

## CONDITIONS OF KAOLINITE FORMATION DURING ALTERATION OF SOME SILICATES BY WATER AT 200°C

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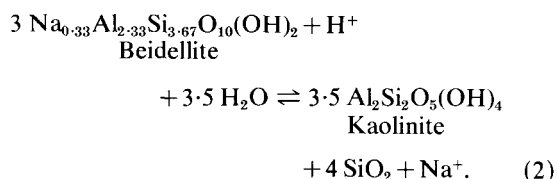
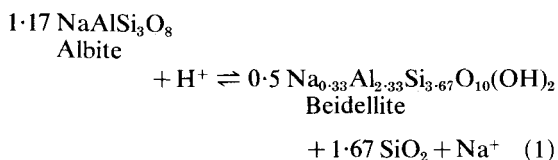
**Abstract**—When a mineral of the montmorillonite group, saturated with Na cations, is placed in a dilute solution of hydrochloric acid, and maintained at 200°C, it should alter and produce the corresponding mineral of the kaolinite group, according to the following reaction: triphormic clay + H<sup>+</sup> ⇌ diphormic clay + SiO<sub>2</sub> + Na<sup>+</sup>. The formation of the diphormic clay should depend only on the value of the [Na<sup>+</sup>]/[H<sup>+</sup>] ratio, for the various temperatures used in the process. In a number of experiments, a few minerals of various types were subjected to this alteration process, carried out under a wide variety of conditions; namely, duration of the alteration treatment, clay and acid concentrations and value of the [Na<sup>+</sup>]/[H<sup>+</sup>] ratio. Formation of kaolinite, was not found but instead either an amorphous gel, or a well-crystallized boehmite, or else no dissolution at all of the initial mineral. We have already shown that a feldspar, when subjected to an alteration under similar conditions, never produces kaolinite, but forms a poorly crystallized boehmite instead. This intermediate product is the only one able to fix silica in its numerous active sites, and thus produce kaolinite. In this investigation we sought to induce a formation of poorly crystallized boehmite, from montmorillonites, with a view to a subsequent growth of kaolinite. This was achieved by inserting layers of aluminum hydroxy-polymer between the layers of a montmorillonite, followed by an alteration conducted under the same conditions as previously. At the end of a 17 hr treatment, a number of fibers of poorly crystallized boehmite (pseudo-boehmite *b*) appeared. At the end of a 15 days period, large amounts of kaolinite were formed, and kaolinite alone remained at the end of one month. These experiments substantiate the need of some 'storage' of the aluminum in an intermediate poorly crystallized mineral. This is an essential preliminary condition to any formation of clay. This clay can be formed only when the silica-monomer can be fixed on active sites of the intermediate product.

It is well known that a silicate, such as feldspar, may produce various clay materials during weathering. The clay minerals can be either triphormic clays (2:1 minerals such as montmorillonite), or diphormic clays (1:1 minerals such as kaolinite). Similarly, the 2:1 minerals can alter to form 1:1 minerals. It is commonly assumed that, in acid environments, 1:1 minerals are preferably obtained, while in more alkaline media mainly 2:1 phyllites are formed. Finally, it was thought for years that, during the hydrolysis of a feldspar, a gel layer was formed around the grains of this mineral. The secondary minerals were supposed to arise within this gel layer, or within the solution, without any direct connection with the original feldspar.

During the last decade, experimental investigations, conducted by Hemley (1959), Hemley, Meyer and Richter (1961) and Lagache (1965), were devoted to the study of the dissolution of feldspars, in presence of acid aqueous solutions, under medium conditions of temperature and

pressure (above 200°C, and of the order of a few bars). Their studies allowed to investigate the equilibrium fields of the various secondary minerals likely to be formed under different conditions of temperature of reaction.

In the case of albite NaAlSi<sub>3</sub>O<sub>8</sub> for instance, Hemley, Meyer and Richter (1961) suggested the following reactions:



The law of mass action can be applied to these reactions, and, on condition that the solution is actually saturated with silica, the activity of this silica can be considered as constant, leading thus to the following relations:  $[Na^+]/[H^+] = k_1$  for reaction (1), and  $[Na^+]/[H^+] = k_2$  for reaction (2).

Basically, these relations permit the prediction of the formation of either beidellite or kaolinite, according to the value of the  $[Na^+]/[H^+]$  ratio.

Figure 1 (full curves) shows the equilibrium fields for the various minerals, as Hemley, Meyer and Richter (1961) determined them. It can be seen that these curves have been established only for temperatures above 250°C. They report that silica shows a strong tendency not to crystallize below 300°C. This aptitude to form supersaturated solutions increases the activity of the silica present in the solution, and the reaction can no more be considered as being under equilibrium conditions. Albite can even be stabilized for acidity values above those corresponding to the equilibrium state.

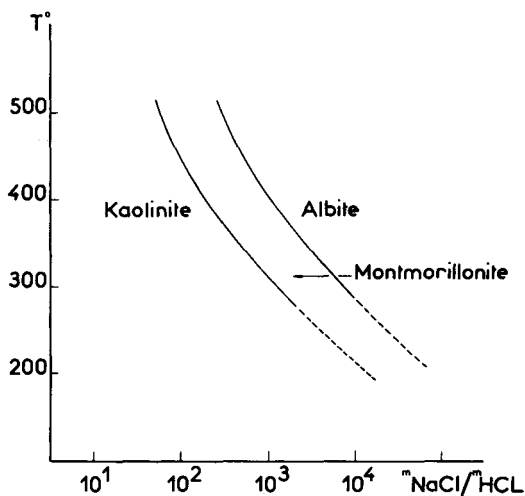


Fig. 1. Stability curves for albite, montmorillonite and kaolinite from Hemley *et al.* (1961).

Lagache (1965) started experiments on the dissolution of albite at 200°C, in water containing dissolved  $CO_2$  and showed that the progressive decomposition of feldspar does not occur through an intermediate gel, but that the amount of Na cations present in the solution increases regularly, while the silica content reaches quite rapidly a threshold attributed to the saturation of the solution. Finally, the amount of alumina still existing in the solution at the end of the process is negligible. The obtained results have also permitted the extrapolation of the curves of Hemley *et al.* (dashed curves in Fig. 1) down to 200°C.

In previous investigations (Tchoubar and Oberlin, 1963; Wyart, Oberlin and Tchoubar, 1963; Tchoubar, 1965; Oberlin and Tchoubar, 1966), conducted to localize and identify the insoluble material containing aluminum, we had the feeling that it would be profitable to repeat these experiments, starting from monocrystals, and to use electron microscopy and electron diffraction to investigate the formed products. These techniques are suitable to describe and identify very small particles.

We have shown that the etch pits appearing first on the cleavage face (001) of albite are very soon followed by occurrence of an insoluble mineral, namely boehmite  $AlOOH$ , epitaxially oriented to albite. It is only after this that clay minerals appear, due to a reaction between the formed solid and the silica present in the solution. Moreover, the formed boehmite must be poorly crystallized to be able to react with silica. It has been shown that, when boehmite precipitates on the feldspar surface, this mineral always takes the form of fibers, the crystalline organization of which is good only along the *c* axis (i.e. the fiber axis).

The alteration of a monocrystal in a large volume of liquid gives only a highly dilute solution of silica monomer: if so, the boehmite fibers have time enough to develop and produce beautiful three-dimensional crystals, and in this case, clay minerals are never formed. When on the contrary pure water is substituted by a solution containing about 100 ppm of silica monomer, into which the fresh crystal is immersed, fibers of poorly crystallized boehmite appear again, but these fibers find themselves in contact with silica, as soon as they are formed. This boehmite, rich in active sites, then reacts with  $Si(OH)_4$  to form a significant amount of kaolinite. Finally, when, instead of using a solution containing 100 ppm of silica, a certain amount of amorphous silica, able to give a solution of higher concentration, is added into the autoclave, kaolinite does not form any more, and a 2:1 clay, i.e. beidellite, is found instead, (Oberlin and Tchoubar, 1967). This shows that in the reactions (1) and (2) above, the activity of silica, then considered as variable, should be taken into account.

Thus, we see that the formation of clay from albite is always preceded by the appearance of boehmite  $AlOOH$ , which can be converted into a 2:1 or a 1:1 clay, only when it is poorly crystallized from the start. The triperiodic crystals of boehmite are stable and never lead to formation of phyllite even in extremely small amounts. The same is also true for gibbsite crystals  $Al(OH)_3$  (De Kimpe, Gastuche and Brindley, 1964).

In this investigation, we intended therefore to check the important part played by the poorly crystallized boehmite as *initiator* in the formation

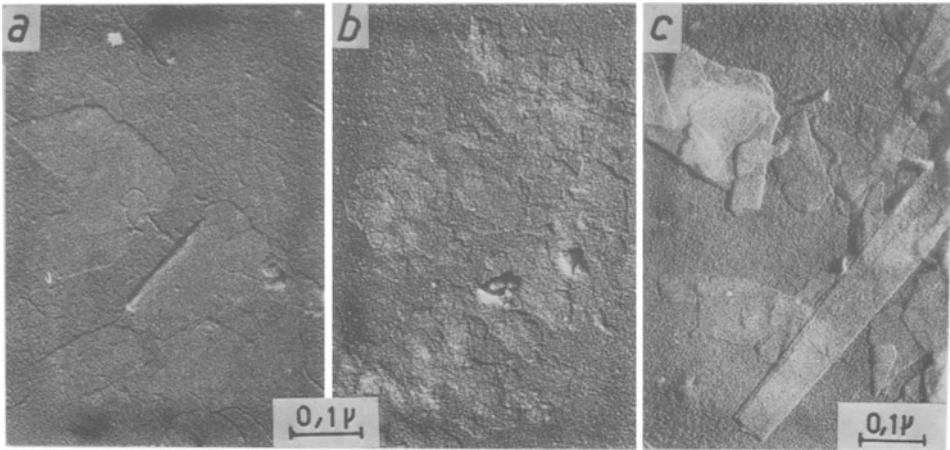


Fig. 2. Carbon-platinum shadowing, reversed print (a) Na montmorillonite from Wyoming; (b) Na montmorillonite from Camp-Berteau; (c) Synthetic-beidellite.

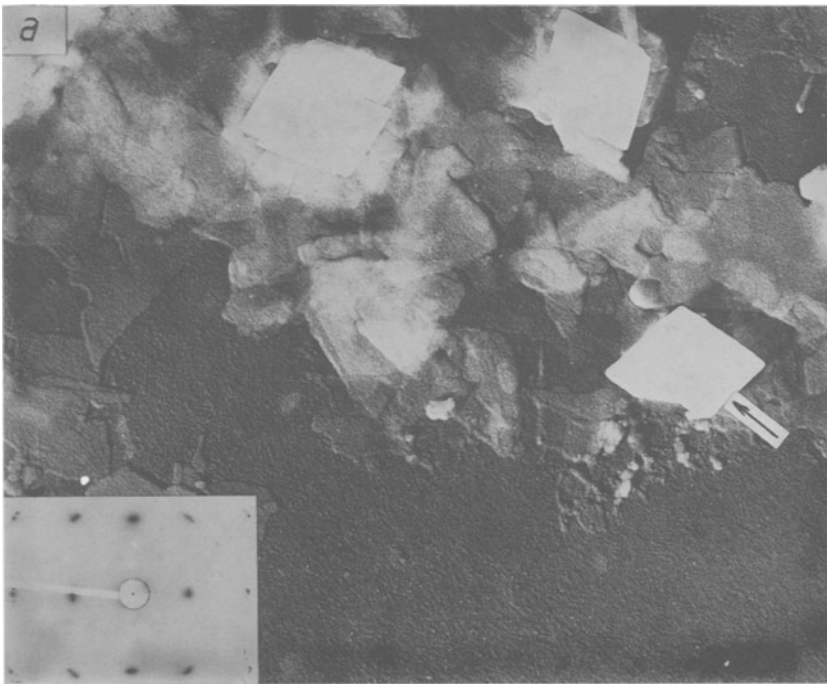


Fig. 3. (a) Boehmite crystals in beidellite sample BIO; (b) selected area electron diffraction diagram of boehmite.

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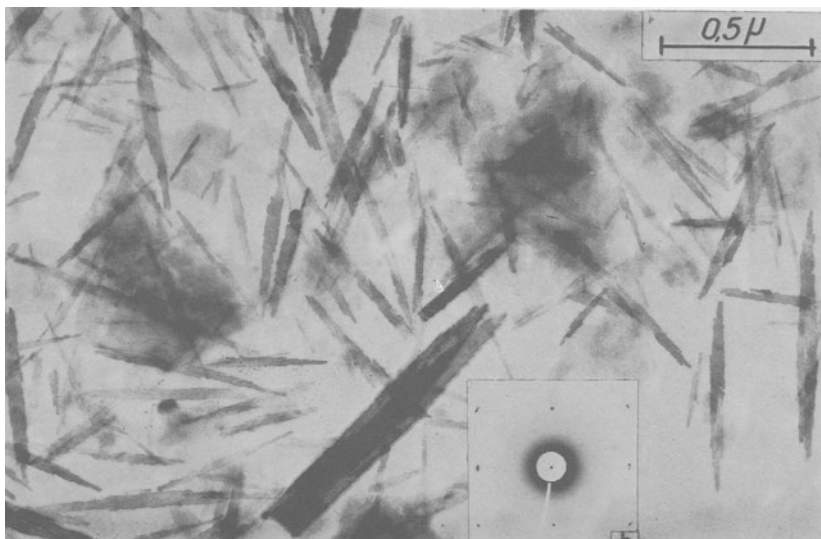


Fig. 4. (a) Al-OH montmorillonite treated 17 hours (sample W 28); (b) selected area electron diffraction diagram of pseudoboehmite.

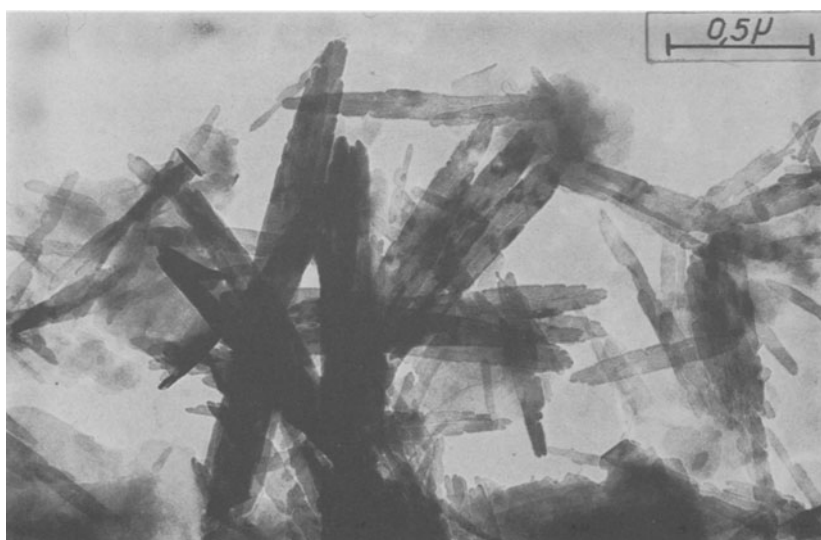


Fig. 5. Al-OH montmorillonite treated 7 days (sample W29).

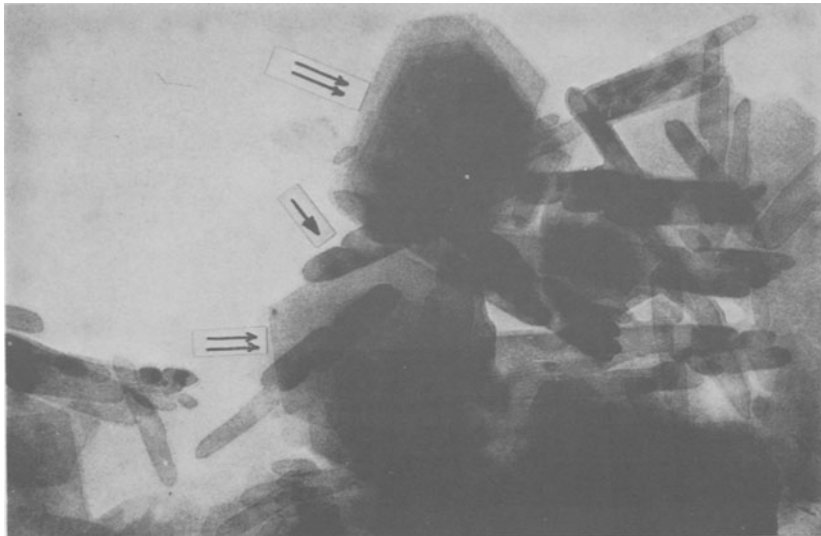


Fig. 6. Al-OH montmorillonite treated 15 days (sample W30).

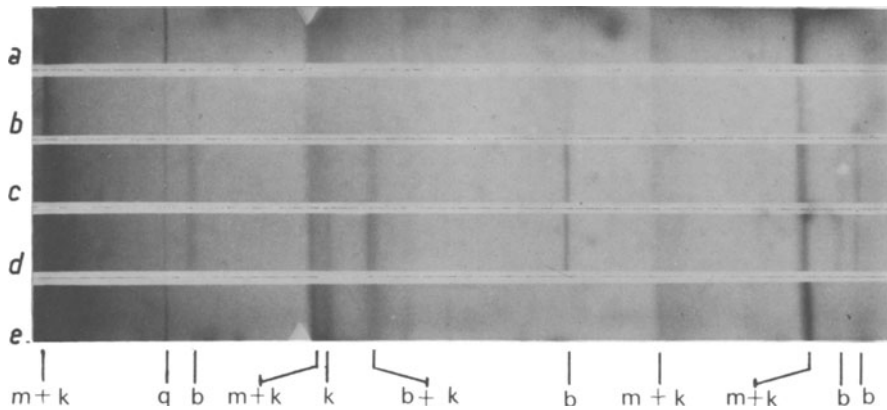


Fig. 7. X-ray diagrams (Guinier de Wolff chamber) using  $\text{CoK}\alpha$  radiation (a) Na montmorillonite; (b-e) Al-OH montmorillonites treated 17 hr, 7 days, 15 days and 1 month.

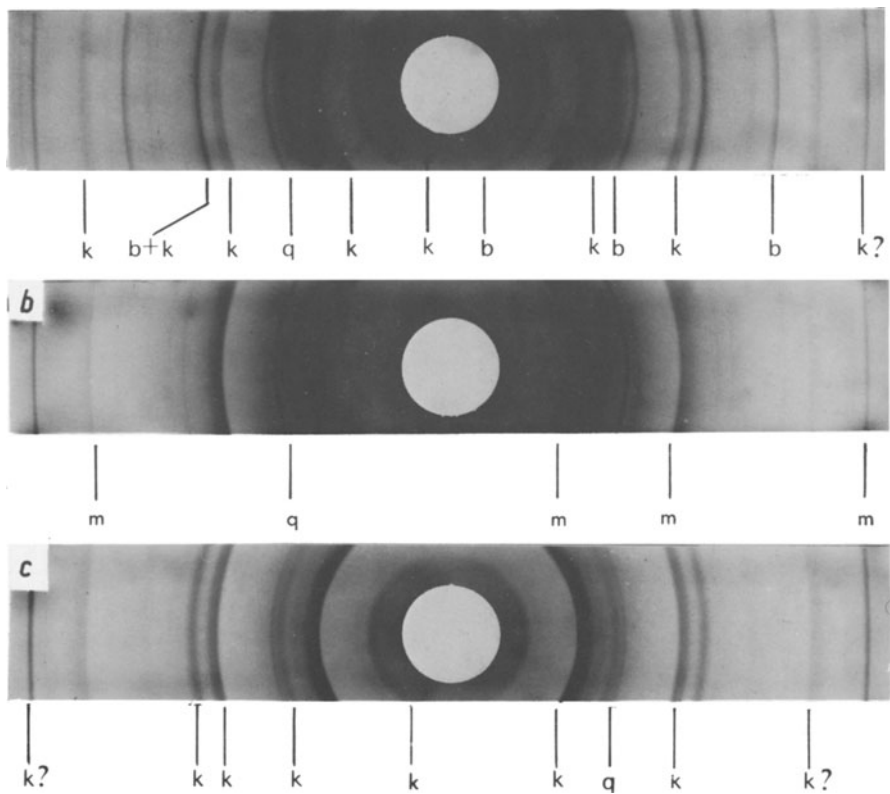


Fig. 8. X-ray diagrams (using  $\text{CoK}\alpha$  radiation) (a) Al-OH montmorillonite treated 15 days; (b) Na montmorillonite; (c) Al-OH montmorillonite treated 1 month.



of kaolinite (Oberlin and Couty, 1969), when starting from a clay of the montmorillonite group (reaction 2).

**1. ALTERATION OF 2:1 DIOCTAHEDRAL PHYLITES**

We used three samples of appreciably different degrees of crystalline organization because it was not evident that the mechanism of alteration would be the same for the tri-periodic and the bi-periodic crystals. We chose two montmorillonites, both consisting of turbostratic stacking layers, but of different origins, and considerably different from each other as regards their rheological properties, namely: one clay from Wyoming (U.S.A.) and one clay from Camp-Berteau (Morocco). The third sample was a synthetic beidellite of three-dimensional crystallization.\*

In all cases, after purification, clays were sodium saturated, and their morphology was examined by electron microscopy (Fig. 2(a,b,c)). Mixtures of clay suspensions of various concentrations and hydrochloric acid of various normalities, were placed into gold tubes. These were sealed and placed into an autoclave, heated up to a temperature of 200°C, maintained during various times from 2 hr to 2 months. After quenching, the content of each tube was poured into water, where it was dispersed by means of ultra-sonic waves, to make a stable dispersion. One part of the sample was then examined either by electron microscopy, or by electron diffraction, while the rest was used to obtain X-ray Debye-Scherrer diagrams (a Guinier-deWolff chamber, and a cylindrical chamber were used with filtered CoK<sub>α</sub> radiation).

The various conditions selected for the experiments together with the obtained results are shown in Table 1, where symbols W, CB and B indicate the Wyoming clay, the Camp-Berteau clay and the beidellite respectively. The C concentrations are expressed in terms of grams of calcinated clay per liter of solution, and the acid concentrations in terms of fractional values of the normality N. Evaluations of the [Na<sup>+</sup>]/[H<sup>+</sup>] ratios were based on an exchange capacity of 80 m-equiv./100 g of calcinated clay for the Wyoming mineral, and 120 m-equiv./100 g for the mineral from Camp-Berteau (Glaeser, 1954). For the beidellite, a value of 92 m-equiv./100 g was used. It was also assumed that HCl remains a strong acid in our experimental conditions.

Table 1, shows that all the experiments corres-

pond to the field of kaolinite stability, as indicated by the dotted curves in Fig. 1. However, whichever the selected sample, the acid normality, the clay concentration and the value of the [Na<sup>+</sup>]/[H<sup>+</sup>] ratio, *no kaolinite was obtained*, even in very small amounts.

*Effect of H<sup>+</sup> concentration*

As long as the concentration of the hydrochloric acid is higher than 10<sup>-3</sup> N, and whichever the value of the [Na<sup>+</sup>]/[H<sup>+</sup>] ratio, the clay particles are completely dissolved, and the solid product recovered after quenching is an amorphous gel (samples 1, 2, 3), as shown by an examination in an electron microscope, by electron diffraction and by X-ray diagrams.

When the pH value is sufficient to reach the field of precipitation of the hydroxides (which corresponds to a normality of the hydrochloric acid below or equal to 10<sup>-3</sup> N), boehmite AlOOH may appear.

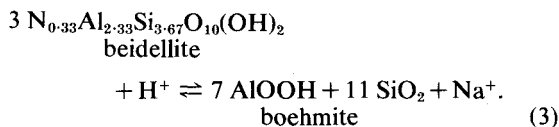
*Effect of time*

In view of the above findings we chose an acid concentration corresponding to the field of possible appearance of boehmite, and dilute clay solutions, which we subjected to alterations of increasing durations (samples 4-13). For the three investigated minerals, we found that boehmite appears from 14 hr on, following which the amount formed remains constant, even after 2 months duration (compare samples 6 and 7). This allowed us to adopt a minimum duration of 16 hr for the experiments.

*Effect of clay concentration*

The treated samples, hereafter compared to each others, differ only in their clay concentration C (samples 4, 6 and 14-21). It can be seen that there is a threshold for the appearance of boehmite, which appears only with clay concentrations below a certain value, (indicated by block letters in Table 1) depending on the type of the mineral treated. Thus, in the case of the Camp-Berteau clay, boehmite appears with all concentrations below or equal to 0.4 g/l (samples 17-21). With beidellite, the threshold lies between 0.20 and 0.25 g/l (samples 18-21) and with the Wyoming mineral, the clay concentration should be reduced to 0.075 g/l (samples 20 and 21).

The reaction of the clay decomposition (of beidellite for instance), when boehmite only is formed, can be written:



\*This sample was supplied by T. Iiyama, who made synthesis. The composition, calculated from the mixture of oxides, is the following:



Table 1. Experimental results (sodium saturated samples)

Samples*	Acid normality	C (g/l)	Time (hours: h; days: d)	$[\text{Na}^+]/[\text{H}^+]$	Results
W1	1	40	7 d	$10^{-1.5}$	gel
CB1	—	—	—	$10^{-1.3}$	gel
W2	0.5	0.4	—	$10^{-3.2}$	gel
CB2	—	—	—	$10^{-3}$	gel
W3	—	0.024	—	$10^{-4.4}$	gel
CB3	—	—	—	$10^{-4.2}$	gel
W4	$10^{-3.30}$	0.024	24 h	$10^{-1.4}$	non altered clay + boehmite (small quantity)
W5	—	—	3 d	—	<i>idem.</i>
CB6	—	0.2	16 h	$10^{-0.3}$	non altered clay + boehmite (small quantity)
CB7	—	—	60 d	—	<i>idem.</i>
B8	$10^{-6.30}$	0.25	5 h	$10^{-2.7}$	non altered clay
B9	—	—	24 h	—	non altered clay + boehmite (very small quantity)
B10	—	—	2 d	—	<i>idem.</i>
B11	—	—	3 d	—	<i>idem.</i>
B12	—	—	5 d	—	<i>idem.</i>
B13	—	—	10 d	—	<i>idem.</i>
CB14	$10^{-3.30}$	2	16 h	$10^{0.7}$	non altered clay
CB15	—	0.8	—	$10^{0.3}$	<i>idem.</i>
W16	—	0.6	—	1	<i>idem.</i>
CB17	—	0.4	—	1	non altered clay + boehmite (very small quantity)
B18	—	0.25	—	$10^{-0.4}$	<i>idem.</i>
W18	—	0.2	—	$10^{-0.5}$	non altered clay
CB6	—	—	—	$10^{-0.3}$	non altered clay + boehmite (small quantity)
W19	—	0.09	—	$10^{-0.8}$	non altered clay
W20	—	0.075	—	$10^{-0.9}$	non altered clay + boehmite (very small quantity)
CB20	—	—	—	$10^{-0.7}$	non altered clay (small quantity) + boehmite (numerous)
B21	—	0.035	—	$10^{-1.2}$	non altered clay + boehmite (medium quantity)
W4	—	0.024	24 h	$10^{-1.4}$	non altered clay + boehmite (small quantity)
CB21	—	—	—	$10^{-1.2}$	pure boehmite
CB22	$10^{-3.30}$	0.075	16 h	$10^{-0.7}$	non altered clay
CB23	—	—	—	$10^{-0.7}$	non altered clay
W24	$10^{-3}$	40	15 d	$10^{1.5}$	non altered clay
CB24	—	—	—	$10^{1.7}$	non altered clay
W25	$10^{-6}$	—	—	$10^{4.5}$	non altered clay
CB25	—	—	—	$10^{4.7}$	non altered clay

\*Symbols W, CB and B indicate Wyoming montmorillonite, Camp-Berteau montmorillonite and beidellite respectively.

Considering this reaction, it can be assumed that, when the clay concentration is very low, and therefore the amount of acid considerably in excess, the amount of boehmite obtained under such conditions corresponds to a total decomposition of the clay; on the other hand, with a high clay concentration, the obtained amount of boehmite should correspond only to a total consumption of the available acid. On this basis, calculations of the boehmite concentrations for the montmorillonite from Camp-Berteau

give for the two extreme cases (samples 21 and 14), 0.005 g/l and 0.20 g/l respectively. In the first example, boehmite only is present; in the second one, boehmite represents about the tenth part of the weight of the clay. Therefore, it can be assumed that boehmite should be detectable in all cases. Now, Table 1 shows that in fact boehmite does not appear with high clay concentrations (sample 14). As pointed out in the introduction, at 200°C we meet the conditions where silica forms highly super-



saturated solutions. If the investigated minerals contain a certain proportion of excess silica, the dissolution of this silica will tend to shift the equilibrium of the reaction, and to stabilize the initial clay minerals, which will not dissolve any more. The great differences between the limiting values of  $C$ , for the three investigated minerals, would then result from differences between the amounts of silica in the initial clays. It is known (Mering, 1968) that the Wyoming montmorillonite contains a slight excess of amorphous silica located around the elementary particles which may explain the apparent resistance of this mineral to acid attack (sample 20, threshold value 0.075 g/l). If this interpretation were justified, it should be assumed then that the synthetic beidellite also contains an excess of silica, playing the same role, and that the Camp-Berteau montmorillonite is the mineral with the lowest silica content.

The same experiments were repeated, taking care to maintain constant all the conditions of alteration needed to produce an important amount of boehmite; however, we added a known quantity of amorphous silica to the acid solution.\* Therefore, we started from one sample containing 0.075 g/l of Camp-Berteau montmorillonite (thus similar to sample 20 which is boehmite-rich) to which was added first 0.06 g/l of calcinated silica (sample 22) and then 0.12 g/l of calcinated silica (sample 23). In the first example a small quantity of boehmite is still present, in the second one, no boehmite appeared. These results signified that in the last case we attained the level of sample 17 ( $C = 0.4$  g/l) which is the threshold of boehmite appearance. So, it can be assumed that montmorillonite from Camp-Berteau (and probably all other minerals studied) contains some excess amorphous silica. From the above experiments it seems to be necessary to add more than 20 per cent of silica by weight compared with the total weight of clay to stop boehmite formation. Correlatively, if we assume for the Camp-Berteau montmorillonite a 50 Å wide amorphous silica fringe surrounding each particle (the dimensions of which being about 1000 Å diameter and 10 Å thickness), we find a mean value of 20 per cent in weight of silica in respect to the total amount of clay. That is to say, the same order of magnitude as above. In any case the precise estimation of amorphous silica content of the various samples should be done only with help of further experiments.

\*We used a commercially available silica containing 98.5 to 99.0% of  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ , 0.15–0.20% of  $\text{Fe}_2\text{O}_3$ , 0.50–0.70% of  $\text{Al}_2\text{O}_3$ , 0.10% of  $\text{CaO}$ , traces of  $\text{TiO}_2$ , 0% of  $\text{Cu}$  and  $\text{Mg}$ , and indeterminable amounts of alkali metals.

#### *Investigation on boehmite*

When it appears, boehmite is very easily identified, both because of its appearance, and by selected area electron diffraction (SAD) diagrams. Crystals of large dimensions and of quite regular external shape are obtained (arrows in Fig. 3(a)). These tabular crystals rest on the supporting film on their (010) faces. Most frequently, they are limited by (101) faces. Their average thickness, estimated from shadowed specimens, varies from 500 Å to 1000 Å. As an examination of the contour of the cast shadow of several particles allows the selection of those in close contact with the support, it is then possible to measure the angle of the (101) and  $(\bar{1}01)$  faces, under full scale conditions. The average value obtained this way is  $103^\circ$ , which corresponds to that of  $104^\circ 26'$  reported elsewhere (Bosmans and Michel, 1959). An examination of SAD diagrams shows that the crystals are resting on their (010) face, and are elongated in the  $c$  direction (Fig. 3(b)). There is no visible disorder in these diagrams, and measurements of the parameters, made on ( $h0l$ ) reflections, gave the following values:  $a = 3.66$  Å,  $c = 2.89$  Å, in good agreement with those reported by Milligan and McAtee (1956) (the (06) ring of the residual clay has been used as internal standard).

The above described results show that kaolinite cannot be obtained when starting from montmorillonite, whatever the value of the  $[\text{Na}^+]/[\text{H}^+]$  ratio (samples 1, 24 and 25), even with alteration times up to two months (sample 7).

In all the cases where the investigated clay is not stabilized by an excess of silica in the solution, the result is either a complete solubilization of silica and alumina, subsequently leading only to the formation of an amorphous gel, unable to evolve further; or a precipitation of a well-crystallized boehmite, which does not allow any further evolution to clay minerals, even in the presence of silica in the solution. Consequently, we sought, starting from montmorillonite, to induce a formation of poorly crystallized boehmite, hoping in this way to trigger a formation of kaolinite. In conducting these tests, we were guided by the work of Poncelet and Brindley (1967) who succeeded in producing kaolinite from Al-OH montmorillonites i.e., montmorillonites containing more or less incomplete layers of aluminium hydroxy-polymers inserted between the layers of clay, (Rich, 1968).

## 2. ALTERATION OF Al-OH MONTMORILLONITES

Samples of Al-OH montmorillonites were prepared according to Sawhney's method (1968), and, to obtain a montmorillonite as stable as possible, we selected an OH/Al ratio of 2.7, and a total quantity of 13 m-equiv. Al/g of dried clay (about

16 m-equiv. Al/g being necessary to obtain a complete hydroxide layer between two consecutive layers of montmorillonite).

As a first step, the hydroxy-polymer is prepared. To make this, 160 ml of NaOH 0.25 N are added very slowly (addition rate: 5 drops per min) to 90 ml of an AlCl<sub>3</sub> solution, 0.5 N. Throughout this addition, the AlCl<sub>3</sub> solution is briskly stirred to avoid too great local increases of the pH value, which would cause some precipitation of Al(OH)<sub>3</sub>. The clear solution of aluminum hydroxy-polymer prepared this way can remain stable for several months.

A suspension, containing 1% of montmorillonite from Wyoming is converted first into calcium montmorillonite by means of cation exchange. An appropriate quantity of this suspension is then mixed with the necessary amount of the hydroxy-polymer solution, to give a final mixture containing 13 m-equiv. Al/g of dried clay. The mixing is carried out by adding, drop by drop, 30 ml of the hydroxy-polymer solution to 50 ml of the clay suspension, the latter being briskly stirred throughout the process. The presence of interlayer hydroxide has been checked by means of X-rays, measuring the interlayer spacing of the mineral, saturated with K cations, and dried at 100°C. The spacing remains 14Å, and the clay does not swell any more in the presence of water vapour. Even after a 7 month ageing, the Al-OH clays prepared this way do not show any perceptible evolution, when checked by means of either X-ray or electron microscope techniques.

As above, samples were checked by electron microscopy. Their aspect was similar to that shown in Fig. 2(a), although the individual particles were more difficult to disperse on the supporting film. Mixtures of clay suspensions and hydrochloric acid of various normalities were placed into gold tubes, and the concentration of clay was maintained constant at a 4 per cent level. After treatment at 200°C, in an autoclave for various durations,

each sample was dispersed by means of ultrasonic waves, and examined in an electron microscope. Moreover, each sample was subjected to an X-ray diffraction test. The experimental results are shown in Table 2.

As for the samples shown in Table 1, we found that the use of 1 N HCl solutions (samples 26 and 27) causes the formation of amorphous gels, which do not evolve further.

On the other hand, when the acid concentration is below or equal to 10<sup>-3</sup> N (Table 2—samples 28–32), boehmite appears very quickly (at the end of a 17 hr period), and is found mixed with unaltered montmorillonite (Fig. 4(a)). The aspect of the particles is quite different from that shown in Fig. 3 for instance. Instead of thick and well-shaped crystals, thin, transparent and elongated particles (about 1000Å wide and 1 μ long) are found, with edges of very irregular shape, all of them apparently consisting of smaller elements (a few tens of angstroms), more or less completely connected laterally to each other. This mineral cannot be identified from its facies; its identification however can be assured by means selected area electron diffraction (Fig. 4(b)). No disorder is found, and measurements carried out on (*h0l*) reflections again give the values *a* and *c* of boehmite.

After a seven day period (sample 29), the facies of the boehmite particles change slightly and become less irregular (Fig. 5). Some montmorillonite remains unaltered, and a few particles with a neat hexagonal contour are visible. It seems that these particles are already kaolinite, but this mineral cannot be distinguished from montmorillonite solely by means of SAD diagrams. After an alteration period of 15 days (samples 30 and 32), montmorillonite is no longer visible in the electron microscope. Only boehmite particles (arrows in Fig. 6) and microcrystals, consisting of pseudo-hexagonal flakes, previously identified with kaolinite (double arrows in Fig. 6), are present. At the

Table 2. Experimental results (Al-OH montmorillonite)

Samples	N (normality)	C (g/l)	Time (hours: h; days: d)	Results
W26	1	40	17 h	gel
W27			7 d	gel
W28	10 <sup>-3</sup>	40	17 h	non altered clay + pseudo boehmite <i>b</i>
W29			7 d	non altered clay + pseudo boehmite <i>b</i>
W30			15 d	pseudo boehmite <i>b</i> + kaolinite
W31			30 d	pure kaolinite
W32	10 <sup>-6</sup>	40	15 d	pseudo boehmite <i>b</i> + kaolinite

Table 3. X-ray identification of alteration products from Al-OH samples

Na montmorillonite check sample		Al-OH montmorillonite 17 hr		Al-OH montmorillonite 7 days		Al-OH montmorillonite 15 days		Al-OH montmorillonite 30 days	
d(Å)	r.i.*	d(Å)	r.i.*	d(Å)	r.i.*	d(Å)	r.i.*	d(Å)	r.i.*
mineral†	mineral†	mineral†	mineral†	mineral†	mineral†	mineral†	mineral†	mineral†	mineral†
4.56	10	4.56	10	4.56	10	7.49	5	7.44	5
	m		m		m	6.12	5		k
3.34	6	3.34	6	3.34	6	4.44	10	4.46	10
	q		q		q	3.55	3	3.54	3
						3.34	2	3.34	5
2.57	8	3.18	1	3.18	3	3.18	6		q
	m	2.60	5	2.60	5				b
						2.55	5	2.55	5
						2.49	3	2.49	5
2.23	4	2.35	1	2.34	3	2.35	10	2.34	6
	m	2.23	1		b				k
					m				k
									k†
1.70	1	1.86	3	1.86	6	2.14	1		
	m	1.71	1	1.71	1	1.86	6		
					m			1.70	3
									k?
1.50	8	1.52	8	1.52	8	1.68	3		
	m	1.46	1		m				
		1.43	1		b			1.50	8
					b				k?
					b				
					b				
					b				

\*r.i.: relative intensities.

†q: quartz (used like an internal standard), m: montmorillonite, b: boehmite; k: kaolinite.

‡k: kaolinite identified only because all boehmite reflections are lacking.

end of a one month period, neither montmorillonite, nor boehmite can be seen: only kaolinite is visible.

All the samples mentioned in Table 2 have been studied by means of X-ray diffraction, using either a Guinier-de Wolff chamber, or a cylindrical chamber, or a cylindrical chamber with  $\text{CoK}_\alpha$  filtered radiation. Figures 7 and 8 show quite a definite and progressive variation of the diagrams. Measurements carried out on the various diagrams (Table 3) have permitted the identification of all the constituents already shown by electron microscope and electron diffraction techniques, i.e., the initial montmorillonite (indicated by symbol *m* in Fig. 7 and 8, and in Table 3), the boehmite *b* and the kaolinite *k*. The latter has been more surely identified by measurements of the  $d_{001}$  spacing, using the cylindrical chamber (Fig. 8 and Table 3).

The observed boehmite is not a boehmite of quasi 'monoperiodic' crystallization, like that obtained in the alteration of albite (Tchoubar, 1965), but a pseudo-boehmite *b*, identical with that described by Papée, Tertian and Biais (1958). The mineral in question thus consists of independent (010) monolayers biperiodically crystallized. This is shown in the Debye-Scherrer X-ray diagrams, by a frequent disappearance of the (020) reflection at 6.11 Å, and the appearance of diffuse bands replacing the other reflections. These results substantiate those given by the SAD diagrams, where no disorder of any kind appears between (*h*0*l*) spots. The kaolinite formed under these experimental conditions is also a kaolinite of a rather poor crystallization (Brindley and Robinson, 1946 and 1947), as shown by the value of the  $d_{001}$  spacing, namely 7.4 Å. However, from the morphological standpoint, the particles are very well shaped.

In short, whatever the technique used to study the formed products, consistent results are obtained, which prove that montmorillonite initially forms first the turbostratic stacking of boehmite layers; subsequently this poorly crystallized boehmite layers; subsequently this poorly crystallized boehmite induces a progressive formation of kaolinite. As the amount of kaolinite formed increases, the quantities of montmorillonite and intermediate boehmite decrease to zero (Table 2).

If we compare our results to those of Poncelet and Brindley (1967) we see that they did show the formation of well crystallized kaolinite. Their best products gave basal spacings up to (005). Thus it would seem that their conditions permitted kaolinite to form somewhat better than in our experiments. However the mechanism involved in their case was entirely different because, for some unknown reason, kaolinite formation occurs entirely by means of solid reaction inside Al-OH samples.

In any case we are concerned here mainly with the mechanism involving boehmite and not with forming kaolinite directly from montmorillonite.

### CONCLUSION

(1) The alteration of a smectite by an acid solution of high concentration gives an amorphous gel. In such cases, no formation of any other clay mineral is observed.

(2) Under lower acid concentration conditions, supersaturation with silica can cause an apparent stabilization of the initial material.

(3) We have shown that the only other possibility is a formation of a well-crystallized boehmite. In this case, the solubilization of each elementary layer of the clay occurs in homogeneous manner (no etch pits are observed). The obtained boehmite forms within the solution without any epitactic connections with the initial clay (such connections being impossible when starting from the turbostratic stacking of the clay). The boehmite is well crystallized, for the dilution of the solution, the pH, pressure and temperature conditions, correspond to the field of stability of this mineral. Therefore, under conditions leading to a triperiodic crystallization, the microcrystals do not present any available active sites and cannot fix the silica present in the solution.

(4) It is also proved that an *initiator, poorly crystallized and rich in active sites*, is essential to induce a formation of kaolinite. The selection of appropriate conditions, causing a formation of pseudo-boehmite *b*, triggers an immediate formation of kaolinite (incidentally, let us note that we can expect a production of biperiodic layers rather than fibers of boehmite, for this mineral results from insertion of more or less complete layers of  $\text{Al}(\text{OH})_3$  between disordered layers of smectite). Therefore, it is practically sure that, to obtain a phyllite, starting from a silicate in the course of alteration, the aluminum should be temporarily 'stored' in a poorly crystallized mineral (oxide or hydroxide). This allows the silica monomer, contained in the solution, to saturate the active sites, to give a 2:1 or a 1:1 phyllite, according to its concentration.

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**Résumé**—Quand un minéral du group montmorillonite, saturé par des cations Na, est placé dans une solution faible d'acide chlorhydrique, et maintenue à 200°C, il doit s'altérer et produire le minéral correspondant du groupe kaolinite, selon la réaction suivante: argile triphormique +  $\text{H}^+$   $\rightleftharpoons$  argile diphormique +  $\text{SiO}_2 + \text{Na}^+$ . La formation de l'argile diphormique doit seulement dépendre de la valeur du rapport  $[\text{Na}^+]/[\text{H}^+]$ , pour les différentes températures utilisées dans le processus. Au cours d'un certain nombre d'expériences, quelques minéraux de types variés ont été soumis à ce processus d'altération, effectué dans des conditions très diverses: nommément, durée du traitement d'altération, concentrations d'argile et d'acide et valeur du rapport  $[\text{Na}^+]/[\text{H}^+]$ . Aucune formation de kaolinite n'a été notée mais, à sa place, on a remarqué soit un gel amorphe, ou une boémite bien cristallisée ou encore pas de dissolution du tout du minéral d'origine. Nous avons déjà montré qu'un feldspar, soumis dans des conditions similaires à un phénomène d'altération, ne produit jamais de kaolinite mais forme au contraire une boémite pauvrement cristallisée. Ce produit intermédiaire est le seul capable de fixer la silice dans ses nombreuses zones actives et produire ainsi la kaolinite. Dans cette étude, nous avons recherché à induire une formation de boémite pauvrement cristallisée à partir de montmorillonites, en vue d'une croissance ultérieure de kaolinite. Ceci a été effectué par l'insertion de couches de polymères hydroxy d'aluminium entre les couches d'un montmorillonite, suivi par une altération effectuée dans les mêmes conditions que précédemment. A la fin d'un traitement de 17 heures, un certain nombre de fibres de boémite pauvrement cristallisée (pseudo-boémite *b*) sont apparues. A la fin d'une période de 15 jours, de grandes quantités de kaolinite ont été formées et, à la fin d'une période d'un mois, seule la kaolinite était restée. Ces expériences établissent le besoin en quelque sorte "D'emmagasinage" d'aluminium dans un minerai intermédiaire pauvrement cristallisé. Ceci est une condition préliminaire essentielle à toute formation d'argile. Cette argile ne peut être formée que lorsque la silice-monomère peut être fixées sur des terrains actifs du produit intermédiaire:

**Kurzreferat**—Wenn ein Mineral der Montmorillonitgruppe, gesättigt mit Na Kationen, in eine verdünnte Lösung von Salzsäure gebracht, und auf 200°C gehalten wird, sollte es eine Veränderung erfahren unter Bildung des entsprechenden Minerals der Kaolinitgruppe, gemäss folgender Reaktion: trimorpher Ton +  $\text{H}^+$   $\rightleftharpoons$  dimorpher Ton +  $\text{SiO}_2 + \text{Na}^+$ . Die Bildung des dimorphen Tons sollte allein vom Wert des  $[\text{Na}^+]/[\text{H}^+]$  Verhältnisses für die verschiedenen in dem Prozess verwendeten Temperaturen abhängen. In einer Reihe von Versuchen wurden einige Minerale verschiedener Arten diesem Veränderungsprozess unterworfen, der unter den verschiedensten Bedingungen in Bezug auf Dauer der Veränderungsbehandlung, Ton- und Säurekonzentrationen sowie Wert des  $[\text{Na}^+]/[\text{H}^+]$  Verhältnisses durchgeführt wurde. Es konnte keine Bildung von Kaolinit festgestellt werden, hingegen jedoch die eines amorphen Gels oder eines wohlkristallisierten Boehmits, oder aber es kam zu keiner Auflösung des ursprünglichen Minerals. Wir haben bereits gezeigt, dass ein Feldspat, wenn er unter ähnlichen Bedingungen einer Veränderung unterworfen wird, niemals Kaolinit liefert, sondern anstatt dessen einen mangelhaftkristallisierten Boehmit bildet. Dieses Zwischenprodukt ist das einzige, das an seinen zahlreichen aktiven Stellen Siliziumdioxid binden, und so Kaolinit liefern kann. In der



gegenwärtigen Arbeit versuchten wir die Bildung mangelhaftkristallisierten Boehmits aus Montmorilloniten hervorzurufen, im Hinblick auf nachfolgende Bildung von Kaolinit. Das gelang durch Einfügung von Schichten von Aluminiumhydroxy-polymer zwischen die Montmorillonitschichten mit nachfolgender Änderung unter den gleichen Bedingungen wie vorher. Am Ende einer siebzehnstündigen Behandlung erschienen eine Anzahl von Fasern von mangelhaft kristallisiertem Boehmit (Pseudo-Boehmit *b*) Am Ende eines Zeitraumes von 15 Tagen hatten sich grössere Mengen von Kaolinit gebildet, und nach einem Monat war ausschliesslich Kaolinit vorhanden. Diese Versuche bekräftigen den Bedarf für eine 'Einlagerung' des Aluminiums in einem mangelhaft kristallisiertem Mineral als Zwischenprodukt. Das ist eine wesentliche Vorbedingung bei der Bildung von Ton. Dieser Ton kann sich nur bilden wenn das Siliziumdioxidmonomer an Aktivstellen des Zwischenproduktes gebunden werden kann.

**Резюме** — При выдерживании минералов монтмориллонитовой группы, насыщенных катионами Na, в разбавленном растворе соляной кислоты при температуре 200° должно происходить их изменение с образованием соответствующих минералов каолинитовой группы согласно следующей реакции: трехэтажная глина + H<sup>+</sup> ⇌ двухэтажная глина + SiO<sub>2</sub> + Na<sup>+</sup>. Образование двухэтажной глины при различных температурах процесса должно зависеть только от значения отношения [Na<sup>+</sup>]/[H<sup>+</sup>]. В большом числе проведенных опытов некоторые минералы различных типов подвергались подобному изменению, осуществлявшемуся в широком диапазоне условий — при разной продолжительности опытов, концентрации глины и кислоты и отношении [Na<sup>+</sup>]/[H<sup>+</sup>]. Образование каолинита не было обнаружено; конечным продуктом реакции являлись либо аморфный гель, либо хорошо окристаллизованный бёмит, либо вообще не происходило разложения исходного материала. Ранее было показано, что полевоы шпат, подвергающийся изменению в аналогичных условиях, никогда не переходит в каолинит, но образуеться вместо него плохо окристаллизованный бёмит. Только один этот промежуточный продукт способен фиксировать кремнезем в многочисленных активных центрах и служить основой для образования каолинита. В проведенных исследованиях авторы пытались получить из монтмориллонита плохо окристаллизованный бёмит с целью последующего образования каолинита. Это могло быть достигнуто внедрением слоев гидрокси-алюминиевых полимеров между слоями монтмориллонита с изменением промежуточного продукта при тех же условиях, что и первоначальные. В конце 17-ти часовой обработки появилось большое количество волокон плохо окристаллизованного бёмита (псевдобёмита *b*). В конце 15-ти дневного периода образовалось большое количество каолинита, который оставался единственным конечным продуктом реакции и по истечении месяца. Эксперимент доказывает необходимость некоторого «избытка» алюминия в промежуточном плохо окристаллизованном минерале. Это является существенным предварительным условием при любом образовании глинистого минерала, который может возникать только в тех случаях, когда мономеры кремнезема имеют возможность фиксироваться на активных центрах промежуточного продукта.