SWELLING PROPERTIES OF SYNTHETIC SMECTITES IN RELATION TO LATTICE SUBSTITUTIONS*

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ABSTRACT

SYNTHETIC clays were prepared hydrothermally at 300° to 350°C and 15,000 psi from gels with compositions calculated to give a series of octahedrally and tetrahedrally substituted, 2 : 1-type layer silicates with charges of 0.5N, 1N, 1.5N, 2N, 2.5N, and 3N, where N equals the " normal " layer charge of montmorillonite. Besides montmorillonites and beidellites, the products also contained other components, kaolinite, saponite, paragonite and possibly amorphous materials, depending on the initial gel compositions. Cation exchange capacities of $<2\mu$ fractions treated for removal of amorphous constituents were within the narrow range of 0.95–1.35 meq per g rather than 0.45–2.70 meq per g as calculated from initial gel compositions.

Comparisons between the expanding properties of these materials showed that the beidellites expanded less readily than the montmorillonites upon solvation with glycerol vapor and tended to give single interlayer complexes. These differences were most pronounced when Mg was the saturating ion, although they were also apparent with Ca.

The K-saturated montmorillonites gave greater expansion than the beidellites on hydration at 100 per cent r.h. The montmorillonites also exhibited greater rehydration than the beidellites after heating at 400°–500°C.

Beidellite exhibits properties of expansion that are intermediate between those of montmorillonite and vermiculite. The results of this investigation are consistent with the existence of somewhat stronger ionic attractions in the beidellites than in the montmorillonites. The source of the charge thus has an effect upon the properties of expansion.

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INTRODUCTION

DIFFERENCES in the expansion and collapse of smectites* and vermiculites have been of interest to clay mineralogists for some time. Much of the discussion has concerned the relative influence of source of charge and charge density. Studies have involved both expansion on solvation and K fixation or lattice collapse. The data reported have led to various interpretations. Wear and White (1951) concluded that the total K in the structure, after subjecting the sample to a K-fixation procedure, was related to the proportion of layer charge arising from tetrahedral substitution. They pointed out that, because of differences in the distances from octahedral and tetrahedral layers to interlayer cations, the force of attraction for ions balancing tetrahedral charge should be four times that for octahedral charge. On the other hand, Barshad (1954) concluded that magnitude rather than the origin of the interlayer charge determines K fixation. Weaver (1958) agreed that an interlayer charge greater than 1.5 meq per g was responsible for K fixation but also indicated that, with minerals having an interlayer charge of less than 1.5 meq per g, the origin of the charge was quite significant in regard to the ability to fix K or for the lattice to contract to 10 Å.

Barshad (1950) reported that Ca- and Mg-saturated vermiculites gave mono-interlayers on solvation with glycerol, while the montmorillonites gave duo-interlayers. He stated that one of the factors that determines expansion is the total interlayer charge. Walker (1957, 1958) studied five vermiculites and obtained differences in (001) spacings for both saturating cation and solvating agent. He concluded that the rate and degree of expansion upon solvation are related to layer charge and recommended that Mg saturation and glycerol solvation be used to differentiate vermiculites from smectites. However, he recognized that, if the groups grade one into another with respect to layer charge, the question of where the dividing line occurs is one of terminology and the criterion selected.

The differentiation of beidellite from montmorillonite is even less clear. The scant information on beidellite may be attributed in part to the fact that this mineral came into disrepute (Grim, 1953). However, in view of recent work by Weir and Greene-Kelly (1962) on a sample from the Black Jack Mine and by Koizumi and Roy (1959) on synthetic clays, it is clear that beidellite must be considered. Since beidellite has an exchange capacity similar to that of montmorillonite and a tetrahedral source of charge as do vermiculites, one would expect it to be intermediate between those of montmorillonite and vermiculite. Weir and Greene-Kelly (1962) reported that the beidellite from the Black Jack Mine gave basal spacings corresponding to duo-interlayers of ethylene glycol and glycerol when the sample was Ca-saturated.

It should be mentioned also that, in addition to the source of charge and

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* Smectites is used to denote expanding montmorillonite-group clay minerals of 2 : 1 type with exchange capacity in the order of 0.7–1.5 meq per g. The term *montmorillonite* will refer to the specific mineral and here is not used as a group name.

charge density, other factors related to experimental methods, such as initial moisture status and methods of solvation, have some effects on the results obtained in the expansion of smectites and vermiculites.

One of the difficulties encountered when the vermiculites are compared with smectites with respect to source of charge and charge density is that both factors are variables. The mineral montmorillonite is characterized by a lower charge and substitution of Mg for Al in the octahedral layer, while vermiculite has a higher charge arising from substitution of Al for Si in tetrahedral layers. There are two ways by which the problem might be approached. The first involves the proper selection and characterization of natural samples to permit segregation into those with similar origin of charge but differing charge density, and those with the same charge density but differing source of charge. This approach contains some inherent difficulties in quantitatively determining the amounts of substitution in tetrahedral and octahedral layers of natural samples. It also requires a number of samples of beidellite clays, which are difficult to obtain. A second approach involves the use of synthetic clays. Recent progress in the synthesis of clay minerals suggested that it might be possible to control the kind and amount of isomorphous substitution (Roy and Sand, 1956; Koizumi and Roy, 1959; Roy, 1962), and thereby permit a resolution of the effects of these two variables. Such studies may yield a better understanding of the relationships between structure and properties of expansion or collapse and provide a better basis for distinguishing between minerals in natural samples. This paper is concerned with this latter approach.

EXPERIMENTAL

The work of Koizumi and Roy (1959) was used as a guide in the synthesis of the clay minerals. The procedure involves preparation of gels of different compositions from salt solutions. The gel compositions were calculated on the basis of theoretical formulae for the clay minerals desired. Two series of samples were prepared, a " beidellite " series and a " montmorillonite " series with theoretical silicate-layer charges of 0.5N, 1N, 1.5N, 2N, 2.5N and 3N where N equals the " normal " (see Koizumi and Roy, 1959) layer charge of montmorillonite (Table 1).* A layer charge of 2N corresponds roughly to that of many vermiculites and 3N corresponds to that of muscovite. The dried gels were placed in gold tubes together with sufficient H_2O to provide a solid : solution ratio of approximately 2 : 1. The tubes were sealed, placed in hydrothermal equipment, and heated at 300°–360°C (the exact temperature depending on composition of the gel) under a pressure of 15,000 psi for seven days. The conditions of equilibration were selected on the basis of Koizumi

* It is realized that the use of beidellite and montmorillonite to cover this range exceeds what is customary. However, the use of these terms to designate the series of samples refers to the type of substitution and source of charge. It will be shown that exchange capacities of the purified products remain within the appropriate limits for those minerals.

Table 1.—Compositions of Gels and Theoretical Formulae of Clay Products Anticipated

Gel	Mole ratios of gels				Theoretical corresponding clay product
	SiO_2	Al_2O_3	MgO	Na_2O	
					"Beidellite" series
0.5N-B	3.83	1.085	—	0.085	$(Si_{7.66}Al_{0.34})Al_4O_{20}(OH)_4$ $\downarrow$ $Na_{0.34}$
1N-B	3.67	1.165	—	0.165	$(Si_{7.34}Al_{0.66})Al_4O_{20}(OH)_4$ $\downarrow$ $Na_{0.66}$
1.5N-B	3.50	1.250	—	0.250	$(Si_7Al)Al_4O_{20}(OH)_4$ $\downarrow$ Na_1
2N-B	3.33	1.335	—	0.335	$(Si_{6.66}Al_{1.34})Al_4O_{20}(OH)_4$ $\downarrow$ $Na_{1.34}$
2.5N-B	3.16	1.420	—	0.420	$(Si_{6.32}Al_{1.68})Al_4O_{20}(OH)_4$ $\downarrow$ $Na_{1.68}$
3N-B	3.00	1.500	—	0.500	$(Si_6Al_2)Al_4O_{20}(OH)_4$ $\downarrow$ Na_2
					"Montmorillonite" series
0.5N-M	4.0	0.915	0.17	0.085	$Si_8(Al_{3.66}Mg_{0.34})O_{20}(OH)_4$ $\downarrow$ $Na_{0.34}$
1N-M	4.0	0.835	0.33	0.165	$Si_8(Al_{3.34}Mg_{0.66})O_{20}(OH)_4$ $\downarrow$ $Na_{0.66}$
1 5N-M	4.0	0.75	0.5	0 25	$Si_8(Al_3Mg_1)O_{20}(OH)_4$ $\downarrow$ Na_1
2N-M	4.0	0.665	0.67	0.335	$Si_8(Al_{2.66}Mg_{1.34})O_{20}(OH)_4$ $\downarrow$ $Na_{1.34}$
2.5N-M	4.0	0.58	0.84	0.42	$Si_8(Al_{2.32}Mg_{1.68})O_{20}(OH)_4$ $\downarrow$ $Na_{1.68}$

and Roy's data, the only differences being the use of larger sized gold tubes (10 mm i.d.) to accomodate larger samples (approximately 4 g air-dry gel).

After equilibration, the samples were removed, air dried and lightly ground in a mortar. The products were analyzed by X-ray diffraction and for cation exchange capacities.

During the investigations it was determined that considerable "amor-

phous " material was present in the products.* Therefore samples were treated for differential dissolution of " free " Al and Si and amorphous components using the procedure of Hashimoto and Jackson (1960). The material was dispersed in dilute Na_2CO_3 and the $<2\mu$ fraction separated (Jackson, 1956). Characterization studies of the products were made on the " cleaned " $<2\mu$ fractions.

Samples were saturated with Ca, Mg or K by washing two or three times with 1 N chloride salt solutions followed by two or three washings with H_2O. In the case of Ca-saturated samples required for determination of cation-exchange capacities, two additional washings with methanol were made.

X-ray diffraction analyses using Cu $K\alpha$ radiation and a recording diffract-ometer were made on powder samples and on oriented specimens prepared by a paste technique (Harward and Thiesen, 1962). Some of the samples were pre-equilibrated over salt solutions to provide a given per cent relative humidity. During diffraction analyses of the hydrated samples, the humidity around the sample was controlled by passing air through columns of salt solutions and then into the goniometer shield, the inner part of which was sealed with cellophane tape. Periodic checks of relative humidity control were made with a hygrometer previously calibrated over salt solutions. In cases in which analysis under dry conditions was desired, the dried samples were stored over P_2O_5. Air to the diffractometer enclosure was passed through columns of " Drierite " and concentrated H_2SO_4 in succession and a small container of P_2O_5 was placed in the enclosure just underneath the sample. No attempt was made to control the humidity of samples after solvation with ethylene glycol or glycerol.

Samples of Ca- and Mg-saturated clays were solvated using ethylene glycol vapor as recommended by Kunze (1955). Duplicates were solvated with glycerol vapor (Brown and Farrow, 1956) or by the addition of glycerol with a dropping tube until the slide was visibly moist (Walker, 1957, 1958). The solvated slides were allowed to stand overnight before analysis. In order to evaluate the effect of moisture status (Walker, 1957; Jackson 1956), samples were dried at 105°C or equilibrated at 55 per cent relative humidity prior to solvation with glycerol vapor.

Cation exchange capacities were determined by procedures essentially the same as those described by Rich (1961) except that the Ca was displaced by two extractions with 1 N NaCl. The supernatant extracting solutions were separated by centrifugation and then filtered. Exchangeable Ca was deter-mined by titration with cyclohexanediamine tetra-acetic acid (CyDTA) using Calcien as the indicator (Carlson and Johnson, 1961). The CyDTA was stan-dardized against standard grade $CaCO_3$ dissolved in HCl and titrated in the presence of 1 N NaCl. A 1 N NaCl blank was used to assist in obtaining the end point during titration of unknowns. Analyses were made on duplicate samples of clay.

* Unpublished data by P. Denny, Pennsylvania State University and M. E. Harward, Oregon State University.

RESULT AND DISCUSSION

Products obtained

The gel compositions were chosen initially with the object of obtaining a wide range of charge densities originating in the octahedral and tetrahedral sites of the layer structures (see Table 1). The cation exchange capacity measurements, however, fell within narrower limits and generally were smaller than the anticipated values (Table 2). This was attributed to the fact that the products did not yield monomineralic clays but contained other components, depending on the composition of the initial gel.

TABLE 2.—CATION EXCHANGE CAPACITIES (CEC) AND PRODUCTS OF HYDROTHERMAL SYNTHESIS

Initial gel	Theo. CEC meq/g	Observed CEC meq/g		Components in initial product
		Initial product	$<2 \mu$ after " clean-up "	
		BEIDELLITE SERIES		
0.5N-B	0.45	0.44	0.81(1.13)*	Beidellite, Kaolinite, amorphous
1N-B	0.90	0.61	1.21	Beidellite, amorphous
1.5N-B	1.35	1.24	1.35	Beidellite, amorphous
2N-B	1.80	1.16	1.31	Beidellite, amorphous, Paragonite?
2.5N-B	2.25	0.74	0.79	Paragonite?, mixed layer expanding and non-expanding phases, amorphous
3N-B	2.70	0.43	—	Paragonite?, amorphous
		MONTMORILLONITE SERIES		
0.5N-B	0.45	0.35	0.95	Montmorillonite, amorphous
1N-M	0.90	1.11	1.21	Montmorillonite, amorphous
1.5N-M	1.35	0.70	1.26	Montmorillonite, Saponite?, amorphous
2N-M	1.80	0.75	1.30	Montmorillonite, Saponite?, amorphous
2.5N-M	2.25	0.74	1.17	Saponite?, amorphous

* The content of kaolinite was estimated to be 31% based on the weight loss on dehydration. Assuming an exchange capacity of the kaolinite to be 0.1 meq/g, the exchange capacity of the beidellite would be approximately 1.13 meq/g.

The high background in the X-ray diffraction patterns and results of electron-probe analyses† indicated that amorphous impurities were present. It was evident that some " clean up " treatment of the initial products was desirable, and the procedure of Hashimoto and Jackson (1960) was used for this purpose. This treatment materially increased the peak : background ratio in the diffraction records. As a result of the differential dissolution treatment, weight losses of selected samples were in the order of 30 to 50 per cent for the products, while a sample of the initial gel was all essentially

† Unpublished data by P. Denny and M. E. Harward.

dissolved with this treatment. Considering the pH conditions under which the exchange capacity determinations were made, it is expected that the exchange capacity of amorphous constituents would be small. The cation-exchange capacities of the $<2\mu$ fractions of the " cleaned " samples were higher than those of the initial products (Table 2). The results are consistent with the removal of amorphous material that would act as a dilutant during the exchange capacity measurements.

Results of diffraction analyses provided direct evidence of crystalline impurities in some preparations. Kaolinite was observed in the 0.5N-B preparation. Correction for the presence of kaolinite gave an estimated exchange capacity of 1.13 meq/g for this beidellite (see footnote to Table 2). As the content of Al and Na increased and Si decreased for 2N, 2.5N and 3N gels of the " beidellite " series, the exchange capacities of the products decreased. Diffraction analyses indicated that the products from 0.5N-B (with the exception of kaolinite), 1N-B, 1.5N-B and 2N-B contained only expanding phases. The products from the 2.5N-B composition contained a nonexpanding component with d_{001} of approximately 9.7 Å plus randomly mixed layers of expanding and nonexpanding material. The products from the 3N-B composition gave only the basal 9.7 Å line and expanding phases were not evident. The 060 lines indicated only the presence of dioctahedral components. It is believed that paragonite formed from the gels with higher amounts of Al and Na. A chemical analysis of the Ca-saturated $<2\mu$ fraction from 2N-B indicated 0.96 per cent Na_2O, although the nonexpanding phase was not evident on the diffraction patterns. The Na_2O contents of $<2\mu$ 1N-B and 1.5N-B were 0.26 and 0.35 per cent respectively. The presence of Na-mica in some of the samples would account for the observed decreases in cation exchange capacities.

The cation exchange capacities for initial products in the " beidellite " series may be compared with the results of Koizumi and Roy (1959). Their observed cation exchange capacities, determined by Mn saturation and X-ray fluorescence analysis, were 0.33, 0.75 and 1.08 meq per g for 0.5N, 1N and 2N " beidellites " respectively. Their curve of exchange capacity vs. composition of gel deviated from the ideal and appeared to level off at values slightly in excess of 1 meq/g in a manner similar to that noted here. They suggested several possible reasons for the observed values being lower than the expected, although they favored the view that some Na remained in the solution or vapor phase during hydrothermal synthesis. The data obtained here support one of their other suggestions, namely, that the beidellite may be mixed with other materials such as talc, kaolinite or paragonite, which have little or no exchange capacity. In addition it appears that the presence of amorphous material may be a factor.

The products for all samples of the " montmorillonite " series contained expanding phases, and no nonexpanding components were evident on the X-ray patterns. Changes in the b-axis parameters, however, were evident from 060 reflections of the Ca-saturated $<2\mu$ fractions. The products from the

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0.5N-M and 1N-M gels gave 060 reflections corresponding to the dioctahedral minerals only, while that from 2.5N-M gave an 060 reflection corresponding to a trioctahedral product. The patterns for 1.5N–M and 2N–M products contained 060 reflections corresponding to both dioctahedral and triocta-hedral components. It appears that, as the Mg content of the gel is increased and Al decreased, there is a tendency to form separate mineral phases rather than an increasing substitution of Mg for Al to give high charge " montmorillonite ". Since trioctahedral phases are formed from the high Mg compositions, the question arises as to the source of charge. It seems likely that tetrahedral substitution of Al for Si in a saponite structure may occur in this case. However, it is difficult to confirm this and it is recognized that both tetrahedral and octahedral substitution may be present in some samples if Na is also present in the octahedral layer. On the basis of the 060 reflec-tion and the expansion properties, it is assumed that the product from the 2.5N-M composition was saponite.

Certain " cleaned " samples were available to develop the relationship of charge to properties of expansion. The presence of kaolinite in the 0.5N-B product did not interfere with studies of expansion of the beidellite compo-nent, and it was possible to obtain an estimate of its exchange capacity. The products for 1N-B and 1.5N-B appeared to be monomineralic. Considering that the 0.5N, 1N and 1.5N " beidellite " products could only contain Si, Al and Na, that the structures were dioctahedral with expanding lattice and that the exchange capacities were in the proper orders of magnitude, it is concluded that these materials may properly be called *beidellites*. Similarly, since the 0.5N and 1N " montmorillonite " products, which contained Mg in addition to Si, Al, and Na, were expanding dioctahedral minerals that possessed the proper range in exchange capacity, it is concluded that these products may properly be called *montmorillonites*.

The cation exchange capacities of $<2\mu$ samples treated for removal of amorphous materials all fell within the same general order of magnitude for both series. If the samples known to contain Na-mica (2.5N-B and 3N-B) or saponite (1.5N-M, and 2.5N-M) are omitted and the exchange capacity of 0.5N-B is corrected for the presence of kaolinite, the exchange capacities fall within the range 0.95 to 1.35 meq per g. Since a range from low to high charge density within each series was not obtained, comparisons of the effect of charge density within each series were not possible in this study. It is possible to make a comparison of the effect of the source of the charge by proper selection of the beidellite and montmorillonite samples. The remainder of the study was therefore directed along these lines.

Expansion on solvation

A basic question is the ease of expansion of beidellite relative to that of montmorillonite on the one hand and of vermiculite on the other. It was considered that beidellite should show properties intermediate between those of the other two minerals. This question was tested by measuring the expan-

sion upon solvation of selected samples of the synthetic clays. Results revealed that the beidellites show greater resistance to expansion than do the montmorillonites. The differences were dependent on saturating cation, initial hydration of the sample and method of solvation (Table 3).

Table 3.—Expansion of Synthetic Beidellites and Montmorillonites; Values of d_{001} in Å*

Treatments			Beidellites			Montmorillonites	
Saturating Cation	Moisture Conditioning†	Solvation	0.5N-B	1N-B	1.5N-B	0.5N-M	1N-M
Ca	55% r.h.		15.2	15.0	15.1	15.2	15.2
Ca	Dried at 105°C	Eth. Glycol Vapor	17.0	16.9	16.8	16.9	16.8
Ca	Dried at 105°C	Glycerol Vapor	14.6	14.5	14.6	17.6	17.6
Ca	55% r.h.	Glycerol Vapor	15.9‡	16.1‡	14.4	17.6	17 6
Ca	Dried at 105°C	Glycerol Liquid	17.8	17.8	17.8	—	—
Mg	55% r.h.		15.0	14.9	14.8	15.0	15.2
Mg	Dried at 105°C	Eth. Glycol Vapor	17.0	16.9	16.8	16.9	17.0
Mg	Dried at 105°C	Glycerol Vapor	14.5	14.3	14.2	17.8	16.7§
Mg	55% r.h.	Glycerol Vapor	14.5	14.2	14.2	17.6	16.1§
Mg	Dried at 105°C	Glycerol Liquid	17.9	17.8	17.9	17.9	17.9

* Spacings reported are averages of all (001) orders observed except where the orders were irregular or for mixed layer systems where the reported spacing is for the first order only.

† Equilibration prior to solvation.

‡ Irregular orders.

§ Possibly mixed 14 Å and 17 Å layer spacings.

Ethylene glycol solvation resulted in expansion of both montmorillonite and beidellite to thicknesses equivalent to the formation of double interlayer complexes. The use of glycerol vapor, however, differentiated the two minerals; glycerol vapor always gave rise to higher (001) spacings for montmorillonite than for beidellite. The beidellite tended to form single interlayer complexes and montmorillonite double layer complexes when glycerol in the vapor form was used. Jackson (1956) and Walker (1958) have pointed out that the hydration state of the mineral prior to solvation is of importance in the formation of the glycerol complex. In this study, expansion to a thickness greater than that for mono-interlayer occurred in montmorillonite regardless of hydration treatment. Hydration of Ca-saturated beidellites prior to exposure to glycerol vapor resulted in some increased expansion in two of the samples, although it was not complete and irregular orders were observed. Only the single interlayer complex of Mg-saturated beidellites was formed by glycerol vapor, even though the samples were hydrated. It was possible to form the

duo-interlayer complex of beidellites by exposure to an excess of glycerol liquid.

It is of interest to compare these data with those of Walker (1958) for vermiculite. He reported that the majority of vermiculite samples expanded when treated with ethylene glycol, although the spacings reported (approximately 16 Å) were slightly less than observed here with the beidellites. His Mg-saturated samples were the most reluctant to expand and two of them gave 14.3 Å spacings. Walker observed only the mono-interlayer complex with glycerol when the samples were Mg-saturated but obtained duo-interlayers for all but one of the Ca-saturated samples. It is important to emphasize that Walker's solvation treatment involved contact with a large excess of the organic liquid, which was similar to the liquid treatments used here. Nevertheless, the effects of hydration, saturating cation and solvating agent, which Walker observed on vermiculites, are somewhat similar to the observations here on beidellite using the organic vapor. It is to be stressed that such differences were not obtained with the montmorillonites. Thus, it appears that the beidellite clays are intermediate between vermiculites and montmorillonites with respect to expansion. It follows that care must be exercised in the identification of these different minerals. Walker interpreted the greater reluctance of vermiculite to expand with glycerol and ethylene glycol as compared with the behavior of smectites as being due to the greater electrostatic charge between the silicate layers of the former group. The data presented here clearly indicate that the source of the charge also must have an important effect on the expansion.

K saturation and hydration

There has been some question of the effect of source of charge on lattice collapse and of K fixation in K-saturated clays. It was desired to study the properties of the synthetic clays in this respect. Comparisons were made of the behavior of K-saturated beidellites and montmorillonites in response to different levels of relative humidity. Since the basal orders on the diffraction patterns were not always regular and in some cases the peaks were broad or asymmetric, only data for the first-order reflection are given. The spacings were estimated by taking the center of the peak at half-peak height.

Expansion of the K-saturated clays occurred upon equilibration of the samples in humidity chambers. As the relative humidity was increased from zero, the (001) spacing increased sharply at first and then leveled off at a thickness corresponding to approximately one interlayer of H_2O. At 100 per cent r.h., the montmorillonite samples expanded further to a thickness equivalent to two layers of H_2O, while the beidellite samples remained with one interlayer of H_2O (Fig. 1).

It is commonly regarded that K saturation results in a collapse of the lattice of expanding-type clays. Relative to Ca- and Mg-saturated clays, this is true. It is apparent, however, that expansion of K-saturated montmorillonites and beidellites to a thickness of one interlayer of water readily occurs.

These results are similar to those of Hendricks, Nelson and Alexander (1940) on Mississippi montmorillonite, although they did not report spacings obtained below 25 or above 90 per cent r.h. They reported spacings of 11.9 Å with the peaks becoming diffuse above 70 per cent r.h. Sayegh, Harward and Knox (1964) also have called attention to the sensitivity of dehydrated K-saturated clays to expansion upon exposure to higher humidity. The princi-
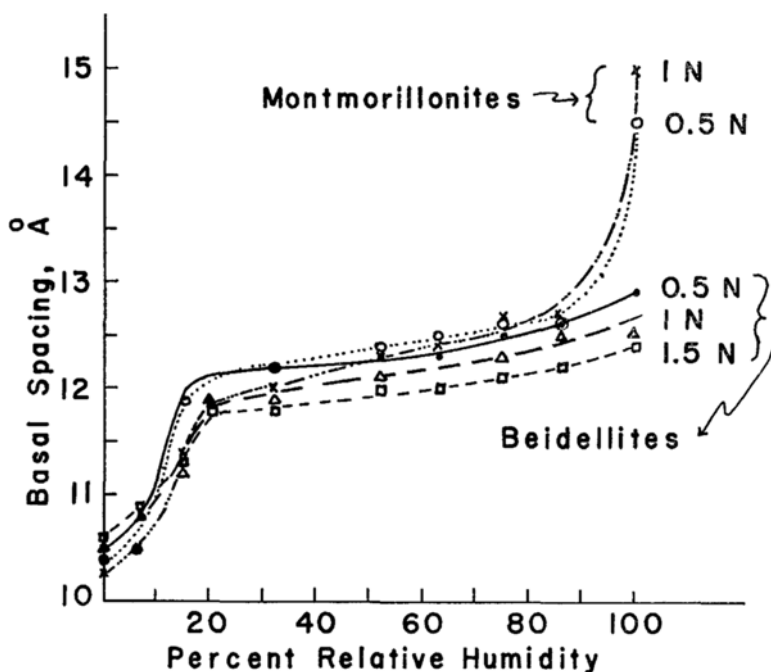

FIG. 1. Effect of humidity on expansion of synthetic montmorillonites and beidellites after heating to 150°C. (The N numbers refer to clays derived from different gel compositions—see text.)

pal point here, however, concerns the difference in behavior between the montmorillonite and beidellite samples. It was initially expected that the beidellites would be intermediate between montmorillonite and vermiculite with respect to collapse and resistance to expansion on hydration. Greater collapse (or less expansion on hydration) of the K-saturated beidellite was expected than was observed in the present work. Montmorillonite and beidellite behave very similarly over most of the range in humidity.

In view of these results on the hydration of K-saturated clays, the question arose as to a possible difference in irreversible collapse after heating. Oriented slides of each of the K-saturated synthetic clays were heated successively at

100°, 200°, 300°, 400° and 500°C for $3\frac{1}{2}$ hr. After each heat treatment the samples were X-rayed and then placed in a moisture chamber at 55 per cent r.h. overnight, and again X-rayed to determine whether rehydration had occurred. After treatment at temperatures up to 300°C, the clays rehydrated as indicated by a shift of the first-order reflection to lower angles of 2θ. As the
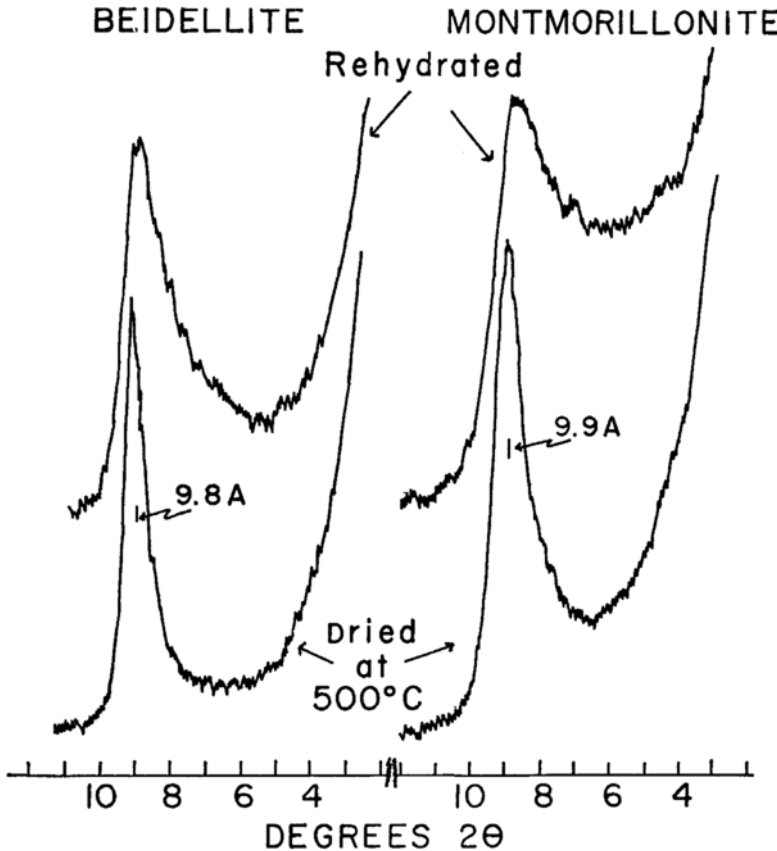

FIG. 2. Rehydration of beidellite and montmorillonite. Samples were equilibrated overnight at 55% r.h. after the heat treatment.

temperature of heating increased, the (001) spacing in dry air decreased, and the amount of expansion on rehydration also gradually decreased. For the higher temperatures of heating, the peaks of the rehydrated samples became more asymmetric toward the low angle side. The montmorillonites exhibited more of this asymmetry than the beidellites. The differences between these clays were most apparent for rehydration after the 400° and 500°C heat

treatments. Data shown in Fig. 2 are typical of the results obtained. The low angle scatter is much greater for the montmorillonite than for the beidellite clay. It is assumed that these diffraction effects are due to expansion of some layers to form a mixed-layer system. It appears that montmorillonites show greater rehydration than do beidellite after heating at 400°–500°C.

CONCLUSIONS

The amount of isomorphous substitution in synthetic montmorillonite and beidellite minerals falls within a relatively narrow range. In some instances, as the composition of initial gels is varied in order to increase the amount of substitution, other phases are formed. Differences in the cation-exchange capacities of synthetic smectite samples that have been observed may be ascribed to the occurrence of other phases in the sample.

Synthetic montmorillonites, with octahedrally located layer charges, and synthetic beidellites, with tetrahedrally located layer charges, both with exchange capacities in the range 0.95–1.35 meq per g, show differences in swelling properties that are consistent with there being somewhat stronger ionic attractions in the beidellites than in the montmorillonites. Beidellite is intermediate between montmorillonite and vermiculite with respect to expansion upon solvation. Source of the charge (type of isomorphous substitution) thus has an effect upon the properties of expansion.

From the present experiments, it appears that a clear distinction between montmorillonite and beidellite minerals on the basis of their swelling behavior is possible only under certain specific conditions. Solvation with ethylene glycol or with liquid glycerol affords no clear differentiation. However, with glycerol vapor, and with Mg- and Ca-saturated clays previously dried at 105°C, there is a clear distinction between the montmorillonites, which expand to about 16.7–17.7 Å, and the beidellites, which expand to about 14.2–14.6 Å. If the clays are equilibrated at 55 per cent r.h. prior to the glycerol vapor treatment, Mg saturation again results in differentiation of the minerals; however, on Ca saturation, the beidellites show some expansion, up to about 16 Å, and the differentiation is then less clear.

K-saturated montmorillonites and beidellites show little difference with respect to humid atmospheres over the range 0–86 per cent r.h. but at 100 per cent r.h., K-montmorillonites expand toward a two-layer complex with d_{001} of approximately 15 Å, while the K-beidellites expand only toward a one-layer complex with d_{001} of approximately 13.7 Å. K-montmorillonites also showed a greater tendency than K-beidellites toward rehydration after heat treatment at 400°–500°C. The differences in hydration of K-saturated beidellites and montmorillonites are also attributed to an effect of the source of the charge.

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