

EXPERIMENTAL FORMATION OF KAOLINITE FROM MONTMORILLONITE AT LOW TEMPERATURES

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ABSTRACT

Na- and Al-montmorillonites under hydrothermal conditions at 175° and 220°C for periods of seven days yield no more than very minor amounts of kaolinite and then only under strongly acid conditions. Al-OH polymers, formed under appropriate ratios of NaOH/Al, have been introduced into the interlayers of montmorillonite in amounts of 300 meq Al/100 g. clay and 1500 meq Al/100 g. clay; the latter corresponds to a nearly complete gibbsitic layer and the resulting montmorillonite approximates to a dioctahedral chlorite. Hydrothermal treatment readily generates kaolinite in quantity, and strongly acid conditions are no longer necessary. The process is followed by X-ray diffraction and IR spectroscopic data. The hydrated state of the kaolin when first formed is noted.

INTRODUCTION

As a part of a program for studying the formation of kaolinite at low temperatures, and in continuation of previous investigations in this laboratory (Brindley and De Kimpe, 1961; De Kimpe *et al.*, 1964), investigations have been made of the formation of kaolinite by alteration of montmorillonites under various conditions of cation saturation and of acid environments. To expedite the very slow reactions at temperature less than 100°C, most of the experiments have been conducted hydrothermally in the temperature range 175°–220°C, and with pressures of the order 4000 or 8000 psi; it is believed that the results will be comparable with those obtained under natural conditions over much longer periods of time.

EXPERIMENTAL

Materials. Montmorillonites from Texas and from Little Rock, Arkansas, were used. The natural material from Texas contained cristobalite as an impurity, but a refined variety contained negligible cristobalite. Na- and Al-saturated samples were prepared by treating the clays four times overnight with normal chloride solutions followed by washing till a negative chloride test was obtained. The washed clays were dried and stored at room temperature.

Montmorillonites containing aluminum hydroxy-polymers, designated Al-OH-montmorillonites, were prepared by methods similar to those described by Sawhney (1960) and by Barnhisel and Rich (1963). Solutions of 0.1 N NaOH and 0.2 M AlCl₃ were added dropwise under vigorous stirring to 0.4 percent Na-montmorillonite suspensions. The total amounts of Al in two series of preparations were 300 meq and 1500 meq per 100 g. of clay. The NaOH/Al molar ratios 0.6, 1.5, 2.25, 2.7 and 3.0 were prepared and aged for two weeks. Barnhisel and Rich (1963) have shown that maximum interlayering of hydroxy-polymers occurs for molar ratios from about 2.25 to 3.0. After centrifugation, the samples were washed and air dried. Hsu (pers. comm.) has observed that negligible Al is removed

during washes. X-ray examination and Al analysis of the centrifugates revealed an increasing fixation of Al hydroxy-polymers with increasing NaOH/Al molar ratios (see Table 1).

In column (II), Table 1, the content of polymer fixed for the NaOH/Al ratio 2.7 is close to the value given by Slaughter and Milne (1960) (1600 meq Al/100 g. of clay) to yield a complete gibbsite-like interlayering. Since completion of the present work, a paper by Brydon and Kodama (1966) has appeared stating that about 1125 meq Al/100 g. clay will be taken up within the montmorillonite structure. Whether the extra alumina taken from solution, as shown in Table 1, is in gel form or held externally by the montmorillonite is not clear.

Additionally Al-OH forms of hectorite, vermiculite and a synthetic fluorhectorite were prepared.

Treatments. Sealed gold capsules (35 mm long and either 2.5 mm or 5.0 mm o.d.) containing known amounts of reactants (generally about 30 mg of solid material and 20–25 mg of liquid) were heated in test-tube type bombs at temperatures ranging 175–220°C, $\pm 3^\circ\text{C}$.

TABLE 1. FIXATION OF ALUMINUM HYDROXY-POLYMERS BY MONTMORILLONITES

Total Al content in initial systems	meq Al per 100 g. of clay	
	300	1500
Total Al found in solutions for NaOH/Al molar ratios:	(I)	(II)
0.6	145.0	1220.0
1.5	45.8	695.0
2.25	0.0	274.0
2.7	1.7	16.7
3.0	14.7	66.7

After reaction, products were quenched. Capsules were weighed before and after treatment to check for leaks. The techniques followed the descriptions given by Roy *et al.*, (1950, 1952).

Product examination. Products were X rayed using Ni-filtered $\text{CuK}\alpha$ radiation and a Philips Norelco diffraction unit.

IR absorption spectra were obtained using vacuum-pressed KBr pellets with a Perkin-Elmer, model 221, spectrometer for the range 2–15 microns, and a Beckman DK2 instrument for the range 2–3 microns.

RESULTS

Na-montmorillonite. In most experiments conducted at 175°C, and at 220°C, for periods of seven days, the initial montmorillonite remained as the predominant component. With 1 N HCl, and with 1 N HCl plus AlCl_3 , at 220°C, a small amount of kaolinite (shown by its 7.2 Å reflection) was formed. With water, with 0.1 N NaOH, and with HCl solution at pH 4.8, no kaolinite was detected. With N HCl plus gibbsite, abundant boehmite (presumably from the gibbsite) was obtained. It should be

noted that with 0.1 N NaOH, no analcime was observed, although under somewhat different conditions, the formation of analcime has been observed by McCaleb (1961), by Van Moort *et al.* (1966), and also by the present writers.

Al-montmorillonite. Only with 1 N HCl at 220°C for seven days was a small amount of kaolinite obtained. A trace of kaolinite was detected with 0.1 N NaOH solution.

With a solution of pH 4.8, with water and at a temperature of 175°C, no kaolinite was detectable. Although there was little difference from the results obtained with Na-montmorillonite, the Al-montmorillonite seemed to show a greater alteration.

Al-OH-montmorillonite, I (300 meq Al/100 g. of clay). As shown by the data in Table 1, most of the available Al-OH polymers was taken up by the montmorillonite when the NaOH/Al ratio was in the range 2.25–2.7. The Al-OH-montmorillonite, prepared as mentioned, was treated hydrothermally with 1 N HCl for seven days at 175°C. Little difference was observed between the products formed by the samples prepared with various NaOH/Al ratios; in each case, a small amount of kaolinite was obtained, with a preponderance of unreacted montmorillonite. The yield, though still small, was an improvement over the previous experiments which showed not even a trace of kaolinite for a reaction temperature of 175°C.

Al-OH-montmorillonite, II (1500 meq Al/100 g. of clay). With this amount of aluminum added to 100 g. of clay and with NaOH/Al ratio of about 2.7, a large amount of Al-OH polymers is taken up by the montmorillonite (see Table 1) and indeed is almost enough to form complete gibbsite-like layers between the montmorillonite layers.

Treated with 1 N HCl at 220°C for 7 days, the Al-OH-montmorillonites prepared with NaOH/Al molar ratios of 2.25 and 2.7 yielded abundant well-crystallized kaolinite. The yield and the degree of crystalline regularity improved slightly by extending the treatment to 28 days; the improvement was seen more clearly by IR absorption spectroscopy than by X-ray diffraction. Even after only one day of treatment, the formation of a kaolin mineral was detectable by both methods, together with traces of boehmite, but after four days, the boehmite and the initial montmorillonite were entirely absent. Further examination of the product formed in quantity at 240°C for 21 days was made by thermogravimetric analysis and by electron microscopy. Material dried in vacuo at 110°C gave a thermogravimetric curve agreeing with that of a well-

formed kaolinite and a total weight loss of 13.2 percent as compared with that of 13.9 percent for the theoretical composition. Electron micrographs showed well-formed, pseudo-hexagonal particles of about 0.2–0.5 μ size.

A major difference between the present results and those reported earlier is that kaolinite was obtained without the use of strongly acid media and even with water, a kaolin mineral was always detected in experiments at 220°C for seven days. At lower temperatures, 190° and 175°C, and with 1 N HCl, the resulting kaolinite was less well crystallized and, at 175°C, traces of boehmite were seen. At a still lower temperature, 150°C, and with 1 N HCl, even after 28 days kaolinite could not be detected by X rays; however the montmorillonite appeared to be altered and possibly diffraction effects from freed silica layers were detected. That the montmorillonite was in process of alteration was indicated by the IR spectra, which showed after only one week of treatment, four distinct absorptions in the OH region at about the same frequencies as those given by kaolinite. The sensitivity of IR spectra for showing short-range order effects before X-ray diffraction can pick up long-range order effects is strikingly demonstrated in this work.

Experiments with 0.1 N NaOH yielded very poor kaolin at 175°C. At 220°C, analcime and other zeolites, possibly sodalite and cancrinite, were formed but no kaolinite was observed.

Al-OH-vermiculite, Al-OH-hectorite and Al-OH-fluorhectorite. Al-OH-vermiculite prepared with NaOH/Al molar ratio of 2.55 has been treated hydrothermally with N HCl at 230° and 360°C. No trace of kaolinite (or a 1:1, 7 Å mineral) was found after seven days. Traces of poorly crystallized boehmite were detected, together with a mixed-layering of 12.5 Å and 14.0 Å phases, with a small 10 Å reflection attributable to small amounts of biotite in the original material.

Al-OH-hectorite and Al-OH-fluorhectorite prepared with NaOH/Al molar ratio of 2.25 were submitted to the same hydrothermal treatment as the vermiculite. In both cases, small amounts of boehmite were detected, but no 7 Å phases.

Sand (1955), and Ames and Sand (1958), studying the hydrothermal stability of montmorillonites, have shown that the trioctahedral 2:1 minerals are more stable than the dioctahedral, and this may account for the negative results obtained with these minerals, at least for the hectorites.

X-ray diffraction data. It suffices to consider the products formed when 1500 meq Al in the form of aluminum hydroxy-polymer prepared with

NaOH/Al molar ratio 2.25 were added to 100 g. montmorillonite. When taken from the sealed gold capsules, the products were given extra water and examined prior to any drying treatment. Part of the sample was air-dried, equilibrated for two months at room conditions, and subsequently heated at 105°, 200° and 300°C. The second part of the sample

TABLE 2. BASAL SPACINGS OF KAOLINITE (OR KAOLIN MINERAL) FORMED FROM Al-OH-MONTMORILLONITE AT 220°C BY TREATMENT WITH 1 N HCl FOR PERIODS UP TO 28 DAYS

Days of reaction	1	2	4	7	14	28
In water prior to drying	8.6	8.4	7.3	7.2 ₅	7.2	7.2
Air-dry	8.0	(9.0) 7.8	7.3 ₅	7.2 ₅	7.2	7.2
After two months at room conditions	9.0	8.3	8.0	7.3 ₇	7.2	7.2
After 105°C	9.0	8.3	8.2	7.2 ₅	7.2	7.2
After 200°C	9.0	8.3	8.2	—	7.2	7.2
After 300°C	8.4	8.3	8.0	—	7.2	7.2
Ethylene glycol added to wet product	8.8 ₅	8.6	8.1	—	7.2	—
After 105°C	8.4 7.2 ₅	8.6 7.2 ₅	7.8 7.2 ₅	7.3	7.2 ₅	—
After 200°C	—	8.2 7.2 ₅	7.9 7.2 ₅	7.3 ₇	7.2 ₅	—
After 300°C	8.2 ₅ 7.2 ₅	8.2 7.2 ₅	7.8 7.2 ₅	7.4	—	—
After 400°C	—	8.3 7.2 ₅	7.8 7.2 ₅	7.4	—	—

was treated with ethylene glycol, and subsequently heated. Table 2 records the basal spacings of the products formed after 1, 2, 4, 7, 14 and 28 days of hydrothermal treatment at 220°C with 1 N HCl. The better crystalline products are those with a basal spacing around 7.2 Å, and with the best products it was possible to measure up to 005 by using the oriented aggregate technique.

The results indicate that the kaolin mineral when first formed has an expanded basal spacing of the order of 8.5 Å which remains fairly stable

up to about 300°C. With four or more days of hydrothermal treatment, the spacing is reduced to 7.3–7.2 Å, a value slightly greater than the value 7.15 Å normally found for well-crystallized kaolinite. If the expanded phase is due to inclusion of water molecules between the layers, possibly in the ditrigonal holes of the silica network, then these are not easily removed by heat treatment. The expanded spacings also may reflect to some extent a poor articulation of the successive layers which is supported by the poor appearance of nonbasal reflections. Heat treatment gives an inhomogeneous product, in that part of the material develops a sharp 7.2 Å reflection when the remainder still gives a broader reflection from the expanded spacing. Ethylene glycol produces only very slight expansion showing that little penetrates into the structure.

Expanded and hydrated forms of kaolin minerals have been studied also by Wada (1965) and by Deeds, van Olphen and Bradley (1966). Intersalation complexes, formed particularly with potassium acetate, when thoroughly washed with water, gave hydrated forms with basal spacings as follows: Halloysite with $4\text{H}_2\text{O}/\text{unit cell}$ and $d(001)\simeq 10.1$ Å, nacrite with about $2\text{H}_2\text{O}/\text{unit cell}$ and $d(001)\simeq 8.4$ Å, kaolinite gave $d(001)\simeq 7.8$ Å and dickite alone appeared not to form a hydrated complex. Both Wada, and Deeds *et al.*, remarked on the thermal stability of the hydrated forms of nacrite and kaolinite, up to at least 200°C. It seems very probable that the expanded spacings observed in the present studies arise from the early formation of similar hydrated forms.

Infrared absorption analysis

OH stretching vibrations. Figure 1 shows the IR frequencies obtained for Al-OH-montmorillonite II after 1, 2, 4, 7 and 14 days reaction at 220°C with 1 N HCl; values for a Florida kaolinite also are shown. After only one day of hydrothermal treatment, four bands appear at about the same positions as those of a well-crystallized kaolinite. Between one and two days of reaction, the absorption labeled MF_2 occurs at the same frequency as the corresponding vibration in kaolinite and keeps this value throughout the sequence of transformation. Such constancy means that the dipole moment associated with this vibration is unaffected during the further development of kaolinite. Only OH groups with their dipole moments parallel to the sheet would stay unaffected by the collapse or the contraction of the sheets. The almost constant value of MF_1 likewise points to OH groups of essentially the same type. These conclusions are very close to those of Farmer and Russell (1964) who attributed these two bands to vibrations in the OH plane.

The continuous shift of the frequency labeled HF could be accounted for, either by an increasing interaction O-H-O, or as a consequence of

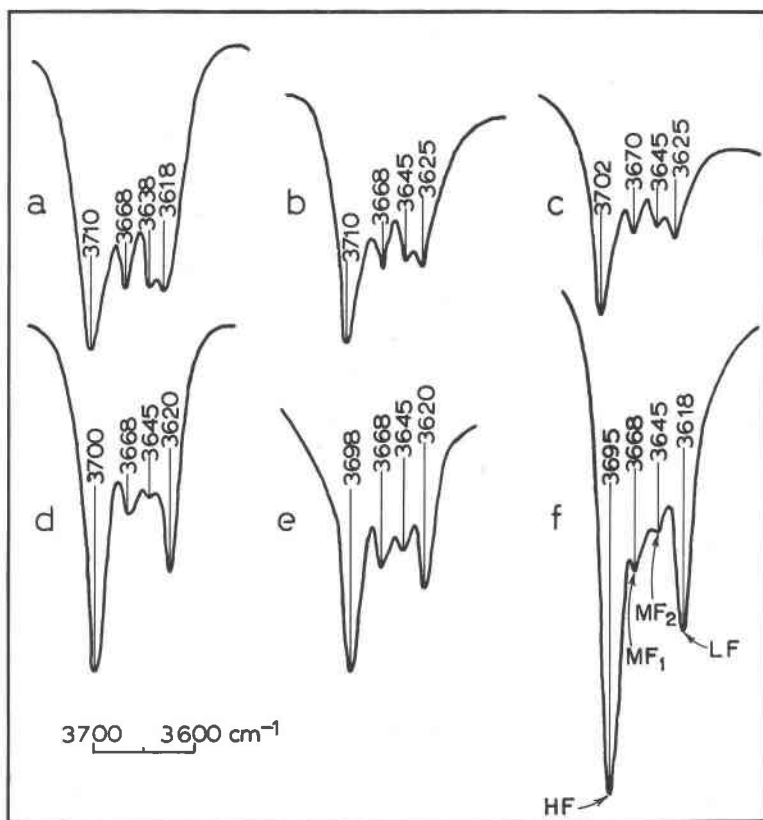


FIG. 1. IR absorption spectra for Al-OH-montmorillonite II after (a) 1 day, (b) 2 days, (c) 4 days, (d) 7 days, (e) 14 days, of hydrothermal treatment with 1 N HCl at 220°C. (f) shows a corresponding spectrum for a Florida kaolinite.

progressive shortening of the bonds O-Al-OH. In the first case, the diminution of $d(001)$ observed by X-ray diffraction (see Fig. 1) should reinforce the hydrogen bond between adjacent sheets and lead to a diminution of the OH stretching frequency, as observed. However the alternative explanation cannot be ruled out, at least as a partial explanation.

The shift of the frequency labeled LF, first towards higher and then back to lower frequencies is not clearly understood but presumably arises from the structural rearrangements during the reaction.

Figure 2 shows frequency differences as indicated, plotted against duration of the hydrothermal treatment. It is evident that the main structural rearrangements occur before seven days. With increasing

duration, the differences between $(HF - MF_2)$ and $(MF_1 - LF)$ and between $(HF - MF_1)$ and $(MF_2 - LF)$ decrease slowly and tend towards the corresponding values for the Florida kaolinite, for which, (perhaps fortuitously), $(HF - MF_2) = (MF_1 - LF) = 50 \text{ cm}^{-1}$ and $(HF - MF_1) = (MF_2 - LF) = 27 \text{ cm}^{-1}$.

Lattice vibrations. Frequencies observed in the range $1100\text{-}600 \text{ cm}^{-1}$ are shown in Figure 3. Here also, after one day of treatment, all the bands present in the spectrum of the Florida kaolinite make their appearance apart from one of the doublet near 918 cm^{-1} . Furthermore, all bands characteristic of montmorillonite disappear before four days, in agreement with the X-ray observations. It is evident that the main lattice reorganization is complete before seven days.

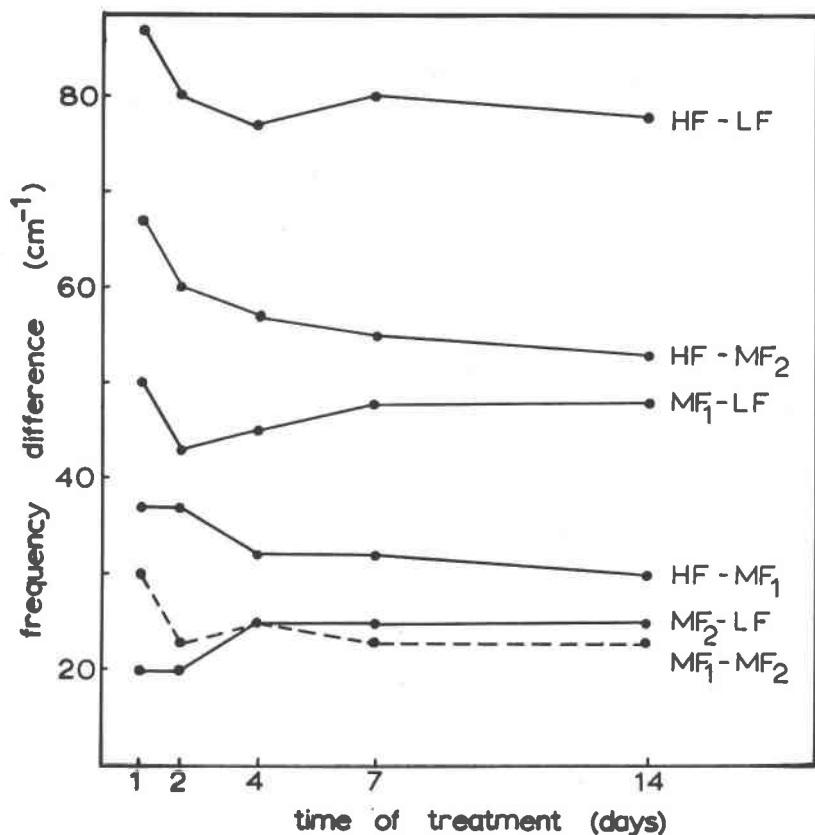


FIG. 2. Differences between IR absorption frequencies in the OH-stretching region, plotted against time of hydrothermal treatment, with 1 N HCl at 220°C

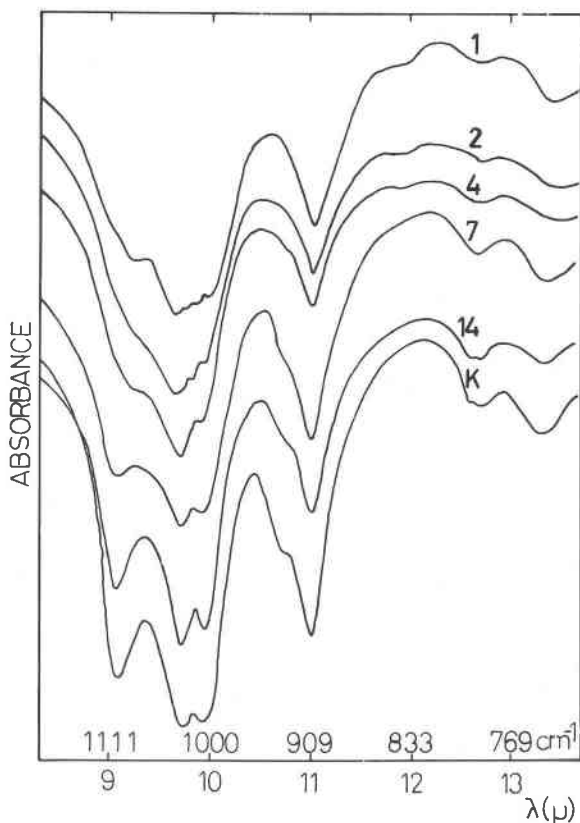


Fig. 3. IR absorption spectra for Al-OH-montmorillonite II after 1, 2, 4, 7 and 14 days hydrothermal treatment with 1 N HCl at 220°C. Curve K is for Florida kaolinite.

The intensity of the absorption at 910 cm^{-1} is greater than expected for pure montmorillonite, which, according to Oinuma and Hayashi (1965, 1966), reflects the presence of a kaolin mineral, and its increasing intensity is expected during the formation of kaolinite, (Gastuche and Fripiat, 1962). The same remarks are true for the absorptions at 1038 and at 1003 cm^{-1} (Touillaux *et al.*, 1960).

Two interpretations are possible of the bands at 790 and 752 cm^{-1} . Either they will be expected as soon as Si-O-Al (their assignments by Stubican and Roy, 1961a, b) bonds are formed, which will occur at the very beginning of the kaolin formation. Or they are a consequence of the removal of one silica layer in montmorillonite, which diminishes the "symmetrical interaction" of the silica layers with the octahedral layer; the absence of these bands in montmorillonite may be attributed

to the associated dipole moments having similar orientation and magnitude but in opposite directions, which thereby cancel each other. To account for two bands, two different Si-O-Al orientations seem to be required.

Whatever the exact explanation, these data, together with the X-ray data, indicate the progressive improvement in the crystallinity of the kaolinite.

DISCUSSION

The form and quantity of added alumina. The results show that a relation exists between the amount of kaolinite formed and the total Al content of the montmorillonite, increasing in the sequence.:

Na-montmorillonite \rightarrow Al-montmorillonite \rightarrow Al-OH-montmorillonite I \rightarrow Al-OH-montmorillonite II. The influence of an acid environment also changes significantly through this sequence.

Na- and Al-montmorillonites do not contain sufficient alumina in relation to silica to form more than a small proportion of kaolinite, the amount depending on how the available alumina may be partitioned between kaolinite and any other phase or phases present. Increasing the amount of Al in the system does not necessarily give more kaolinite. Thus addition of AlCl_3 to an Al-montmorillonite does not increase the yield of kaolinite. Addition of gibbsite leads to the appearance of boehmite, but not to more kaolinite. But when Al-OH-polymers are added, the yield of kaolinite is greatly increased, for several possible reasons. In the first place, cations such as $\text{Al}(\text{OH})_2^+$ and the more complex forms probably present in the Al-OH-polymers, (*cf.* Hsu and Bates, 1964a) increase the proportion of Al in the system as compared with that of an Al-montmorillonite. Secondly, the Al is introduced throughout the inter-layer region of the montmorillonite and thereby is brought into intimate contact with the silica layers, an arrangement which will facilitate kaolinite formation. Thirdly, the Al-OH polymers introduce the OH ions also required in kaolinite formation. Evidently the *internal* formation of gibbsite-like layers is much more effective than the addition of *external* gibbsite.

Formation of dioctahedral chlorite-like intermediate phase. An interesting aspect of this mode of kaolinite formation is that it resembles the relation between serpentine minerals and chlorites. When gibbsitic layers are introduced into montmorillonite, the resulting structure is close to that of a wholly dioctahedral chlorite and it has some of the properties of a chlorite in that it no longer collapses to a 10 Å basal spacing with mild heat-treatment, (Sawhney, 1960; Barnhisel and Rich, 1963;

Hsu and Bates, 1964b; Turner and Brydon, 1965). The 2:1 layer structure of montmorillonite develops towards a 2:1:1 dioctahedral chlorite structure, which then transforms to the 1:1 layer structure of kaolinite.

Acid environment. The role of the acid environment seems to be mainly to break down the initial montmorillonite structure and is found to be essential when Na- or Al-montmorillonite is the starting material. The acid probably also converts the Na- to a H,Al form of montmorillonite. When the Al-OH polymers are "loaded" into montmorillonite sufficiently to give nearly gibbsitic layers, then a strongly acid environment is no longer essential and kaolinite forms even when the liquid medium is water. However, an acid environment may still develop possibly from the Al-OH polymers. In any case a slightly acid environment (e.g. pH 4.8) seems to be conducive to the formation of kaolinite, probably because it assists the breakdown, *i.e.*, reorganization, of the montmorillonite.

Field evidence. Many workers have reported the presence of aluminum interlayered 2:1 minerals in soil clay fractions. Among others, Keller (1952) found a "chlorite clay mineral" in a Missouri diaspore clay deposit, Klages and White (1957), a chlorite-like mineral in some Indiana soils, interstratified minerals were found by Tamura (1956) in several New England soils, Dixon and Jackson (1959) described 2:1-2:2 intergrades, Weed and Nelson (1962) mentioned chlorite-like intergrade minerals in soils of North Carolina, Glenn and Nash (1964) refer to an expansible 2:1 chloritized mineral in soils from the lower Mississippi Coastal Plain.

The occurrence of these Al interlayered minerals seems to be common to the soil clay fraction and is considered by Jackson (1963) as being a stage in the natural weathering sequence in the alteration of 2:1 minerals to kaolinite. Several of the workers cited above have shown a correlation between the decreasing percentage of interlayered minerals and the increasing kaolinite content with a higher degree of weathering. Jackson (1963) points out that vermiculite, of greater particle size, will alter more slowly than montmorillonite and may weather in a first step into montmorillonite.

Possibly the clearest evidence comes from a recent study by Altschuler, Dwornik and Kramer (1963), who have proposed that extensive developments of kaolinite several feet thick over hundreds of square miles in Florida were formed by a transformation of montmorillonite during low-temperature supergene weathering. They note, for example, that in one locality a "green clay is composed of disorganized montmorillonite and

poorly crystallized kaolinite," but a gray clay, stratigraphically equivalent, "is almost entirely kaolinite of improved crystallinity, with barely detectable. . . . montmorillonite." Evidence is also obtained for an alumina-interlayered material, and possibly a mixed-layering between montmorillonite and kaolinite. These descriptions fit many of the present observations, though so far no experimental evidence has been obtained for a kaolinite-montmorillonite interlayering. The altering medium is suggested to be mildly acidic ground water, probably rain water enriched with humic acids and with a pH possibly 6.5-5.0.

The experiments do not, as yet, provide any clear confirmation of the particular mechanisms suggested by Altschuler *et al.* Possibly the most important conclusion so far is that the experiments seem to provide data running broadly parallel with the field observations, so that a more searching study of the laboratory preparations may yield further rewarding results.

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