-Å hydrate. The chemical reactions taking place and the influence of different conditions of treatment on the production of the hydrate are of interest. We report here preliminary data on the effects of (1) the time of fluoride treatment, (2) the concentrations of fluoride, (3) the nature of the starting clay, and (4) the intercalating molecule on the formation of the 10-Å kaolinite.

EXPERIMENTAL

Materials

All chemicals were Fisher Certified Reagent grade. X-ray powder diffraction (XRD) scans of the clays were made with a General Electric XRD-6 diffractometer ($\text{CuK}\alpha$ radiation). The pH measurements were made with a Chemtrix pH meter (model 40-E) using a Sen-sorex S200C electrode.

Three well-crystallized kaolinites were examined; a china clay from Cornwall (sample identification RLO1415, from English China Clays, St. Austell), Hydrite UF (lot #1545 from the Georgia Kaolin Company), and Georgia well-crystallized kaolinite (KGa-1 from the Source Clays Repository of The Clay Minerals Society). Two less well-crystallized kaolinites also were included; Georgia poorly crystallized (KGa-2 from the Source Clays Repository of The Clay Minerals Society) and dehydrated, tubular halloysite from Spruce Pine, North Carolina. The Hinckley crystallinity indexes (Hinckley, 1963) for the first four of these clays were 0.92, 0.77, 0.95, and 0.32 respectively. The infrared

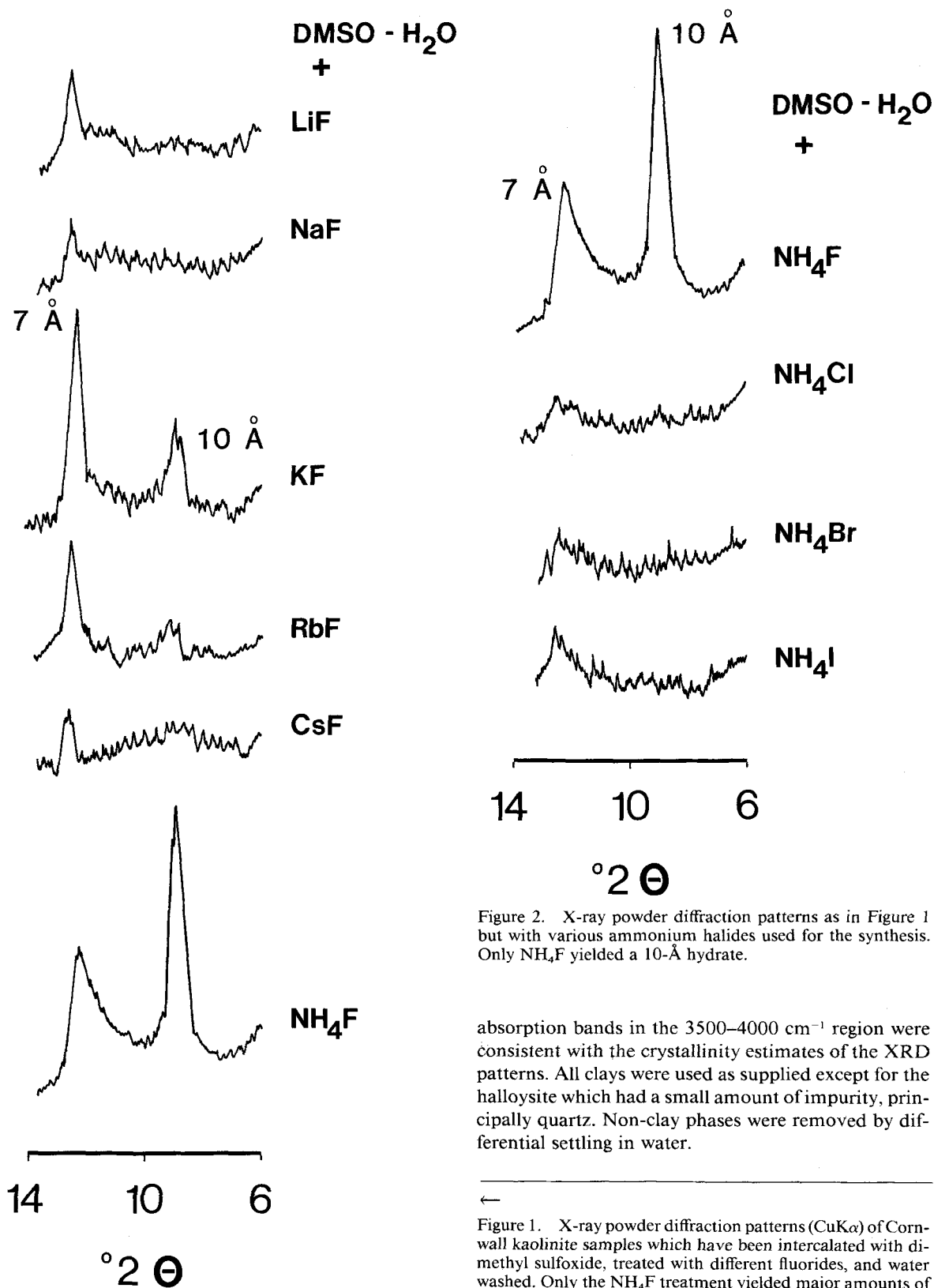


Figure 2. X-ray powder diffraction patterns as in Figure 1 but with various ammonium halides used for the synthesis. Only NH₄F yielded a 10-Å hydrate.

absorption bands in the 3500–4000 cm⁻¹ region were consistent with the crystallinity estimates of the XRD patterns. All clays were used as supplied except for the halloysite which had a small amount of impurity, principally quartz. Non-clay phases were removed by differential settling in water.

Figure 1. X-ray powder diffraction patterns (CuKα) of Cornwall kaolinite samples which have been intercalated with dimethyl sulfoxide, treated with different fluorides, and water washed. Only the NH₄F treatment yielded major amounts of a 10-Å hydrate as shown by the large peak near 9°2θ.

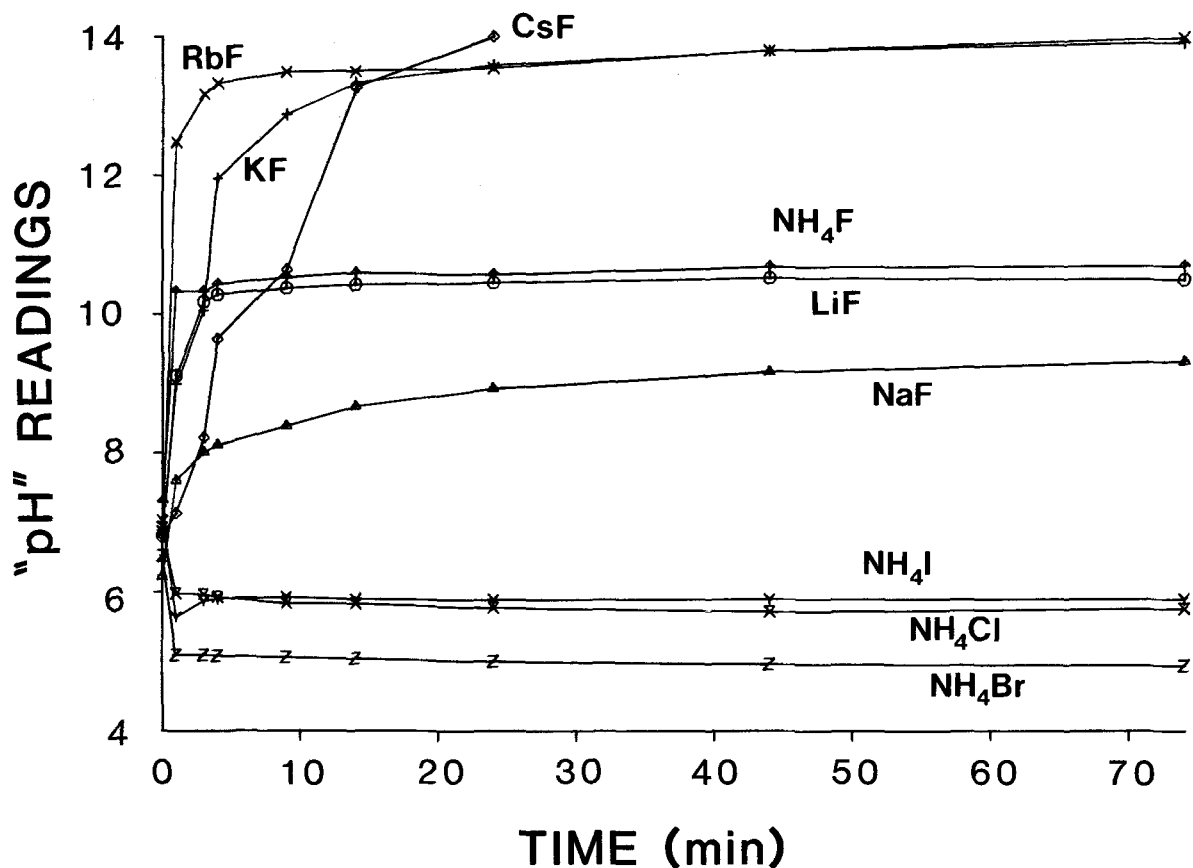


Figure 3. Variation in "pH" (see text for discussion of "pH") with time for Cornwall kaolinite intercalated with dimethyl sulfoxide and various salts.

Nature of the salt

Syntheses were attempted using simple alkali fluorides and ammonium halides, including LiF, NaF, $\text{KF} \cdot 2\text{H}_2\text{O}$, $\text{RbF} \cdot x\text{H}_2\text{O}$, and CsF; and NH_4F , NH_4Cl , NH_4I , and NH_4Br . For each salt, 3 g of clay was added to 20 ml of DMSO (8% water). After complete intercalation ($d(001) = 11 \text{ \AA}$) had taken place, as indicated by the replacement of the 7- \AA peak by an 11- \AA peak in the diffraction pattern, 1.3 g of the salt was added. All salts dissolved readily in the DMSO-water solution. The clay was kept in suspension with a magnetic stirrer and the solution was maintained at 60°C in a water bath for several hours. As evaporation reduced the volume of liquid, fresh DMSO was added. The mixture was then centrifuged, decanted, and water washed three times to remove the DMSO and salt. After being left in contact with distilled water overnight, a small amount of the wet clay was smeared on a glass microscope slide and quickly scanned from 6° to 14°2 θ in the diffractometer. The XRD scans of the kaolinites treated with the fluorides and the ammonium salts are presented in Figures 1 and 2. Of all the salts tested, ammonium fluoride gave the best defined and most abundant yield

of the 10- \AA hydrate. KF gave a small amount of a reasonably well-defined hydrate, RbF gave a small amount of a poorly defined hydrate, and CsF yielded only a broad, weak band centered at 10 \AA . None of the other salts produced any detectable 10- \AA phase.

Changes in pH as a function of time can be useful in following the reactions of silicates suspended in aqueous solutions (Lin and Clemency, 1981). Such measurements were made on the DMSO-salt solutions, but the interpretation of the pH meter readings is not simple. For dilute aqueous systems containing simple solutes, pH has a well-defined meaning (Bates, 1973). The DMSO-water system does not fall into that category; DMSO is non-aqueous, the concentration of the salt is not dilute, and an insoluble phase (clay) is suspended in the liquid. As a result, the readings from the pH meter cannot easily be interpreted in terms of acidity/basicity of the system. For example, Ritchie and Uschold (1967) measured hydrogen ion activity in DMSO with a glass electrode and observed "pH values" as large as 25. In spite of the difficulties in the interpretation of the "pH" readings in such systems, they are still useful in following the reactions which

take place. The initial "pH" reading for the DMSO and water alone was 8.2; the addition of the clay increased the "pH" to 10.0. The "pH" reading immediately after the addition of the salt was difficult to measure because it changed very rapidly during the first minute or so. This was the time during which the salt was dissolving. Figure 3 shows the "pH" values determined for the Cornwall kaolinite with several ammonium halides and alkali fluorides. Starting "pH" readings for the clay, DMSO, and salt mixtures were in the range of 6.0 to about 7.5 and rapidly changed with time (Figure 3). The ammonium salts tended to have "pHs" less than 7 while those of the alkali fluorides were above this value. The ammonium fluoride reaction mixture produced a "pH" higher than the other ammonium halides. As indicated above, the only other salt to produce noticeable yields of the 10-Å hydrate was KF; this salt also produced high "pH" conditions. All but two samples reached steady "pH" readings within 5 min of initial mixing, and for most samples, 1 or 2 min was sufficient.

Concentration of ammonium fluoride

The above experiments underline the superior efficacy of ammonium fluoride in the 10-Å hydrate synthesis. If the fluoride from the salt replaces surface hydroxyls, there should be a relationship between the concentration of ammonium fluoride and the yield of 10-Å hydrate. Seven samples of the Cornwall kaolinite were treated in the standard way except that the amount of ammonium fluoride added ranged from 0.1 to 3.0 g (per 3 g of clay). Hydrate yield was estimated by comparing the intensities of the 7-Å and 10-Å (001) peaks. In the absence of ammonium fluoride, no hydrate is formed (Costanzo *et al.*, 1980). As soon as some salt was added, small amounts of hydrate were produced, and the yield increased rapidly to a maximum of about 65% for the addition of 1.3 g of ammonium fluoride per 3 g of clay (Figure 4). For greater salt concentrations the amount of hydrate decreased slightly. The increase in hydrate yield that accompanied the addition of small amounts of ammonium fluoride suggests that fluoride replaced hydroxyls. The complexity of chemical reactions taking place is suggested by the observation that a new crystalline phase began to appear at ammonium fluoride concentrations greater than 1.3 g. This phase has been identified from its XRD pattern as ammonium aluminum fluoride $(\text{NH}_4)_3\text{AlF}_6$. Infrared absorption bands at 3210 and 1425 cm^{-1} are characteristic of this fluoride and aid in its identification. Scokart *et al.* (1979) reported the appearance of this same material during their ammonium fluoride treatment of aluminum oxides. The high "pH" of the clay-organic suspension coupled with sufficient time and abundant ammonium fluoride will chemically attack the kaolinite liberating aluminum compounds.

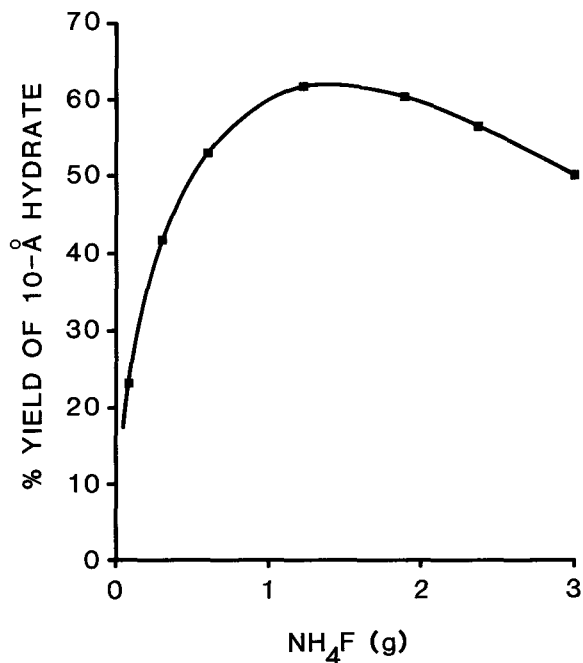


Figure 4. Yield of 10-Å hydrate as a function of the amount of NH_4F added to 3 g of clay which had been intercalated with dimethyl sulfoxide. Approximately 20 ml of liquid (DMSO with 8% water) was present.

Duration of fluoride treatment

The fluoride ions in the bulk solution did not have instantaneous access to the bulk of the inner surface hydroxyls even though the kaolinite layers had been separated by DMSO molecules. If the formation of 10-Å hydrate involves the replacement of inner surface hydroxyls, the process should be time dependent. The increase in $d(001)$ due to intercalation is only about 4 Å, and the interlayer volume is occupied by three DMSO molecules per two unit cells of kaolinite (Olejnik *et al.*, 1968). Under these crowded conditions, even if the electrostatic interaction of NH_4^+ and F^- ions with the highly polar DMSO is not considered, diffusion of these ions into the interlayer volume should be slow. Thus, the amount of OH replaced by F should increase as the time during which the clay is in contact with the NH_4F solution increases.

To test this hypothesis, a series of Cornwall kaolinite samples was treated in the standard manner except that the duration of the fluorination step varied between 1 and 60 min. All samples, including the 1-min treatment produced substantial and very nearly equal amounts of 10-Å hydrate. No time-dependent trend was observed.

Recently, Mohammad (1982) chemically analyzed three series of timed reactions similar to the one described above except that the fluorination times were as long as 49 hr. Georgia well-crystallized and Cornwall

Table 1. Yield of 10-Å hydrate for five kaolinites.

Clay ¹	Intercalate (%)	10-Å hydrate %	Corrected ² yield of 10-Å hydrate (%)
RLO1415	100	79	79
Hydrite UF	90	67	74
KGa-1	95	75	79
KGa-2	77	62	80
Spruce Pine	100	100	100

¹ See text for source, location and description of the clays.

² Corrected yield represents the hydrate formed from the fraction of the clay which was intercalated by dimethyl sulphoxide.

kaolinites were used in these experiments. The results indicated that a small amount of F (~1–4 wt. %) was adsorbed by the DMSO-intercalated clay in fluoride treatments lasting up to 6 hr. Similar small increases in F (~4 wt. %) were observed by Scokart *et al.* (1979) during their fluoride treatment of alumina. Similar fluoride treatment of these same clays but without an initial intercalation with DMSO resulted in the adsorption of between 0.2 and 0.7 wt. % F on the external surfaces of the kaolinites. The fluoride in excess of these latter values must represent replacement of some of the inner hydroxyls. For fluoride treatments in excess of 6 hr, the fluoride content increased rapidly, but the increase was due to the dissolution of the clay and the formation of the aluminum ammonium fluoride phase. The fluorine content of the clay itself could not be determined because it was impossible to remove the ammonium fluoride phase completely.

Nature of the kaolin

The five kaolins, Georgia well- and poorly crystallized kaolinites, Cornwall kaolinite, Hydrite UF kaolinite and Spruce Pine halloysite, when treated in the standard manner, yielded substantial quantities of 10-Å hydrate. Under the conditions of the experiment, the degree of DMSO intercalation varied among the five clays. Inasmuch as DMSO intercalation is necessary for hydration, the percentage of intercalated layers which hydrate is the important factor. The yields of hydrate along with the percentage of intercalate and the net hydrate yield (corrected for the non-intercalated clay) for the five clays are shown in Table 1. The Spruce Pine halloysite intercalated and hydrated most easily and to the greatest extent. This behavior presumably is related to the greater amount of structural disorder in this clay.

Intercalating agent

The organic intercalating molecule may simply expand the clay layers or it may take an active part in the chemical and physical modification of the inner surfaces, facilitating hydroxyl replacement by fluorine.

Table 2. Synthesis of hydrated kaolinite using different intercalating molecules.¹

Intercalating molecule	Final "pH" ²	Initial intercalation (%)	Yield of 10-Å hydrate (%)
Dimethyl sulfoxide	10	92	76
Hydrazine	10–11	>95	85
Formamide	~7	72	81
N-methyl formamide	8.5	>95	39

¹ All experiments used RLO1415 kaolinite.

² See text for discussion of "pH."

Costanzo *et al.* (1980) used DMSO which is an aprotic molecule with a sulfonyl oxygen capable of participating in hydrogen bonding. To examine the relative activity of the different intercalating agents, hydrazine, which is protic with no oxygen, and formamide and N-methyl formamide (NMF), both of which are protic and have a carbonyl oxygen, were used. Samples of the Cornwall kaolinite were intercalated with each, treated with ammonium fluoride, and washed as before. Table 2 summarizes the results of these experiments. The "pHs" of the clay/organic suspensions containing fluoride salt are in the observed range of hydrate formation for DMSO and hydrazine while those for formamide and NMF are lower. The Cornwall kaolinite intercalates nearly completely with each of these molecules except formamide. The final yield of 10-Å hydrate as a percentage of intercalated layers, with the exception of NMF, was high. The non-uniformity in hydration of the Cornwall kaolinite suggests that the intercalating molecule does more than open the clay layers to expose the inner surface hydroxyls to fluoride ions.

Recently, Giese and Costanzo (1982) investigated the heat capacities (C_p) of several kaolin minerals, their intercalates with DMSO, NMF, and formamide, and the same clays after the intercalating molecules had been driven off by mild heating ("de-intercalation"). Their results show that intercalation of the kaolinites by NMF followed by de-intercalation does not markedly change the C_p values of the clays. This is not true for DMSO or formamide where marked increases in C_p were observed. These changes in heat capacity suggest that varying degrees of stacking disorder are created by the process of intercalation followed by de-intercalation. The observation that DMSO is more effective than NMF in the synthesis of the 10-Å hydrate (Table 2) and the C_p values of Giese and Costanzo (1982) suggest that hydration of kaolinites is related to the disordering of the clay as well as to the replacement of OH by F; the greater the degree of disorder (as measured by C_p), the greater the yield of 10-Å hydrate. These differences between the action of DMSO and NMF on kaolinites during intercalation and de-intercalation have been observed in electron paramagnetic and nuclear magnetic resonance studies (M. Lipsicas,

Schlumberger-Doll Research, P.O. Box 307, Ridgefield, Connecticut 068774, personal communication).

CONCLUSIONS

The determining factor in hydrate formation is the ability of the clay to form an intercalate with an appropriate organic molecule such as DMSO. If the clay can be intercalated, a 10-Å hydrate probably can be synthesized.

All of the organic molecules used here functioned well in the synthesis except NMF. The Cp data for NMF intercalated kaolinites indicate that NMF intercalation/de-intercalation introduced relatively little disorder to the kaolinites used in this study. The creation of disorder (probably stacking disorder) seems to be a necessary and integral part of the 10-Å hydrate synthesis. Chemical analysis of 10-Å hydrates for fluoride, the relationship between the amount of ammonium fluoride and the yield of the hydrate, and the "pH" readings as a function of length of fluoride treatment all indicate that small amounts of F were taken up in the structure. More fluoride was adsorbed than can be explained by simple external surface adsorption. The replacement, wherever it took place, was very rapid and appeared to be largely complete after 1 min of exposure to the ammonium fluoride in solution. These observations suggest that F replaced OH at the edges of the 1:1 layers and inner surface OH near the exposed edges. The kaolinites appear to have been disordered by the organic intercalation, and, as a result, more of the individual layers were exposed at the boundaries of the crystallites, allowing increased replacement of OH by F. Disordering of the layer stacking and fluorination of crystallite edges (plus a small number of adjacent-inner-surface OHs) should weaken the interlayer bonding at the crystallite edges thereby reducing the possibility of collapse being initiated at the edges. These reactions help to stabilize the crystallites in an expanded form, and water washing should replace the organic molecules between the layers with water, resulting in a 10-Å hydrate.

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Note added in proof:

We have recently used DMSO as the intercalating agent without adding a fluoride salt. The clay/DMSO suspension was washed three times with absolute methanol followed by three water washings. This sequence of treatments produced substantial yields of the 10-Å hydrate. It is not clear what the methanol washing did to the intercalated clay, but the treatment may have increased the level of stacking disorder and thus increased the stability of the 10-Å hydrate.

Резюме—Гидратированный каолинит ($d(001) = 10 \text{ \AA}$) может быть синтезирован путем умеренного нагрева каолинито-органической суспензии, если имеется достаточное время для того, чтобы органический растворитель включился в глину и для последующего растворения флюористой соли в жидкости. После умеренного нагрева суспензии, соль и органический растворитель удаляются при помощи неоднократных водных промываний. Каолинит удерживает межслойную воду в виде $10\text{-}\text{\AA}$ каолинитового гидрата. Исследовалось влияние прослойного вещества, типа соли, концентрации соли и времени обработки на синтез $10\text{-}\text{\AA}$ гидрата для нескольких каолинитов. Наиболее эффективная соль это NH_4F ; намного меньшие результаты были получены при использовании KF и RbF . Не все органические молекулы давали высокий выход гидрата. Диметилсульфоксид, формамид и гидразин давали хорошие результаты, в то время как N -метилловый формамид не давал таких результатов. В результате реакции между глиной и солью происходило замещение некоторых гидроксидов флюоридами. Это замещение было быстрым, после 1 минуты флюористой обработки был получен значительный выход гидрата. Тонкое включение прослойки разделяло слои, а также приводило к нарушению упорядочения каолинита, облегчая замещение OH флюором на кристаллических гранях. Это замещение ослабляет межслойную связь на гранях и, таким образом, уменьшает возможность разрушения слоя и сопутствующей дегидратации. [E.G.]

Resümee—Hydratisierter Kaolinit ($d(001) = 10 \text{ \AA}$) kann durch mildes Erhitzen einer Suspension aus Kaolinit und einem organischen Lösungsmittel synthetisiert werden, wobei genügend Zeit vorhanden sein muß, damit das organische Lösungsmittel in die Zwischenschichten des Ton eindringen kann, und anschließend ein Fluorid-Salz in der Flüssigkeit aufgelöst werden kann. Nachdem die Suspension mild erhitzt wurde, werden das Salz und das organische Lösungsmittel durch wiederholtes Waschen mit Wasser entfernt. Der Kaolinit hält Zwischenschichtwasser in der Form eines 10 \AA Kaolinithydrates zurück. Der Einfluß des Zwischenschicht-bildenden Agens, der Art des Salzes, der Salzkonzentration und der Behandlungszeit auf die Synthese des 10 \AA Hydrates wurde für verschiedene Kaolinite untersucht. Das wirksamste Salz war NH_4F ; viel kleinere Ausbeuten wurden mit KF und RbF erzielt. Nicht alle organischen Moleküle ergaben hohe Hydratausbeuten. Dimethylsulfoxid, Formamid und Hydrazin hatten einen positiven Einfluß, während N -methylformamid keine Wirkung zeigte. Die Reaktion zwischen Ton und Salz führte zum Ersatz einiger Hydroxidionen durch Fluoridionen. Dieser Ersatz verlief schnell; nach einer Minute der Fluoridbehandlung wurde eine wesentliche Ausbeute an Hydrat erzielt. Der Schritt zur Bildung der Zwischenschicht trennte die Lagen und führte zu einer schlechten Ordnung des Kaolinit, indem er den Ersatz von OH durch F an den Kristallkanten erleichterte. Dieser Ersatz schwächte die Zwischenschichtbindung an den Kanten und verringerte dadurch die Möglichkeit, daß die Schichtstruktur zerstört wird und im Zusammenhang damit eine Dehydratation stattfindet. [U.W.]

Résumé—Une kaolinite hydratée ($d(001) = 10 \text{ \AA}$) peut être synthétisée en chauffant légèrement une suspension organique-kaolinite, donnant du temps pour que l'argile soit intercalée par le solvant organique, et ensuite dissolvant un sel floride dans le liquide. Après avoir légèrement échauffé la suspension, le sel et le solvant organique sont enlevés par des lavements à l'eau répétés. La kaolinite retient de l'eau intercouche sous la forme d'hydrate kaolinite $10\text{-}\text{\AA}$. L'influence de l'agent intercalant, le genre de sel, la concentration du sel, et la durée du traitement sur la synthèse de l'hydrate $10\text{-}\text{\AA}$ ont été examinés pour plusieurs kaolinites. Le sel le plus efficace est NH_4F ; on a obtenu des produits beaucoup moins importants en utilisant KF et RbF . On n'a pas obtenu de grandes quantités d'hydrate de toutes les molécules organiques; la sulfoxyde diméthyle, la formamide et l'hydrazine marchaient bien, mais pas la formamide méthyle- N . La réaction entre l'argile et le sel a résulté en le remplacement de certains hydroxylys par la fluoride. Ce remplacement est rapide; après 1 min de traitement à la floride, une quantité substantielle d'hydrate a été produite. L'étape d'intercalation a séparé les couches et a aussi désordonné la kaolinite, facilitant le remplacement de F par OH aux bords cristallites. Ce remplacement affaiblit les liens intercouche aux bords, et réduit ainsi la possibilité de l'effondrement de couches et la déshydratation l'accompagnant. [D.J.]