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CLAY MINERAL SYNTHESIS. II.[1] A RANDOMLY INTERSTRATIFIED ALUMINIAN MONTMORILLONOID[2]

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ABSTRACT

A randomly interstratified layer lattice silicate (a heteropolytypic montmorillonoid) was synthesized from a starting slurry of diatomite and bayerite in an aqueous solution of NaOH. The synthesis was carried out for varying reaction times at 300°C and the corresponding p_{H_2O}.

Samples quenched at various reaction times were subjected to X-ray diffraction, DTA, surface area and cation exchange capacity determinations, and infrared absorption studies with particular emphasis on the 400–900 cm^{-1} region.

The synthesis process is a crystallization from solution, and is made up of several steps: solution of the solid reactants, nucleation of the layer lattice, and growth of these nuclei to the final crystalline product. The growth step is sufficiently rapid so that the solution and/or nucleation steps become rate controlling.

INTRODUCTION

Synthesis of the three-layer clay minerals, such as montmorillonite, dates from the classic work of Noll (1930). More recently, the subject has been pursued vigorously by Roy (Iiyama and Roy, 1963). For some years, the Research Project at Mellon Institute sponsored by Baroid Division National Lead Company has been studying various facets of clay mineral synthesis, with primary emphasis on the variation of the physical properties of the synthetic clay as a function of the nature and extent of isomorphous substitution. In general, in the work discussed in this paper, reaction conditions were more moderate and vessel sizes larger than those described by the other workers in this field.

One phase of our study has been concerned with the composition

$$[(Al_4)_{octa}(Al_xSi_{8-x})_{tetra}O_{20}(OH)_4]^{x-}\cdot xM^+$$

In this paper, we describe a "big-bomb" synthesis of a heteropolytypic (Iiyama and Roy, 1963) montmorillonoid (or smectite) in which, on the average, $x \cong 1$. Reaction times and temperatures are explored and the various products characterized.

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[1] For the first paper in this series, which was concerned with the synthesis of hectorite, see Granquist and Pollack (1960).

[2] The word "montmorillonoid" is used in the sense in which it was originally proposed by MacEwan (1951); *i.e.*, meaning a mineral of the montmorillonite group. British workers have more recently adopted the name "smectite" for this same group.

EXPERIMENTAL

The feed slurry for each synthesis was prepared by addition, with stirring, of 20 g of acid-washed diatomaceous earth to one liter of distilled water, solution of $AlCl_3 \cdot 6H_2O$ (48.2 g) in the resulting mixture, and precipitation of $Al(OH)_3$ by a 75 ml addition of aqueous ammonia (28% NH_3). This final mixture was filtered and washed by redispersion and filtration through three cycles. The final filter cake was redispersed in distilled water, sufficient NaOH added to establish a $NaOH/Al_2O_3$ mole ratio of 0.4, and the volume adjusted to one liter with additional distilled water.

This slurry was introduced into a Type 347 stainless steel Aminco superpressure bomb, with an inside diameter of 2 9/16 in. and an inside depth of 21 in., equipped with a standard Aminco closure. The head contained three ports; one leading to a rupture disk assembly, a vent, and a pressure gauge: one equipped with a probe thermocouple assembly; and one containing a long tube running from near the bottom of the vessel through the head and terminating in a needle-valve. Heating and stirring were furnished by a standard Aminco heating jacket mounted on a rocker assembly. The jacket temperature was controlled by an off-on temperature control device, and the reading from the thermocouple probe was recorded. Variation from the desired crystallization temperature was approximately $\pm 2°C$.

The bomb was vented, at the boiling point of the contents, without rocking until the air had been displaced from the vessel. The vent was then closed, rocking started, and the temperature allowed to climb to the control point. At the end of the scheduled reaction time, the rocker was stopped with the head of the bomb at the maximum angle above the horizontal, a water-cooled condensing device was connected to the needle-valve, and the contents of the bomb discharged through the condenser. Flow was controlled to maintain total discharge times of the order of 15 min.

The products were washed with distilled water by filtration and redispersion, and oven-dried at 105°C. Examination of the products included: X-ray diffraction studies with both film and diffractometer techniques; DTA of samples equilibrated with 50 percent RH; infrared absorption spectroscopy, with KBr pellets, over the range 400 to 4000 cm^{-1} (a Beckman IR-9 grating instrument was used in this work); surface area by N_2 adsorption (standard Brunauer-Emmett-Teller [BET] method; Emmett, 1942) of samples which had been outgassed at 500°C and at least 10^{-4} mm Hg; and cation exchange capacity (CEC) by a suitable variation of the ammonium acetate technique (Lepper, 1945).

As will be evident, all of these techniques were not applied to all product samples.

In the X-ray studies, powder diffraction patterns (North American Philips camera, diameter 114.6 mm) were first obtained. Diffractometer traces were then made for both random and oriented specimens. Nickel filtered copper radiation was used in both diffractometer and camera work.

Oriented specimens were prepared by suspending the various products in water and then letting the solids settle on glass slides. No dispersing agent was added in this step. A diffractometer trace was made of each of two oriented slides prepared for each clay sample. One slide was then treated with a 10 percent glycerol in ethanol solution and again studied with the diffractometer. The second slide was heated at 440°C and then 500°C (two hours at temperature) and diffractometer traces were obtained corresponding to each temperature.

The intensity of the 06 reflection was measured as follows. Finely ground samples were packed in aluminum holders 20×10 mm in area and 1 mm thick. All intensities were measured under the same instrumental setting on the Geiger counter; that is, a scale factor of 2, multiplier setting of 1, and time constant of 1. The goniometer scanned at a rate of $\frac{1}{4}°$ per minute. The resulting peaks on the chart were symmetrical except for the weak peak for the 12-hour 300°C sample. The integrated intensity was obtained by multiplying the width at half-maximum by the peak height.

Results and Discussion

The results of this study appear in Tables 1 and 2 and Figures 1 through 8. The time-dependent features of particular interest are the change in the integrated intensity of the 06 reflection (see Fig. 1); the behavior of the 001 reflection (before and after glycerol solvation, Figs. 2 and 3); the variation in surface area and CEC; the shifts seen in the 400–900 cm^{-1} region of the infrared; and the changes in the differential thermal analysis patterns.

In the 300°C products, except the 72-hour sample, the montmorillonite is randomly interstratified with mica-like layers. In the 72-hour sample, however, the product is a mixture of montmorillonite and regularly interstratified montmorillonite-mica. This interpretation is based mainly on the behavior of the oriented specimens following glycerol treatment. All the products except the 72-hour sample show an irrational basal sequence and an 001 reflection with a shoulder on the high angle side. The 72-hour sample has an $00l$ sequence which is close to rational and in addi-

TABLE 1. SUMMARY OF SOME TIME-DEPENDENT PROPERTIES OF THE SYNTHESIS PRODUCTS

Time, hours	Temp., °C	Bulk density g/cc[1]	Relative[2] Intensity (06)	Surface area[3] m^2/g	CEC[4] meq/100 g
0	—	0.22	0	66.7	—
24	279	.56	0.68	128	—
35	279	.86	0.84	120	—
46	279	.88	0.97	96.4	—
59	279	.94	1.0	92.3	—
0	—	.22	0	66.7	—
12	300	.47	0.40	133	71.64
24	300	.44	0.84	80	90.46
36	300	.93	1.13	83	110.67
48	300	.99	1.08	77	91.28
72	300	.93	1.13	62	81.92

[1] 30/60 mesh particles, packed to minimum volume.
[2] Relative to sample at 59 hours, 279°C.
[3] Samples outgassed at 500°C and ca. 10^{-4} mm Hg.
[4] Dry clay.

tion a peak at 9.2 Å. This peak is probably the third order of a 1:1 regularly-interstratified structure.

Application of MacEwan's (1961) technique (for 10/12.4 Å and 10/17.5 Å random interstratification) to the observed d_{001} for the oriented specimens of samples near equilibrium before and after treatment with glycerol, leads to a $\rho(10\ \text{Å}) \approx 0.4$. Thus, it is concluded that the samples contain approximately 40 percent mica-like layers and 60 percent mont-

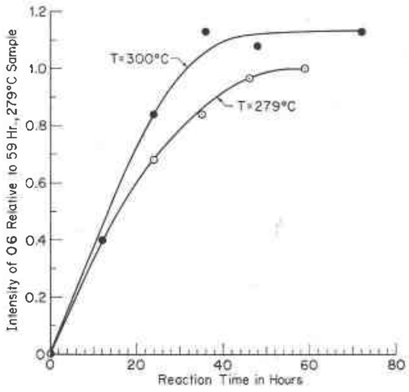


FIG. 1. Variation of intensity of 06 reflection with reaction time.

TABLE 2. X-RAY DIFFRACTION DATA FOR 36-HOUR AND 72-HOUR PRODUCTS SYNTHESIZED AT 300°C

Time, hours	Treatment of oriented slide	Diff. scale settings	*d*	Comments	Half-width deg 2θ	Peak height in chart units
36	25°C	32-1-2	11.8		1.7	62
			7.2	kaol	—	2
			5.79		B	7
			4.45	*hk*	—	2
			4.05	crist.		8
			3.16		B	12
	glycerol solvated 25°C	16-0.8-2	17.3		2.5	26
			9.3–11	shoulder	B	16
			5.98		VB	3
			4.61		B	9
			4.05	crist.	S	11
			3.49		1.4	20
	440°C 2 hrs	32-0.6-2	10.3		1.5	56
			7.2	kaol	B	2
			5.00		1.3	28
			4.46	*hk*	0.5	5
			4.05	crist.	0.3	15
			3.33		1.6	34
	500°C 2 hrs	16-0.8-2	9.9		1.30	60
			4.90		1.0	38
			4.46	*hk*	—	7
			4.07	crist.	0.3	20
			3.22		1.30	70
72	25°C	64-0.8-2	11.8		1.95	43
			7.2	kaol.	S	13
			5.86		B	6
			4.05	crist.	MS	2
			3.57	kaol.	S	7
			3.12		B	10
	glycerol solvated 25°C	32-0.8-2	17.7	mont.	2.0	49
			9.2		1.6	11
			7.2	kaol.	S	18
			5.90	mont.	B	5
			4.52		MS	10
			4.05	crist.	S	5

S = Sharp. B = Broad. MS = Medium Sharp.

TABLE 2—(*Continued*)

Time, hours	Treatment of oriented slide	Diff. scale settings	*d*	Comments	Half-width deg 2θ	Peak height in chart units
			3.56	kaol. +mont.	S	32
			2.96	mont.	B	6
	440°C 2 hrs	32-0.6-2	10.2		1.4	47
			7.1	kaol.	0.6	18
			4.95		1.4	16
			4.48	*hk*	0.8	2
			4.05	crist.	0.4	7
			3.56	kaol.	1.0	15
			3.30		1.9	22
	500°C 2 hrs.	16-1-2	9.9		0.8	53
			4.84		0.7	18
			4.48	*hk*	0.2	3
			4.09	crist.	0.15	8
			3.20		0.8	31

morillonite-like layers randomly interstratified. Therefore, in the unit cell formula presented in the introduction to this paper, x, although over-all approximately equal to unity, must assume two ranges of value:

$$0 < x < 1 \text{ montmorillonite-like,}$$

$$1 < x < 2 \text{ mica-like.}$$

In a random stacking sequence of platelets A and B, when the numbers of A and B are approximately equal, sequences of AAA . . . (or BBB . . .) must occur in the over-all stacking. Weak *hkl* lines appear in these products, presumably because of mica-like sequences occurring for the above reason. These *hkl* lines are best seen in the Debye-Scherrer patterns, but also appear in the diffractometer traces (Fig. 4).

The sharpest clay peak in the diffractometer traces of unoriented specimens of these products is the 11.02 peak, and it is also the first to develop during the crystallization. Figure 5, which shows the region from 19 to 25°2θ, demonstrates the growth of the 11.02 peak and the slow decrease of the 101 peak of accessory cristobalite as a function of reaction time. In general, the crystalline forms of SiO_2 are not suitable as source material for the crystallization; these results show, however, a slow loss of cristobalite to the reaction system.

The integrated intensity of the 06 reflection was considered to be a semiquantitative measure of the amount of montmorillonoid produced in the synthesis. However, since the 06 reflections of the montmorillonoid (~1.50 Å) and kaolinite (~1.49 Å) superimpose, a small part of the 06 intensity of the 24- and 72-hour samples is due to kaolinite. This crystallization of kaolinite introduces another complication by somewhat depleting the system of alumina, causing a slight increase in the SiO_2/Al_2O_3 for the 3-layer material. A further complication arises from the fact that these products are not homoionic, but rather contain a mixture of Na^+ and NH_4^+ in the exchange sites. The ratio Na^+/NH_4^+ undoubtedly varies from platelet to platelet, but we suspect that the NH_4^+ is the predominant cation for the mica-like component and Na^+ for the montmorillonite.

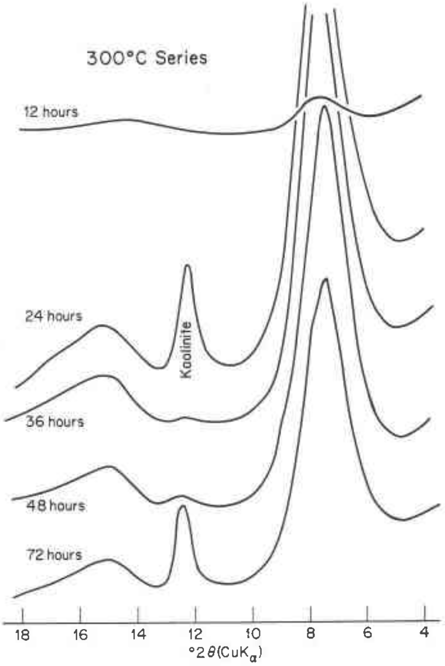


FIG. 2. Behavior of 001 as a function of reaction time, oriented slides, 300°C series.

It is concluded that the product crystallizing initially was montmorillonite-like platelets randomly interstratified with a somewhat lesser amount of mica-like layers, an arrangement that remained essentially constant until the equilibrium amount of crystalline material was obtained (note behavior of the 06 reflection). Beyond this point, the total amount of crystalline material remained constant, but there was an increasing tendency for the interstratified material to separate into a mix-

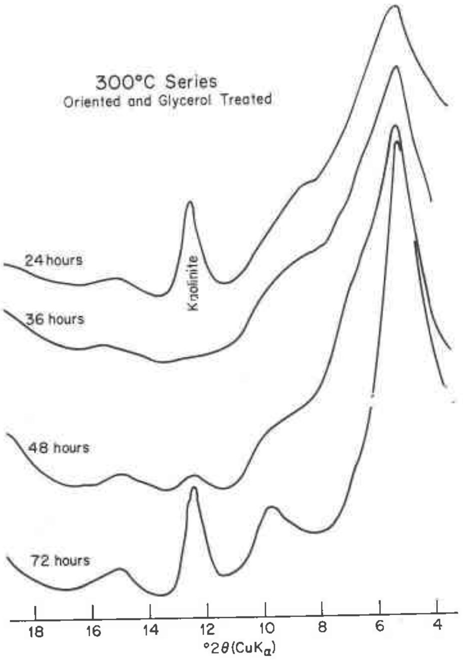


FIG. 3. Behavior of 001 upon glycerol solvation as a function of reaction time, oriented slides, 300°C series.

ture of two separate phases, montmorillonite plus regularly interstratified montmorillonite-mica.

It is of interest to compare the variation of the CEC (Table 1) with these structural changes. The increase of CEC to a maximum in the 36-hour sample parallels the increase in the relative intensity of the 06 reflection. That is, in a mixture which was diatomite and bayerite initially,

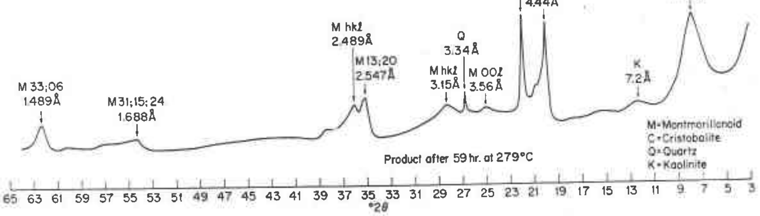


FIG. 4. X-ray diffractometer trace of an unoriented specimen of the 59 hour, 279°C sample.

the CEC of the product (clay+diatomite+bayerite) increased as the amount of clay increased, as would be expected. However, the decrease in CEC beyond 35 hours, corresponding to an increasing separation of the interstratified product into a mixture of two phases, is more difficult to explain. In this region, the relative intensity of the 06 reflection, and, thus, the total amount of clay is constant. Since the CEC obtained by the NH_4Ac technique doesn't necessarily reflect the total charge deficiency of the lattice because some of the charge-balancing cations may be "bound" by the clay, this decreasing "apparent CEC" probably results from an increase in the number of bound cations, perhaps in the regularly interstratified part.

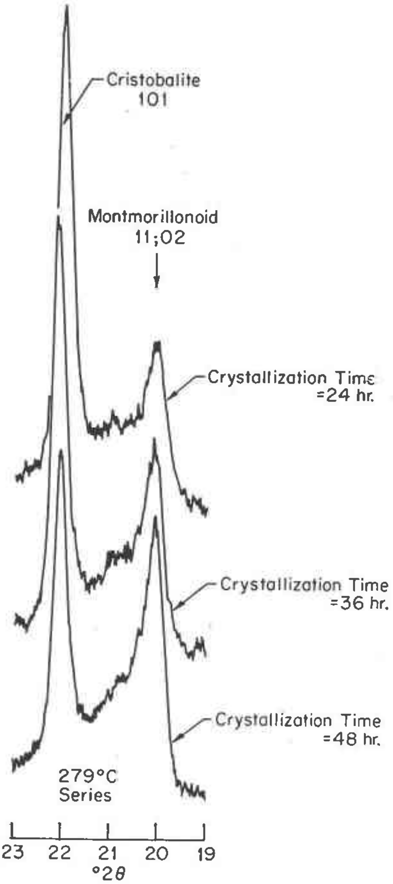


FIG. 5. Region 19 to 23° 2θ for unoriented specimens at several reaction times.

The surface area undergoes an increase during the initial stages of hydrothermal treatment, probably due to the joint effects of breakdown of the diatoms and appearance of montmorillonoid nuclei of small size and correspondingly high area. After this early increase, however, surface area decreases as a function of synthesis time, and this decrease parallels the increase in the amount of crystalline product present. Continuing decrease of area in the region of constant 06 intensity is due to increasing crystallite size. In this discussion of surface area, it is not implied that

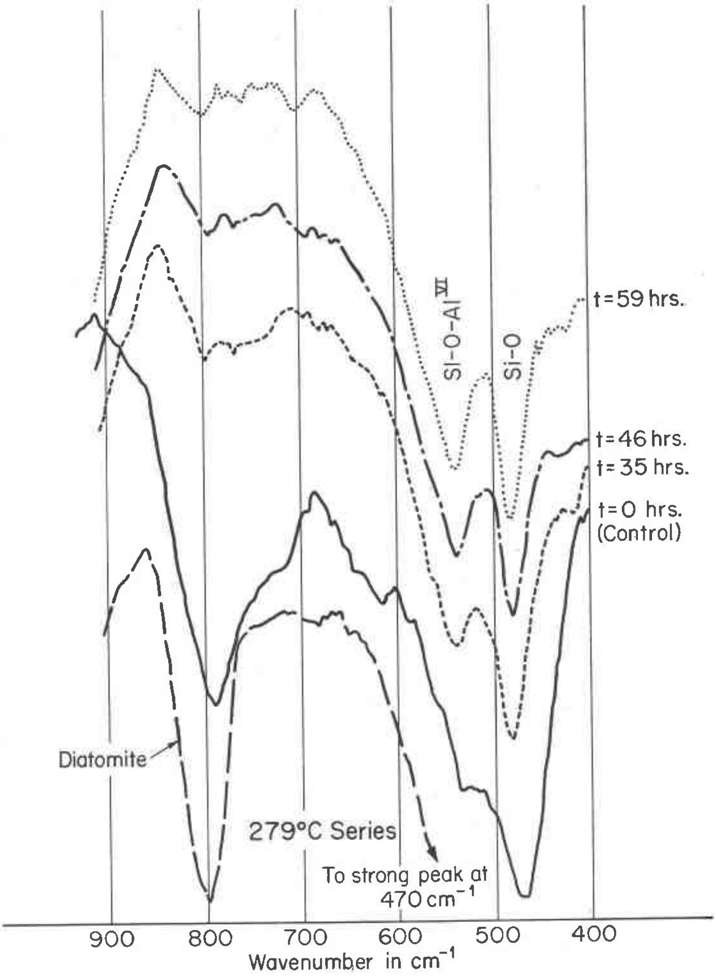


FIG. 6. Infrared spectra in the region 400–900 cm^{-1} for varying reaction times at 279°C.

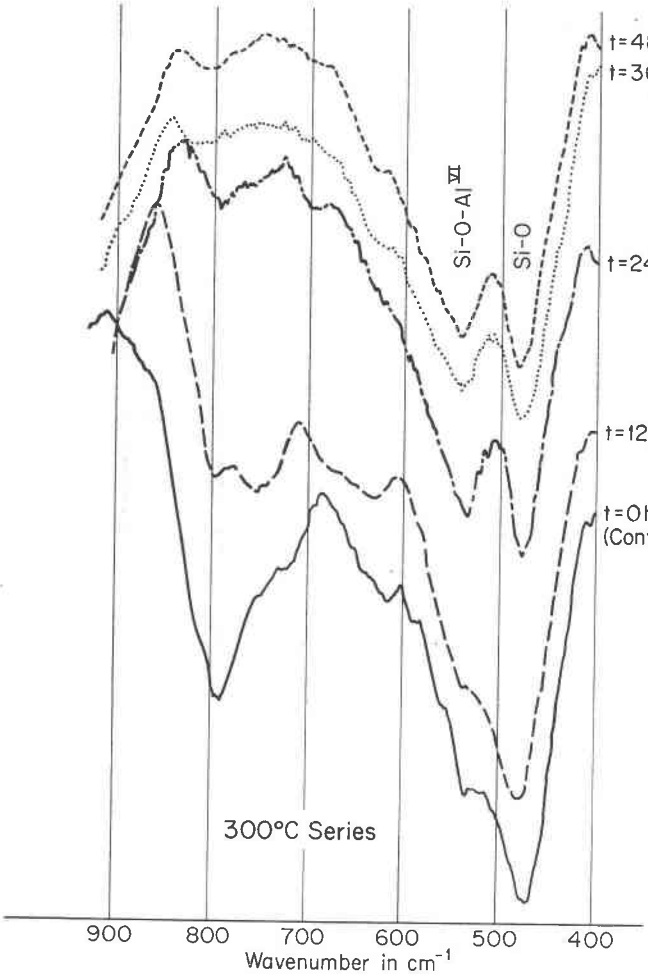


FIG. 7. Infrared spectra in the region 400–900 cm^{-1} for varying reaction times at 300°C.

the BET area, obtained by N_2 adsorption, of samples heated in vacuum to 500°C is indicative of the true area of the crystallites in the reaction mixture. Rather, BET area is reported as an interesting time-dependent parameter.

The apparent density of 30/60 mesh particles of the various products also follows the increase in 06 intensity, and, thus, the increase in the concentration of the montmorillonoid phase. This density increase occurs because the geometry of the platelet stacks is such that more mass can be accommodated within a given volume. From the data in Table 1 it would seem that the apparent density of the product is a simple method of following the course of the crystallization.

The infrared absorption spectra, in the region 400–900 cm^{-1}, of many of the quenched samples appear in Figures 6 and 7. Stubičan and Roy (1959, 1960) have discussed assignments of the various infrared bands of layer silicates. On the basis of their work the band at approximately 480 cm^{-1} is attributed to Si-O, while the band at 540 cm^{-1} is due to some Si-O-Al^{VI} mode. They do not discuss the fairly strong band at 780–800 cm^{-1} which we observe for diatomite and for the 0-hour control sample, but it seems reasonable to attribute this also to an Si-O mode, possibly arising from the accessory cristobalite.

Because of its relationship to the formation of the layer lattice, the band of most interest is that for Si-O-Al^{VI}. That is, this band is apparent only as a trace (if at all) in the control sample, but as crystallization proceeds, it increases in intensity almost in direct proportion to the increase of the 06 reflection intensity. A more quantitative approach is not possible at this stage because of uncertainty in the base line position, but the change in intensity of the 540 cm^{-1} Si-O-Al^{VI} band relative to the 480 cm^{-1} Si-O band certainly supports this statement. Note that the band at *ca.* 800 cm^{-1}, present in the diatomite and in the control sample, diminishes as the crystallization proceeds and the amount of diatomite decreases.

The DTA patterns of the 279°C series of products are presented in Figure 8. The free-water endotherm becomes well-defined after 24 hr. synthesis time; the double-peak feature of this endotherm is undoubtedly related to the presence of Na^+ and NH_4^+ on the exchange sites. The dehydroxylation endotherm increases in intensity and shifts towards higher temperatures as crystallization proceeds. The apparent double dehydroxylation endotherms for the 46- and 59-hour samples result from superposition of an exotherm on an endotherm. In many instances, in our work involving synthetic three-layer clay minerals, a strong symmetrical exotherm has been seen in this region. The process involved may be combustion of NH_3, but tests to establish this point have been inconclusive. The high temperature exotherms increase in intensity with synthesis time and also shift to higher temperatures, indicative of increasing stability of the structure. The high temperature process involved here is the crystallization of cristobalite (major) and mullite and γ-Al_2O_3 (both minor).

Some speculation concerning mechanism. The comments which follow cannot be completely supported on the basis of the preceding information; however, neither are these comments at odds with the data.

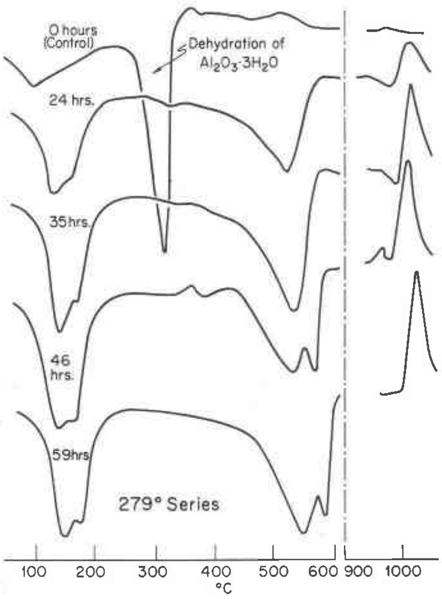
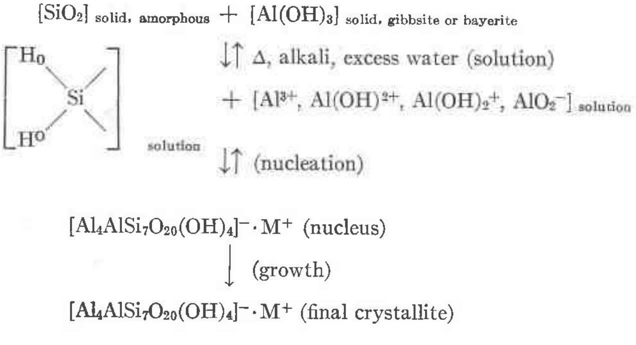


FIG. 8. DTA patterns for the various products synthesized at 279°C.

The process involves the solution of the solid reactants (alumina and silica), nucleation of the layer lattice, and growth of these nuclei to the final crystalline product. Thus, the reaction is a transfer of material from solid reactant to solution to solid product in some variation of the following scheme:



$[SiO_2]_{\text{solid, amorphous}} + [Al(OH)_3]_{\text{solid, gibbsite or bayerite}}$

$\downarrow\uparrow$ Δ, alkali, excess water (solution)

$+ [Al^{3+}, Al(OH)^{2+}, Al(OH)_2^{+}, AlO_2^{-}]_{\text{solution}}$

$\downarrow\uparrow$ (nucleation)

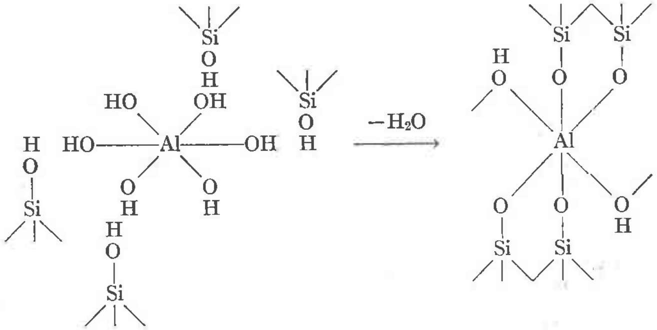
$[Al_4AlSi_7O_{20}(OH)_4]^{-}{\cdot}M^{+}$ (nucleus)

$\downarrow$ (growth)

$[Al_4AlSi_7O_{20}(OH)_4]^{-}{\cdot}M^{+}$ (final crystallite)

It is suggested that the growth step is sufficiently rapid so that the solution and/or nucleation processes become rate-controlling. The nucleation step probably follows the route suggested by Caillère, Hénin and

Esquevin (1953). These authors have stated that the formation of clay minerals under ordinary conditions of temperature and pressure (and surely also under the synthesis conditions used in this work) appears to be determined by the existence of a brucite-type hydroxide layer which induces the SiO_4 tetrahedra to develop a layer lattice. If they are correct in this supposition, then the mechanism would involve the nucleation of $Al(OH)_3$ followed by immediate condensation with Si-OH to produce the desired structure, as illustrated.



This condensation process creates the Si-O-Al^{VI} bonds which give rise to the infrared band at about 540 cm^{-1}. The gibbsite layer would continue to grow with accompanying condensation of the gibbsite-OH with Si-OH to yield a crystallite of increasing size in the *a-b* plane. Finally, these platelets become organized into the randomly interstratified stacks indicated by the X-ray data, probably as the result of an energy minimization process.

We attempted to fit these limited data to the pseudo-first order approach discussed by Granquist and Pollack (1960). That is,

$$\ln \frac{I(\max) - I(t)}{I(\max)}$$

was plotted against t, where $I(\max)$ is the maximum intensity (at a given temperature) of the 06 reflection, and $I(t)$ is the intensity at time t. The data could be fitted satisfactorily by a straight line through the origin. The resulting rate constants (t^{-1}) at the two temperatures were then used to compute the apparent activation energy for the crystallization by means of the integrated Arrhenius equation. The result was 3.9 kcal/mole, a value to which we attach no great significance although it does seem reasonable.

ACKNOWLEDGMENTS

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