SYNTHETIC MONTMORILLONOIDS WITH VARIABLE EXCHANGE CAPACITY*

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Abstract

An attempt has been made to resolve the questions: 1) Do montmorillonoids exist with widely varying exchange capacities: 2) Which of these phases are stable under given conditions of pressure and temperature?

Two series of gels have been prepared in the saponite and beidellite regions respectively, and reacted in sealed inert systems over the range 200°–850° C. at 1000 atmospheres water pressure. The effects of temperature, time, open or closed systems, etc. have geen evaluated. In a time period which is demonstrated to be considerably longer than necessary for the completion of crystallization (as shown by a time-crystallinity study) beidellites can be synthesized with exchange capacities varying from 1/2N to over 2N (where N represents the "ideal" exchange capacity of about 90 m.eq. of the formula $Na_{.33}Al_2Al_{.33}Si_{3.67}O_{10}OH)_2$. These phases are homogeneous and all expand to 17 Å with glycol, the 2N exchange capacity members being the best crystallized. At 300° C. these phases persist for weeks at 1000 atm. and are probably stable. With increasing temperatures only the "N" composition remains single phase up to 425° C.

The range of saponites that can be formed is much narrower. Only the N and 2N members can be prepared as single phases with a stability maximum of about 550° C. Above this temperature a new montmorillonoid (probably a Na-hectorite) is formed and this phase is stable up to 850° C. at 1000 atmospheres.

Cation exchange capacity measurements made by x-ray fluorescence on these Mn-saturated clays shows good correlation with expected values on a relative scale. A wide latitude in compositions for *stable* montmorillonoid formation is thus established especially in the beidellite family. The properties of both low c.e.c. and high c.e.c. members should be of interest.

Two other new phases corresponding to a pure magnesian stilpnomelane and a 14 Å "aluminum chlorite" are encountered in this study.

Introduction

A matter of considerable interest to clay mineralogists can be stated in the questions: Do montmorillonites have a fixed or ideal cation exchange capacity? If so, are the reported variations due to admixture with impurities or faulty measurements? If a real latitude exists in the cation exchange capacity, what are the maximum and minimum limits to the c.e.c. value? Under what conditions do these different montmorillonites form and are they stable?

An analysis of the literature values for cation exchange capacity will show a rather definite peak for values near 90 and a high fraction of values in the range 110–140 m.eq./100 gm. Other values reported range from 40 to over 150 m.eq./100 gm. and it is extremely difficult to obtain

an answer to the questions listed above by a study of whatever sample one obtains from nature. In fact it might be thought, that one of the best ways to solve this problem would be to synthesize various montmorillonites and measure their exchange capacity. The obvious difficulty here as in the natural samples of course is the problem of how to be certain of mineral homogeneity. If the value is low perhaps some low-exchange material is admixed, if high perhaps some high-capacity material, such as an amorphous gel, is included in the sample. Indeed this latter problem is virtually insuperable since the proof of the absence of "gel" in a natural montmorillonite sample is essentially impossible.

It may be argued that, if most montmorillonites showed the same fixed value for the c.e.c., this may be considered an "ideal" composition. This is partly true for the 90 c.e.c. value but definite exceptions are common.

The synthetic approach on a systematic basis was tried by Roy and Roy (1952, 1955) in the system $MgO-Al_2O_3-SiO_2-H_2O$. The range of composition which could be prepared as single phase montmorillonoids was determined. While this did not give unequivocal evidence of the variability of c.e.c., it did, in effect, show that since montmorillonoids could be prepared over such a wide range of composition it was to be expected that both very low and very high exchange capacities should be possible. In Sand, Roy and Osborn's study (1953, 1957) likewise, an unexpectedly wide range of compositions appeared to crystallize in a single montmorillonoid structure. More specific efforts to check this question included Roy and Sand's (1956) measurement of the c.e.c. value of an ideal beidellite; the fact that the c.e.c. was close to that calculated from the total composition lent additional weight to the idea that variability was real. Mumpton and Roy (1956) studied the differences in thermal stability of the compositionally different montmorillonites and showed a continuous variation. The most direct attack on this very problem was that of Karsulin and Stubican (1954) who in their work claimed to show that they had synthesized montmorillonoids with varying compositions and they measured their exchange capacities and showed them to vary also. In their comprehensive study many other measurements, such as the ratio of octahedral to tetrahedral aluminum, were also made to confirm the variation. However, it appeared to us that insufficient emphasis had been placed on verifying the central argument that the phases were both homogeneous and completely crystalline. Moreover, the variations did not follow a simple crystal chemical substitutional scheme.

The work undertaken in the present study was an attempt to demonstrate unequivocally that single phase beidellites and saponites can be prepared with variable exchange capacities, to measure the properties

of these phases including the dehydration-rehydration phenomena, exchange capacities, thermal stability and x-ray properties, and to attempt thereby to derive the limits of solid solution in the montmorillonoid structure. The beidellite family was chosen since in this only tetrahedral substitution of Al for Si is involved and only this changes as one changes the exchange capacity. In the saponite family the desired substitution is likewise the introduction of tetrahedral aluminum, although here one cannot be certain that some alumina does not reside in the octahedral layer.

<div align="center">EXPERIMENTAL</div>

Starting Materials

Mixtures to be used as starting materials in this investigation were prepared as gels. The mixtures were made by mixing calculated amounts of "Ludox" silica sol,* a solution of the nitrates of Al and Mg as required, a NaOH solution of known strength, adjusting the pH to slightly acidic with HNO_3, and evaporating to dryness. They were then fired to about 500° C. until the nitrates were completely decomposed. The products were ground to fine powders.

Techniques of Hydrothermal Synthesis

In every run, the materials were contained in small sealed gold tubes to prevent selective leaching. A small amount of distilled water was added before the tube was sealed. The weight of each sealed tube containing the specimen and water was measured before and after the run to detect any leakage. "Large" batches (0.5 gm.) were made using wider gold tubing in order to prepare enough material for the base exchange capacity measurements. Typical examples of actual weights of the above materials including gold tubing, specimen and water are shown below, especially to convey an idea of the ratio of sample to excess water:

	Small Tubes	*Large Tubes*
Tubing	226.7 mg.	3899.1 mg.
Tubing plus sample	233.9	4419.7
Tubing plus sample and water	247.3	4549.9
Total weight after sealing, before run	236.0	4286.4
Total weight after sealing, after run	236.2	4286.9

The usual hydrothermal equipment was used throughout the investigation. The type of pressure vessel used was the test-tube or cold seal bomb,

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* "Ludox" silica sol is an ammonium-stabilized sol with particles of about 150 Å in size. Analysis shows 0.262% NH_3 and 0.35% Na_2O. This material was generously supplied to us by R. K. Iler of the E. I. duPont de Nemours and Company.

(Roy and Tuttle, 1956) made of Stellite-25 alloy. The pump used for high pressure was an air-operated multiplying-piston type pump.

Up to four gold tubes were placed side by side in the pressure vessel. Temperatures were automatically regulated and measured with chromel-alumel thermocouples. The charge was quenched by removing the furnace from the bomb and immediately placing the bomb in cold water. Upon removal from the pressure vessels, the samples were dried at room temperature in air, and were then powdered, mounted on glass slides with water, and kept at room temperature in air over night.

The products were identified in every case by x-ray diffraction techniques with a wide-range Norelco diffractometer.

The limits of accuracy of the data were as follows: Temperature: $\pm 5°$ C. Pressure: $\pm 5\%$. Spacing: $0.05°$ 2θ fast scan, $0.01°$ 2θ slow scan.

Cation Exchange Capacity Measurements

A rapid instrumental method for determining the cation exchange capacity of small quantities of synthetic clays was developed. A procedure similar to that of Bower and Truog (1940) was used to saturate a clay with Mn^{2+} ions. The manganese content was then measured directly by x-ray fluorescence methods.

A one-half gram specimen of each synthetic montmorillonoid was placed in a 15-ml. centrifuge tube, ten milliliters of a 1N $MnCl_2$ solution, acidified to pH $= 4$–5 with HCl, were added, and then the material was shaken vigorously for a few minutes to obtain a good dispersion. After being shaken automatically for 30 minutes, the material was centrifuged and the supernatant liquid was discarded. This treatment was repeated five times. The residue was washed with water using the shaking and centrifuging procedure four times. In order to remove the excess of $MnCl_2$ completely, the specimen was then washed with water by a dialysis method until the washings no longer gave a test for chloride. One week of washing was usually sufficient. The samples were dried at 110° C.

Manganese is a particularly good element for use in fluorescent x-ray spectroscopy, with LiF as the analyzing crystal, since manganese can be detected in very low concentrations.

A G.E. XRD-5 instrument was used in this x-ray fluorescence work. The intensity of the $MnK\alpha$ peak at $62.95°$ 2θ was measured. The background count was found to be negligible, compared to the intensity of the $MnK\alpha$ peaks for the exchange clays.

Standard samples were made by adding weighed amounts of C.P. grade $MnCO_3$ to clay blanks with the same absorption as the clays to be studied. This was followed by thorough mechanical mixing. The five

standard mixtures of clay samples with 160, 120, 80, 40 and 20 m.eq./100 gms. were prepared in this way. A calibration curve, which was quite close to a straight line, was obtained and extrapolated to 0 c.p.s. at 0% Mn. For each set of measurements made at intervals of several weeks it was found best to re-run the calibration curve and thus to allow for changes in instrumental settings.

The base exchange capacity determination using the x-ray fluorescence method was made on several natural standard clay minerals, the exchange capacity values of which were "known." The three specimens included a purified hectorite from National Lead Company, kaolinite (Lustra clay, RS-286) and montmorillonite clay (FCB) from Filtrol Corporation. They were treated in an indentical manner.

The cation exchange capacity values for those specimens involving the "known" values and the values determined from x-ray fluorescence method are listed below:

Specimen	Base-Exchange Capacity	
	"Known" Value	Value Determined
Purified Hectorite	82.7 m.eq./100 gm. (105° C.)	75 m.eq. Mn²⁺/100 gm.
Kaolinite (Lustra clay, RS-286)	—	2
Montmorillonite clay (FCB)	133 m.eq./100 gm.	116

These results show that the method used gave slightly lower values of base exchange capacity than those obtained by others. One of the possible reasons for these smaller values may be the week-long washing with dialysis. Some leaching of Mn^{2+} may occur.

However, since the relative values appeared to agree within 2% the method used appears quite satisfactory. Increasing our figures by 10% brings them into line with the numerical values obtained by other methods.

<div align="center">RESULTS</div>

Composition of Starting Materials

Eight gels were prepared as starting materials in this investigation. The compositions and the theoretical formulae of the expected types of montmorillonoids are listed in Table I.

Check on Crystallization Rate

Experiments to prove whether or not the entire sample was crystalline were carried out by determining the length of time it takes to achieve crystallinity in the gels used in this investigation.

Several runs were made on three of the beidellite compositions (0.5N,

TABLE I. SYNTHETIC STARTING MIXTURES

Mixture No.	Composition (Mole ratios)							Calculated theoretical formulae

Beidellite Compositions

Mixture No.		Al_2O_3	:	SiO_2	:	Na_2O	Calculated theoretical formulae
B-0.5N		1.09		3.83		0.09	$Al_2(Al_{0.17}Si_{3.83})O_{10}(OH)_2Na_{0.17}$
B-1N		1.17		3.67		0.17	$Al_2(Al_{0.33}Si_{3.67})O_{10}(OH)_2Na_{0.33}$
B-2N		1.34		3.33		0.34	$Al_2(Al_{0.67}Si_{3.33})O_{10}(OH)_2Na_{0.67}$
B-4N		1.67		2.67		0.67	$Al_2(Al_{1.33}Si_{2.67})O_{10}(OH)_2Na_{1.33}$

Saponite Compositions

Mixture No.	MgO	:	Al_2O_3	:	SiO_2	:	Na_2O	Calculated theoretical formulae
S-0.5N	3		0.09		3.83		0.09	$Mg_3(Al_{0.17}Si_{3.83})O_{10}(OH)_2Na_{0.17}$
S-1N	3		0.17		3.67		0.17	$Mg_3(Al_{0.33}Si_{3.67})O_{10}(OH)_2Na_{0.33}$
S-2N	3		0.34		3.33		0.34	$Mg_3(Al_{0.67}Si_{3.33})O_{10}(OH)_2Na_{0.67}$
S-4N	3		0.67		2.67		0.67	$Mg_3(Al_{1.33}Si_{2.67})O_{10}(OH)_2Na_{1.33}$

N and 2N) for various run durations, up to 14 days, at 300° C. and 15,000 psi to determine the effects of run duration on the formation of crystalline phases.

In the one-day run, the 0.5N gel did not crystallize and the other two gels yielded a single phase of very poorly crystallized montmorillonoid. The three-day run gave a single phase montmorillonoid from all three gels, although the phase obtained from the 0.5N gel was still poorly crystallized. After 7 days, a well crystallized montmorillonoid, expanding with glycol to 17–18 Å, was formed from all the compositions. Longer runs of up to two weeks seem to have no further effect.

These results, which are illustrated in Fig. 1, show that in 5- to 7-day runs complete crystallization of such gels to a montmorillonoid phase is achieved. There is considerable crystallization even in a short run of 1–3 days but at this time level it is possible to assume that some material may still be left amorphous. What has been established is the fact that it is not possible to assume that any amorphous phase (with composition near those used) will remain amorphous under the conditions generally used in this investigation.

BEIDELLITE COMPOSITION MONTMORILLONOIDS

Phase equilibrium studies

About 40 runs have been made on the four beidellite composition gels in the temperature range of 260–770° C. at 15,000 psi. Critical runs are summarized in Table II and the results shown in the *t-x* diagram of Fig. 2.

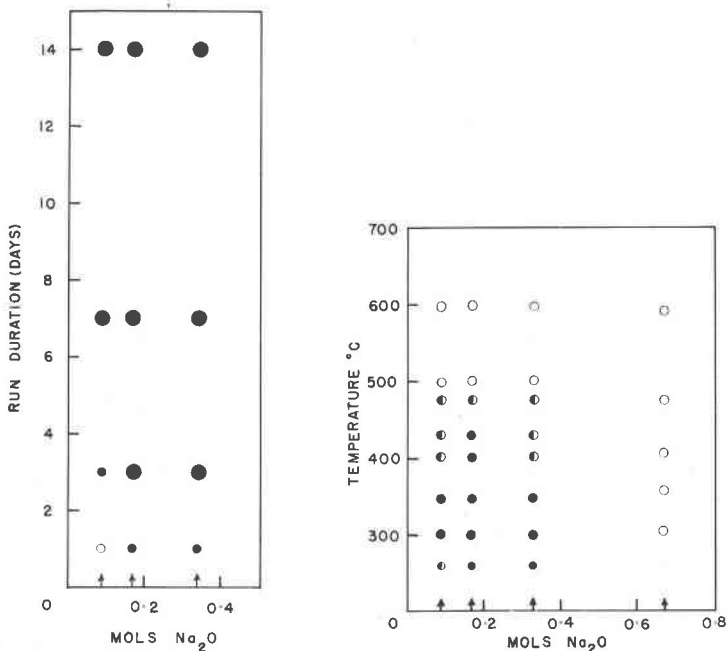From the three beidellite gels including the 0.5N, N, and 2N composi-

FIG. 1 (*left*). Crystallization rate of gels of beidellite composition at 300° C., 15,000 psi. Open circle: no crystallization, small solid circle: poorly crystallized montmorillonoid, large solid circle: well crystallized montmorillonoid.

FIG. 2 (*right*). t-x diagram at 15,000 psi for gels of beidellite compositions. Solid circle: montmorillonoid, open circle: other phases (see Table II), small circle: very poorly crystallized phase.

tions, in the temperature range of 300–350° C. (one-week runs), a single well crystallized montmorillonoid phase was formed. The (001) spacings of the products were 11–13 Å and they expanded with glycol to 17–18 Å. The 4N composition gel did not yield any expanding phase but paragonite alone or paragonite plus analcite was formed. The most favorable conditions for the growth of well crystallized beidellites with variable charge have been therefore fixed as at 300–350° C. and 15,000 psi for 7 days.

At 260° C., single phase montmorillonoids were obtained only from the two gels of N and 2N composition, for the 0.5N beidellite composition gel yielded a kaolinite (or dickite) phase plus a montmorillonoid phase. These expanding phases were not well crystallized.

In the higher temperature range near 400° C. pyrophyllite, mica, or a complex mixed-layer phase of montmorillonoid and mica appeared in

TABLE II. REPRESENTATIVE RUNS FOR THE BEIDELLITE COMPOSITION GELS AT 15,000 PSI

Run No.	Temp. (° C.)	Duration (days)	Products*
Composition $1.09Al_2O_3:3.83SiO_2:0.09Na_2O$			
1,241	262	11	Poorly crystallized mont+kaol (or dickite)
1,341	302	7	Mont (12.2–18.0)
1,351	346	6	Mont (11.1–17.7)+1 pyr (?)
1,301	401	5	Mont+pyr
1,421	430	5	ML (mont, mica)+pyr
1,491	474	4	Al-chlor.+hyd+ML (mont, mica)
1,391	498	5	Al-chor+hyd+pyr+qtz
1,291	598	3	Al-chlor+hyd+qtz
1,331	770	3	Qtz+Ab+mull
Composition $1.17Al_2O_3:3.67SiO_2:0.17Na_2O$			
1,242	262	11	Poorly crystallized mont (12.8–18.0)
1,342	302	7	Mont (12.8–17.7)
1,352	346	6	Mont (12.3–17.3)
1,301	401	5	Mont (12.6–17.7)
1,421	430	5	Mont (12.7–17.7)
1,491	474	4	ML (mont, mica)+hyd
1,391	498	5	Al-chlor+hyd+qtz
1,331	770	3	Atz+Ab+mull
Composition $1.34Al_2O_3:3.33SiO_2:0.34Na_2O$			
1,243	262	11	Mont (12.8–18.0)
1,343	302	7	Mont (12.6–17.6)
1,353	346	6	Mont (12.6–17.3)
1,303	401	5	ML (mont, mica)+mica
1,423	430	5	ML (mont, mica)+mica
1,493	474	4	Hyd+ML (mont, mica)
1,393	498	5	Al-chlor+hyd+mica
1,293	598	3	Al-chlor+hyd+qtz
1,333	770	3	Ab+mull
Composition $1.67Al_2O_3:2.67SiO_2:0.67Na_2O$			
1,514	303	7	Mica+anal
1,484	357	6	Mica
1,524	406	5	Mica
1,494	474	4	Mica+anal+1 cor
1,504	593	3	Ab+cor+neph

* Abbreviations used: mont=montmorillonoid, kaol=kaolinite, pyr=pyrophyllite, ML=mixed layer, Al-chlor=aluminum-chlorite, hyd=hydralsite, qtz=quartz, Ab=albite, mull=mullite, cor=corundum, anal=analcite, neph=nepheline, Mont (12.2–18.0) =(001) spacing of montmorillonoid expands from 12.1 Å to 18.0 Å with glycol, 1=a little, minor.

addition to a montmorillonoid phase. However, the ideal beidellite composition gel (N) still gave a single phase montmorillonoid up to 430° C. At 475° C. only a small amount of the expanding phase persisted. The sodium-poor (0.5N) gel yielded an unexpected chlorite-like phase, with a 14 Å (001) spacing, plus hydralsite besides the mixed-layer phase. Hydralsite is a clay phase found in the study of the system $Al_2O-SiO_2-H_2O$ by Roy and Osborn (1954). The chlorite-like phase will be described later in more detail. The phase assemblage in the products from the N and 2N gels was a mixed-layer phase plus hydralsite. In the above temperature range (400°–500° C.), the sodium-rich gel (4N) gave paragonite plus analcite. The assemblage shown by Sand, Roy and Osborn (1957) consists of these two phases plus alumina; however, no boehmite was found at low temperatures but corundum was found at 500° C.

At 500° C. no expanding phases persisted. The chlorite-like mineral and hydralsite were dominant in all the compositions except the sodium-richest one.

The phase assemblage of chlorite-like mineral and hydralsite was obtained even at 600° C., with quartz appearing as an additional phase at this temperature. From the 4N gel, nepheline plus albite and corundum were obtained.

The runs at 770° C. were made to check the chemical composition of the four beidellite gels. Both the sodium poor gel ($0.09Na_2O$) and the ideal beidellite composition gel ($0.17Na_2O$) gave the three phase assemblage of quartz, albite and mullite, while the gel with the $0.34Na_2O$ yielded albite plus mullite, and the sodium-richest gel gave nepheline, albite plus corundum.

The above phase equilibrium studies suggest that well crystallized montmorillonoids with variable charge, corresponding to $0.09Na_2O$ to $0.33Na_2O$, can be made from the beidellite composition gels and that the optimum condition for obtaining them are the combination of 300° C., 15,000 psi and one week. They also show unequivocally that there is a maximum of stability in the "N" member and in this sense it is an "ideal" composition.

Cation exchange capacity

The cation exchange determinations made on the synthetic montmorillonoids of beidellite compositions with variable charge and with Na_2O from 0.09 to 0.34 are listed in Table III and shown graphically in Fig. 3.

A linear relation with somewhat higher values say 45, 90 and 135 m.eq. would have presented the idealized picture of inter-layer composition

TABLE III. BASE-EXCHANGE CAPACITIES OF THE SYNTHETIC
BEIDELLITE COMPOSITION MONTMORILLONOIDS

Composition (Na_2O Mol)	0.5N 0.09	1N 0.17	2N 0.34
Base-exchange capacity	33	76	110
(m.eq. Mn^{2+}/100 gm. of clay)	33	76	106
average	33	76	108
+10% (see p. 792)	36	84	119

varying with total charge. There are several possible reasons for the deviation of the curve in Fig. 3 from the ideal.

1. Since the values are all low and that for the 2N composition the lowest, it would suggest that not all the Na^+ is entering the inter-layer position. We know only that the total composition within a sealed tube is fixed. It is more than possible that:
   a. Some Na^+ is entering the octahedral sites. (It will be seen that this is probably true in the saponite case.)
   b. Some Na^+ remains in the "solution" or vapor phase.
2. The low values may also be due to admixture of the montmorillonoid with some material such as pyrophyllite, kaolinite or paragonite which has little or no exchange capacity and which escaped x-ray detection though specifically sought.

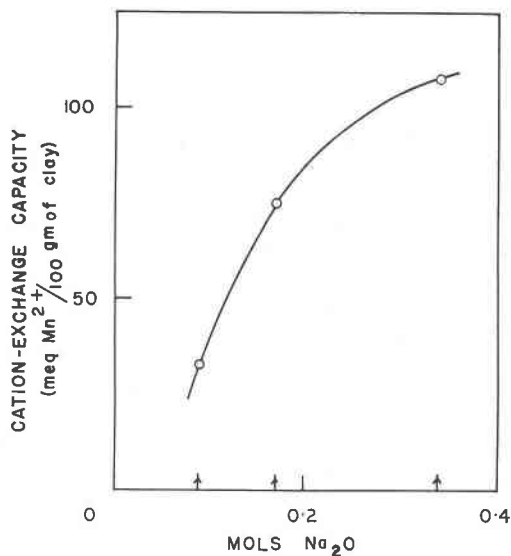The most serious source of error is, in our view, that of Fig. 1*b* the

FIG. 3. Variation of cation-exchange capacity with composition
in the beidellite series of montmorilllonoids.

amount of Na^+ dissolved in the liquid or vapor phase. The problem is an extremely difficult one from the experimental point of view. When a phase such as a montmorillonoid is synthesized under "H_2O" pressure at say 300 or 400° C., the composition of the fluid phase can only be assumed to be that of pure water as a very rough approximation. In fact there is at every temperature and pressure a conode joining the composition of the solid phase and the fluid phase passing through the total composition of solid + water in the system. It is clear therefore that the ratio of solid : water is a critical one in evaluating the change of composition caused by "trading." In Morey-type vessels or in an unsealed envelope in a test-tube bomb the ratio of water : solid (by weight) is frequently of the order of 10:1 or 100:1. Our main direction of effort in keeping the final composition close to the original was by reducing the volume of the water in relation to the solid. Runs were made with low water : solid ratios of 2:1 and much of the actual large sample work was done with a ratio near 1:4 (see page 790). There was a very practical reason why the ratio could not be lowered much further —the gels simply do not crystallize under such conditions, or require prohibitively long times to give decent crystallinity. This small amount of water could, however, alter the composition measurably if the solubility under these conditions were appreciable.

If the "solubility" of the gel were 10%, 0.025 gm. of a 1-gm. sample would be in solution. Of course the composition of the sample would only be altered by the difference in the $Na : Al : Si$ ratio in the fluid and solid phases $\times 0.025$. There is at present no way whatsoever to estimate either the total solubility or the real composition of the solution in equilibrium with the solid. We do know that it is certain that the solution will be rich in soda compared to our composition, but not extremely so, since in this case the alumina and silica will both enter the solution in very large amounts. It is also known that the composition of the fluid phase will vary markedly not only with pressure and temperature but with the solid phase assemblage with which it is in equilibrium. This entire area of the composition of the fluid phase in an alkali-containing system is a major gap in hydrothermal experimentation but one that will only be filled by some years of laborious analytical work. In this study the effort to minimize the extent of solution was considered a satisfactory limitation of the error introduced.

In an attempt to check the influence on hydration characteristics of direct synthesis of a Ca^{2+} beidellite as compared to a synthesized Na^+ beidellite in which Na^+ has been replaced by Ca^{2+} by washing with $CaCl_2$, a "N" Ca-beidellite was synthesized directly from the gels. The effect on hydration characteristics is reported by Gillery (1958). Its

c.e.c. value when measured was found to be only 52 m.eq./100 gm. This low value we ascribe to superior crystallinity and the inability to remove all Ca^{2+} by Mn^{2+} washing.

SAPONITE COMPOSITION MONTMORILLONOIDS

Phase equilibrium studies

Runs have been made on the four saponite composition gels in the temperature range of 260–800° C. at 15,000 psi. Representative runs are listed in Table IV, and the results are illustrated in the *t-x* diagrams of Fig. 4.

From the saponite composition gels, a single phase montmorillonoid expanding to 17–18 Å with glycol was obtained only from the ideal saponite composition gel and the gel with 0.33 Na_2O in the temperature range between 260 and 450° C. In this temperature range, the sodium-rich gel (0.67 Na_2O) yielded a complex mixed-layer including an ex-
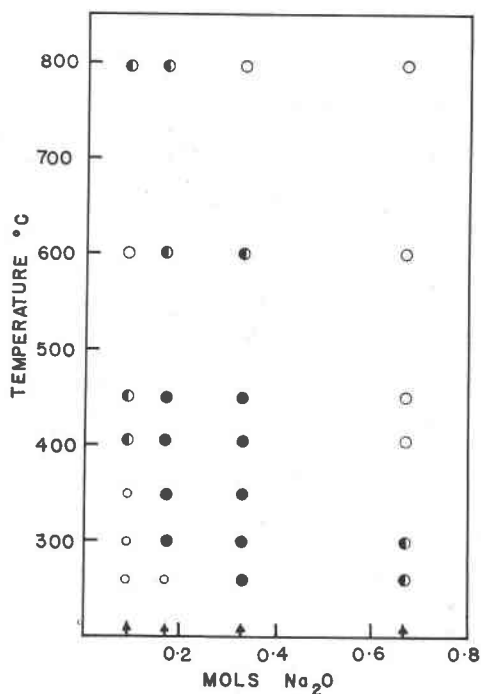

FIG. 4. t-x diagram at 15,000 psi for gels of saponite composition. Solid circle: montmorillonoid, open circle: other phases (see Table IV), small circle: very poorly crystallized and unidentified phase.

TABLE IV. REPRESENTATIVE RUNS FOR THE SAPONITE
COMPOSITION GELS AT 15,000 PSI

Run No.	Temp. (° C.)	Duration (days)	Products*
Composition: $3MgO:0.09Al_2O_3:3.83SiO_2:0.09Na_2O$			
1,261	260	12	Very poor crystallization, unidentified
1,201	300	7	Very poor crystallization, unidentified
1,271	350	6	Very poor crystallization, unidentified
1,121	404	7	Mont+talc
1,281	448	5	Mont+talc
1,321	600	3	Talc+1 mica
1,381	796	3	Mont+talc
Composition: $3MgO:0.17Al_2O_3:3.67SiO_2:0.17Na_2O$			
1,262	260	12	Very poor crystallization, unidentified
1,202	300	7	Mont (12.6–17.7)
1,272	350	6	Mont (12.3–17.7)
1,122	404	7	Mont (12.6–17.7)
1,282	448	5	Mont (12.6–17.0)
1,322	600	3	Mont+1 talc
1,382	796	3	Mont+mica+stilp
Composition: $3MgO:0.34Al_2O_3:3.33SiO_2:0.34Na_2O$			
1,263	260	12	Mont (12.6–17.7)
1,203	300	7	Mont (12.6–17.7)
1,273	350	6	Mont (12.6–17.7)
1,123	404	7	Mont (12.6–17.0)
1,283	448	5	Mont (12.6–17.0)
1,323	600	3	Mont+1 talc+1 mica
1,383	796	3	Stilp+mica
Composition: $3MgO:0.67Al_2O_3:2.67SiO_2:0.67Na_2O$			
1,264	260	12	ML (mont, some other phase)
1,204	300	7	ML (mont, some other phase)
1,274	350	6	Stilp
1,124	404	7	Stilp+1 mica
1,284	448	5	Stilp+mica+chlor
1,324	600	3	Stilp+mica+1 chlor
1,384	796	3	Stilp+mica

* Abbreviations used: Mont = montmorillonoid, stilp = stilpnomelane, chlor = chlorite, ML = mixed layer, Mont (12.6–17.7) = (001) spacing of montmorillonoid, expands from 12.6 Å to 17.7 Å with glycol treatment, 1 = a little, minor.

panding phase at 260–300° C., but above 350° C. gave a "regular mixed-layer" phase with the (001) spacing of 12 Å. This phase was formed not only from the sodium-rich gel for the wide temperature range (350°–800° C.), but also from both the gels of N and 2N compositions at the

TABLE V. BASE-EXCHANGE CAPACITIES OF THE SYNTHETIC SAPONITE
COMPOSITION MONTMORILLONOIDS

Composition (Na_2O Mol)	0.5N 0.09	1N 0.17	2N 0.34
Base-exchange capacity	33	80	126
(m.eq. Mn^{2+}/100 gm. of clay)	33	80	127
Average	33	80	127
+10% (see p. 792)	36	88	140

higher temperatures (750–800° C.). The (001) spacing of these phases obtained from the various conditions is nearly constant at 12 Å. From the constancy of these results, this phase may be considered to be a reproducible single phase, and, as discussed later, this phase may be identified as stilpnomelane.

The sodium-poor gel (0.09 Na_2O) yielded a very poorly crystallized montmorillonoid phase below 350° C., and a montmorillonoid phase plus talc at 400–450° C.

At 600° C., talc and/or mica plus montmorillonoid were formed. This phase combination was found to be stable for the two gels including the sodium-poor one and the one with the ideal saponite composition even at the unexpectedly high temperature of 800° C. The reason for the marked stability of this phase is discussed below and probably bears on the entry of Na^+ into the octahedral layers.

From these results, it was determined that saponites with variable charge cannot be prepared for the whole range corresponding to $0.09Na_2O$ to $0.67Na_2O$, the variability in layer charge, exchange capacity, and Na_2O content extending only from about 0.13 to about $0.5Na_2O$.

Cation exchange capacity

Base exchange capacity values obtained for the synthetic saponites with variable charge and with Na_2O from 0.09 to 0.33 are tabulated in Table V. A large batch of each of the specimens was synthesized at 400° C. and 15,000 psi.

Figure 5 shows a nearly linear relationship in base exchange vs. composition for these materials.

NEW PHASES: SYNTHETIC "ALUMINUM-CHLORITE,"
"SODIUM-HECTORITE" AND STILPNOMELANE

Three interesting new phases were encountered in this study. In the temperature range of 475–600° C., a chlorite-like phase with a basal spacing of 14.0–14.2 Å was developed from the 0.5 N, N and 2N beidel-
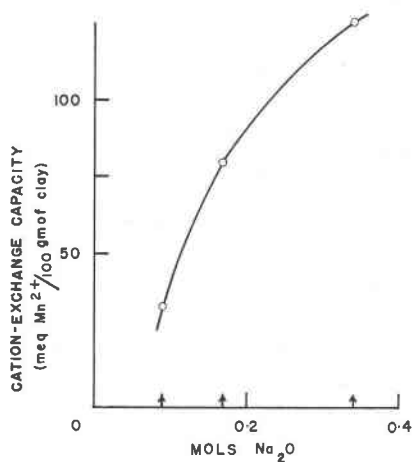
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FIG. 5. Variation of cation-exchange capacity with composition
in the saponite series of montmorillonoids.

lite composition gels. This phase appears quite consistently. The x-ray
pattern of this phase is shown in Table VI. In a parallel concurrent
study, C. M. Warshaw (1958) has consistently encountered the same
phase in the K-deficient muscovite compositions. Unfortunately, as yet
we have not succeeded in obtaining it pure. A reasonable hypothesis is
that this phase represents a dioctahedral-chlorite with a gibbsite layer
between the dioctahedral mica sheets. However, it should be noted that
it has never been observed in the pure Al_2O_3-SiO_2-H_2O system (Roy and
Osborn, 1954) and that some K^+ or Na^+ seem to be essential for its for-
mation. Further studies are in progress on this phase.

Sand et al. (Sand, 1955; Sand and Ames, 1957; Ames and Sand, 1958)
have commented on the "stability" of hectorite to very high tempera-
tures of about 750° C. at 1000 atm. This is very much (200° C.) higher

TABLE VI. X-RAY DIFFRACTION PATTERNS OF NEW PHASES

	"Al-chlorite"			Stilpnomelane	
hkl	d(Å)	I/I_0	hkl	d(Å)	I/I_0
001	14.2	100	001	11.9	100
003	4.647	30			
004	3.480	40	002	5.906	4
	2.344	10	004	2.979	40
	1.828	10	006	1.971	20
009 (?)	1.549	7	008	1.683	2

than the stability of any other montmorillonoid (Mumpton and Roy, 1956). When the "expanding" phase persisted in this work even beyond 800° C., it was obvious that again we were dealing with an exceptional montmorillonoid. It seems possible that we are dealing with a true sodium hectorite of the type $(Mg_{3-n}Na_n)(Si_{4-y}Al_y)O_{20}(OH)_2 Na_{n+y}$. The saponite composition used obviously contains too little Na^+ and too much Mg^{++}, hence other phases appear constantly with the Na-hectorite. Apparently the monovalent ion in the octahedral layer leads to a particularly stable configuration; it may be possible that if the seat of charge could be restricted wholly to the octahedral layer in other montmorillonoids a similar stability would result. Further experimental work on this phase is in progress.

The possible "stilpnomelane" identification arose out of sheer coincidence. During the final weeks of work on this problem we were honored by a visit by Prof. J. W. Gruner of the University of Minnesota, who mentioned his recent re-newed interest in stilpnomelane. This led us to investigate the possibility that the phase obtained from the Na-rich saponite is a magnesium end member of the stilpnomelane family rather than a regular mixed-layer of chlorite and mica. The x-ray pattern of this phase is given in Table VI. It is fairly similar to the x-ray pattern of natural stilpnomelane which was given by Gruner (1937).

MORPHOLOGY OF THE SYNTHETIC MONTMORILLONOIDS

A series of electron micrographs (Fig. 6, *a, b, c,*) of various samples of these synthetic phases was prepared. Two observations are pertinent. The synthetic saponites appeared always to be better crystallized—showing thicker pseudohexagonal discrete crystals (Fig. 6a). In the beidellites of high exchange capacity, there was a definite, elongated, lath-like habit with sharp edges. The crystals were all very thin and in some specimens rolled in from both sides to give a double-barrelled gun effect (Fig. 6c). In most cases the habit and the maximum size appeared to be very similar to those of the natural phases.

DEHYDRATION PROPERTIES OF THESE PHASES

These have been examined in detail by our colleague F. H. Gillery and are reported in this issue on pages 806–818.
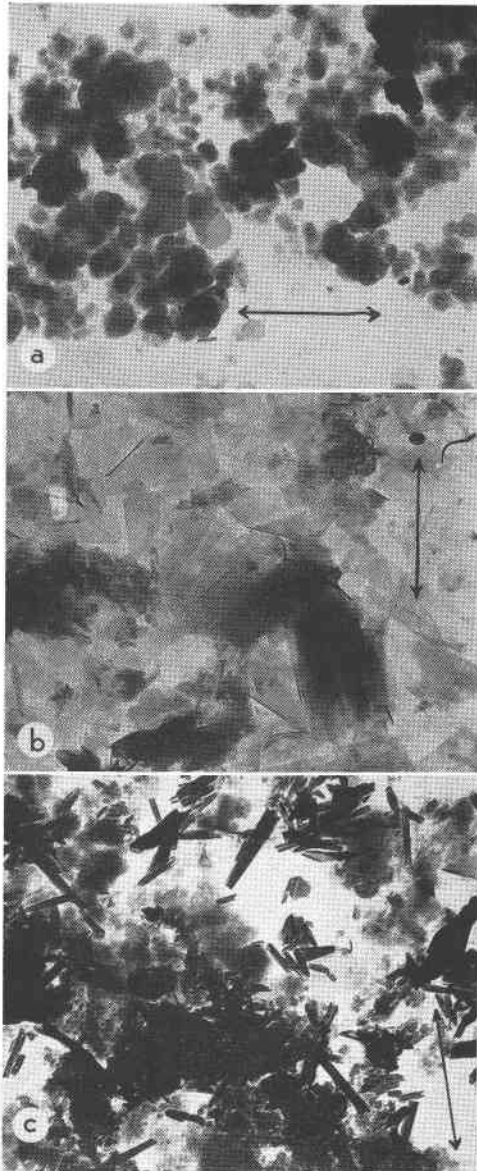
ACKNOWLEDGMENTS

Fig. 6. Electron micrographs of Synthetic Montmorillonoids. (*a*) Saponite (2N) show-ing thick relatively euhedral hexagonal crystals. (*b*) Synthetic beidellite (N) showing fairly typical habit of better formed crystals; which generally show a lath-like habit and are not as poorly formed as natural montmorillonites. (*c*) Synthetic beidellite (2N) showing double-tube effect as though the flat rectangular laths of (*b*) above had been rolled inwards from both edges.

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