ADSORPTION-DESORPTION CHARACTERISTICS OF SYNTHETIC MONTMORILLONOIDS IN HUMID ATMOSPHERES*

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ABSTRACT

A systematic study of the desorption characteristics of synthetic Na and Ca-beidellites and saponites with various exchange capacities has been made. The results show that well defined hydrates exist over certain ranges of water vapor pressure and that between these ranges mixed layers of the hydrates predominate. The valence of the interlayer cation has a greater effect on the desorption characteristics than the exchange capacity or the type of montmorillonoid examined.

INTRODUCTION

Many papers have been published on the subject of the expansion of montmorillonoids in contact with water vapor. The specimens investigated have been of natural origin and therefore of random composition. The use of synthetic specimens in the present investigation has eliminated some of the difficulties which arise in the study of natural specimens and has made possible a systematic study of the effects produced by varying the exchange capacities and lattice composition. The specimens examined have included natural and synthetic montmorillonites, beidellites and saponites saturated with the cations Na and Ca.

PREPARATION OF SPECIMENS

The specimens were prepared hydrothermally from "gels" by M. Koizumi in sealed gold tubes (Koizumi and Roy, 1959). The conditions for optimum crystallinity were, for the beidellites 300° C., 15,000 psi and 7 days, and for the saponites, 400° C., 15,000 psi and 7 days. They were prepared in a Na saturated form and after the expansion characteristics of this form had been examined they were re-saturated with Ca and finally with Mn.

The re-saturations were carried out by shaking about 0.2 gm. of the clay with 10 ml. of 1M. $CaCl_2$ or 1M. $MnCl_2$ for 30 min., centrifuging, and decanting. This procedure was repeated five times. The washing was carried out in precisely the same way using deionized water in place of the 1M. solutions, until the specimens became deflocculated to such an extent that it was difficult to separate them from the water b· centrifugation. At this stage washing was continued by sealing the s)ecimen, suspended in water, in dialysis tubing and passing a slow, continuous

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stream of distilled water around the tubing for about 5 days, until the evaporated washings showed no chloride ion with the $AgNO_3$ test.

For x-ray examination a dilute suspension of the specimen in water was allowed to dry out on a glass slide under room conditions, resulting in a well oriented layer suitable for the examination of the basal reflections.

Table I gives a complete list and details of the specimens examined.

TABLE I. DETAILS OF SPECIMENS EXAMINED

No.	Ex Cap	Sat Cation	Name	Formula
a	$\frac{1}{2}$N	Na	Beidellite	$0.17Na(Al_2)(Si_{3.83}Al_{0.17})O_{10}(OH)_2$
b	$\frac{1}{2}$N	Na	Saponite	$0.17Na(Mg_3)(Si_{3.83}Al_{0.17})O_{10}(OH)_2$
c	N	Na	Beidellite	$0.33Na(Al_2)(Si_{3.66}Al_{0.33})O_{10}(OH)_2$
d	N	Na	Saponite	$0.33Na(Mg_3)(Si_{3.66}Al_{0.33})O_{10}(OH)_2$
e	85†	Na	Montmorillonite	—
f	2N	Na	Beidellite	$0.66Na(Al_2)(Si_{3.33}Al_{0.66})O_{10}(OH)_2$
g	2N	Na	Saponite	$0.66Na(Mg_3)(Si_{3.33}Al_{0.66})O_{10}(OH)_2$
h	2.5N	Na	Beidellite	$0.83Na(Al_2)(Si_{3.17}Al_{0.83})O_{10}(OH)_2$
i	N	Ca	Beidellite	$0.17Ca(Al_2)(Si_{3.66}Al_{0.33})O_{10}(OH)_2$
j	N	Ca	Saponite	$0.17Ca(Mg_3)(Si_{3.66}Al_{0.33})O_{10}(OH)_2$
k	109*	Ca	Saponite	$0.25Ca(Mg_{2.92})(Si_{3.5}Al_{0.5})O_{10}(OH)_2$
l	85†	Ca	Montmorillonite	—
m	2N	Ca	Beidellite	$0.33Ca(Al_2)(Si_{3.33}Al_{0.66})O_{10}(OH)_2$
n	2N	Ca	Saponite	$0.33Ca(Mg_3)(Si_{3.33}Al_{0.66})O_{10}(OH)_2$
o	N	Mg	Beidellite	$0.17Mg(Al_2)(Si_{3.66}Al_{0.33})O_{10}(OH)_2$
p	109*	Na/Ca	Saponite	—

* Natural specimen from Allt Ribhein, Fiskavaig Bay, Skye, Scotland. Mackenzie (1957) Ex. Cap. in meq/100 gms., originally Ca saturated.

† Natural specimen of purified Wyoming Bentonite supplied by the National Lead Company, Houston, Texas. Ex Cap. in meq/100 gms. measured by Dr. M. Rustom.

APPARATUS

A North American Philips Wide Range X-ray diffractometer was used to examine the specimens. The radiation shield covering the specimen was modified to contain a variable humidity atmosphere by lining the slot through which the x-ray beam passes with aluminum foil. The end of the shield was provided with tapped holes and tubes for the entrance and exit of the humid air.

The humidity of the air was controlled by splitting the incoming air from the compressed air line into two streams, one of which was dried by passage through "Drierite" and "Anhydrone" columns, and the other was completely saturated by passing it through four vessels containing

distilled water. The two streams were then remixed in proportions giving the approximate relative humidity required and passed through a saturated salt solution. The salt solution modified the humidity to correspond to that of its water vapor pressure, which was accurately known (O'Brien, 1948). Details of the solutions used are given in Table II.

The relative humidity was measured by means of wet and dry thermocouples connected differentially so that the difference in e.m.f. caused by the difference in temperature between them was measured directly with a potentiometer. The thermocouples were made from 32 B.S.

TABLE II. RELATIVE HUMIDITIES GIVEN BY THE
SATURATED SALT SOLUTIONS*

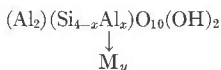|	R.H. at 20° C. (%)	R.H. at 25° C. (%)	R.H. at 30° C. (%)
Distilled Water	100	100	100
NH_4Cl	80	79	78
$NaNO_2$	—	66	—
$Ca(NO_3)_2.4H_2O$	56	51	46
$K_2CO_3.2H_2O$	44	43	—
$MgCl_2.6H_2O$	33	33	32
K. Acetate	20	19	—
H_2SO_4 (Sp. Gr. 1.570 gms/cc)	—	11	—
Anhydrone	0	0	0

* O'Brien (1948).

gauge nichrome and constantan wires giving an e.m.f. of 1mV/22.4° C. The wet junction was wound with thin cotton thread kept wet by immersing a part of its length in distilled water. The two thermocouples were mounted in a 4 mm. I.D. glass tube through which the humid air flowed. In this manner a high air velocity at the thermocouple junctions was maintained and the correct differential temperature produced.

The weight loss against humidity relations were obtained by means of a fused silica spring balance enclosed in a glass tube through which the humid air was passed. The extension of the spiral was measured with a cathetometer. No means of heating the tube was provided so that the specimen had to be removed and heated in a furnace to obtain the weight loss between 0% R.H. and heating to 350° C. This method was not satisfactory since it was suspected that the specimens absorb water very quickly from the atmosphere and also the chances of losing small portions of the sample during transference between the spiral and the furnace and back again were quite high.
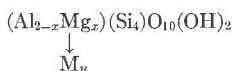
SPECIMENS EXAMINED AND NOMENCLATURE

The general formula for the beidellites is:

$$(Al_2)(Si_{4-x}Al_x)O_{10}(OH)_2$$
$$\downarrow$$
$$M_y$$

for the saponites:

$$(Mg_3)(Si_{4-x}Al_x)O_{10}(OH)_2$$
$$\downarrow$$
$$M_y$$
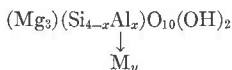
and for the montmorillonites:

$$(Al_{2-x}Mg_x)(Si_4)O_{10}(OH)_2$$
$$\downarrow$$
$$M_y$$

Here M is the exchangeable cation, and $y = x$ if M is monovalent and $y = x/2$ if M is divalent. For most natural montmorillonoids $x \simeq 0.33$ and in this paper, synthetic specimens with this amount of substitution are designated N (normal) montmorillonoids. Similarly specimens with $x = 0.17$ and $x = 0.67$ are designated N/2 and 2N respectively.

RESULTS

The results are summarized in graphical form in Fig. 1. In Figs. $1a–1p$ a full line represents a hydrate, which gives sharp x-ray reflections and integral orders of reflection. The full lines are drawn through points representing an average lattice spacing derived from all the integral basal reflections. Where two full lines cover the same range of relative humidity at different spacings the two hydrates exist at the same humidity as mixed crystals with little or no mixed layering. The broken lines indicate mixed layer formation of the two hydrates on either side of the broken lines. The broken lines are drawn through points representing the positions of the 001 reflections. The mixed-layer regions do not appear to be pure mixed-layers but in most cases show some mixed crystal nature as indicated by the partial resolution of the diffuse mixed-layer peaks.

Specimens $a–p$ are represented in Figs. $1a–1p$ respectively.

Specimen b, Fig. $1b$, was very poorly crystallized and only the 001 reflection could be detected. The results from this specimen were neglected in arriving at the final conclusions.

Figure $1c$ represents a mean of three samples, the results agreeing with each other. Two of the samples were made in different hydrothermal syntheses and since they are identical in characteristics the syntheses can be considered consistent. The third specimen was produced by re-
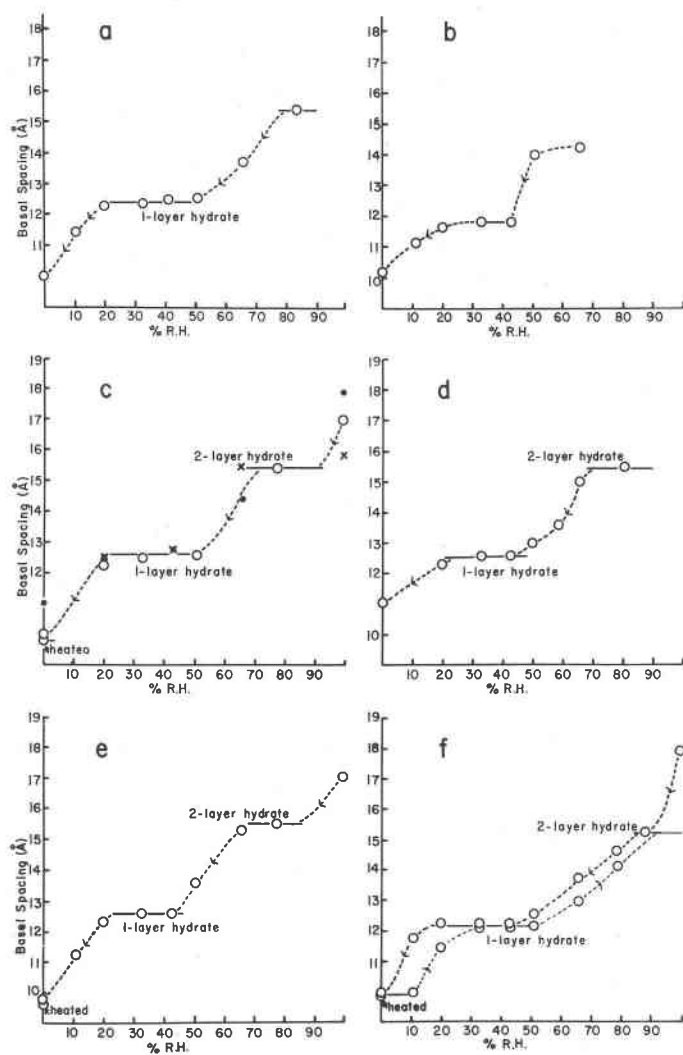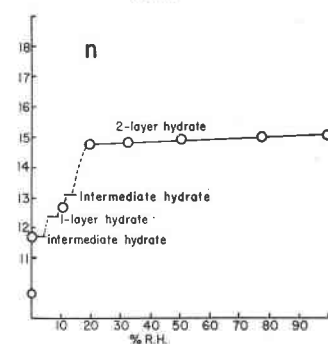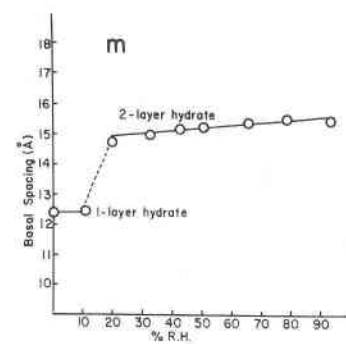
FIG. 1. 1a–1p Basal spacing—Relative humidity relations (R.H.). a) N/2 Beidellite. b) N/2 Na Saponite. c) N Na Beidellite. d) N Na Saponite. e) Nat. Na Montmorillonite. f) 2N Na Beidellite. g) 2N Na Saponite. h) 2.5N Na Beidellite. i) N Ca Beidellite. j) N Ca Saponite. k) Nat. Ca Saponite. l) Nat. Ca Montmorillonite. m) 2N Ca Beidellite. n) 2N Ca Saponite. o) N Mg Beidellite. p) Mixed Na-Ca Saponite. 1q–1r Weight loss—relative humidity relations. q) 2N Na Saponite. r) 2N Ca Saponite.

Panel g: Basal Spacing (Å) vs % R.H. — labels "2-layer hydrate", "1-layer hydrate", "heated"

Panel h: Basal Spacing (Å) vs % R.H. — labels "2-layer hydrate", "1-layer hydrate"

Panel i: Basal Spacing (Å) vs % R.H. — labels "3-layer hydrate", "2-layer hydrate", "heated"

Panel j: Basal Spacing (Å) vs % R.H. — label "2-layer hydrate"

Panel k: Basal Spacing (Å) vs % R.H. — labels "3-layer hydrate", "2-layer hydrate", "intermediate hydrate", "1-layer hydrate", "intermediate hydrate", "heated"

Panel l: Basal Spacing (Å) vs % R.H. — label "2-layer hydrate"

Panel m: Basal Spacing (Å) vs % R.H. — labels "2-layer hydrate", "1-layer hydrate"

Panel n: Basal Spacing (Å) vs % R.H. — labels "2-layer hydrate", "intermediate hydrate", "1-layer hydrate", "intermediate hydrate"

saturation of one of these samples with Na. This specimen is identical with the others and therefore it can be stated that the hydrothermal specimens as produced are fully saturated with sodium ions.

Specimen g (Fig. 1g) appears to be anomalous. It is extremely well crystallized compared with the other synthetic specimens, the hydration and dehydration curves are very sharp, yet the stability ranges of the hydrates do not agree well with those of the other Na saturated samples

Figure 1i shows a curve derived from a mean of two samples. One was a N.Ca beidellite synthesized as such and the other was a N.Ca beidellite prepared as a N.Na beidellite and resaturated by treatment with 1M. CaCl$_2$. The two curves are identical except for the region below 20% R.H. Here the re-saturated sample will not collapse to a basal spacing below about 13 Å, even after heating to 350° C. The N.Mg beidellite sample, o (Fig. 1o), shows a similar effect. These two were treated with 1M. CaCl$_2$ and 1M. MgCl$_2$ solutions of unadjusted pH. The rest of the samples were treated with solutions of pH 4.5–5.0. It is conceivable that under higher pH conditions, some precipitation of CaCl$^+$, Ca(OH)$^+$, MgCl$^+$, or Mg(OH)$^+$, occurred between the montmorillonite layers which prevented the collapse of the structure.

Figure 1l (specimen l) is labelled Natural Ca montmorillonite, but

the appearance of the diagram suggests a mixture of cations rather than pure Ca. A similar effect is illustrated in Fig. 1p. The central curve on the diagram is given by a sample in which an attempt was made to replace Ca with Na as the interlayer cation. The upper curve is that given by the original Ca saponite, while the lower curve is typical of a specimen completely saturated with Na. It is obvious that the center curve is a combination of the other two and that the substitution of Na for Ca is incomplete.

Considered generally, the x-ray diagrams show a trend for the degree of crystallinity to increase with an increasing amount of lattice substitution (x); this is shown by the intensity and sharpness of the reflections in the x-ray patterns. Another general feature of the patterns is a fairly diffuse region of scattering occurring at a spacing corresponding to 2 d_{001}. This is an effect produced by the specimens and not by the equipment since it moves as the 001 reflection moves, always obeying the above condition.

All the specimens were examined under conditions of decreasing humidity; some were also examined under increasing humidity conditions. These few specimens showed varying degrees of "hysteresis" in the mixed-layer portions of the curves, but this does not affect the spacing of the hydrates.

None of the specimens examined will dehydrate completely in dry air but require to be heated to 350° C. Even at this temperature some of the specimens do not collapse completely (to below 10 Å). All the specimens can be rehydrated after heating to this temperature.

On further comparing the results it can be seen immediately that the factor producing the greatest change in the hydration characteristics is the valence of the interlayer (exchangeable) cation. The amount of lattice substitution (x) and the composition (whether the specimen is saponite, beidellite or montmorillonite) have relatively minor effects.

The main features of the diagrams given by the Na saturated specimens are the two hydrates of basal spacings about 12.3 Å and 15.5 Å. The former is stable between relative humidities of about 15 and 50% and the latter stable between about 70 and 95%. The Ca specimens show hydrates with the same spacings but the first hydrate of 12.3 Å has a very small stability range at about 5% relative humidity, while the second hydrate of spacing 15.5 Å has a wide stability range extending from about 35% R.H. to about 100% R.H. In both the Na and Ca specimens there is evidence to show that a further hydrate exists at about 18 Å, but 100% R.H. is not sufficient water vapor pressure to produce this hydrate in a pure form but only in a mixed-layer or mixed crystal form with the 15.5 Å hydrate.

A closer examination of the finer details of the diagrams given by the

Na saturated samples reveals a possible significant trend in the spacing of the first hydrate (12.3 Å). The N/2 and 2N beidellites and saponites give spacings of 12.3 Å for this hydrate whilst the N. synthetic and the natural specimens give spacings of 12.6 Å indicating that a maximum occurs in the lattice spacing–exchange capacity relation at the exchange capacity usually associated with natural specimens. Another trend, less clearly defined, exists in regard to the range and position of the second hydrate of the Na beidellites, as shown in Table III.

The second hydrate of the Ca saturated specimens shows clearly in most cases a continuous decrease in spacing from about 15.5 Å to 15.0 Å

TABLE III. A Possibly Significant Trend in the Range and Position of the Second Hydrate of the Sodium Beidellite in Regard to Humidity

Amount of substitution	Lower humidity limit	Higher humidity limit
$\frac{1}{2}$N	80	90
N	80	95
2 N	90	92
$2\frac{1}{2}$N	100	—

with decrease in relative humidity. The decrease takes place without any observable amount of mixed layering. This effect is easily seen in this case because this particular hydrate has a wide range of stability. It may exist for the other hydrates, but if so it cannot be observed since their range of stability is too small. There is a tendency for the second hydrate (15.5 Å) of the Ca specimens to produce a two phase mixture with the third hydrate (18.0 Å) and not mixed layers. This is noticeable in all the Ca saturated specimens except those where the third hydrate does not appear. The same effect does not occur with the Na saturated specimens.

Specimens k and p show the normal Ca-saturated specimen x-ray diagrams, but careful analysis of the diagrams shows that in addition to the two usual hydrates there are another two occurring at about 0 and 15% R.H. with very small ranges of stability. These have spacings of 11.7 Å and 13.1 Å respectively. It is possible that these two hydrates occur in some other specimens but are difficult to recognize because of their extremely small stability range and the poorer crystallinity of most of the other samples.

The exchange capacity of most of the synthetic samples has been measured (Koizumi and Roy, 1959) using x-ray fluorescence to determine the amount of Mn absorbed into the exchange positions. The results were checked by using the same method on three specimens of previously

determined exchange capacity. The results determined by these methods are always lower than the values given by other methods (Table IV) but this does not detract from the results reported herein.

The weight loss curves shown in Figs. 1q and 1r are not completely satisfactory from a quantitative aspect due to the impossibility of heating the specimen in the present apparatus to determine the amount of water still present in the specimen at 0% R.H. Qualitatively, however, the break in the curve given by the Ca specimen (Fig. 1r) at 20% R. H. indicates a discontinuity in the rate of water desorption when the

TABLE IV. EXCHANGE CAPACITIES OF THE SPECIMENS EXAMINED

No.	Theoretical* meq/100 gms.	Measured, meq/100 gms.	Measured by other methods, meq/100 gms.
a	45	33	—
b	45	33	—
c and i	90	75	—
d and j	90	80	—
k	—	—	109
e and l	—	—	85
f and m	179	107	—
g and n	179	127	—
h	225	—	—
Calibration			
Kaolinite (Lustra Clay) RS-286	2	—	
Hectorite (National Lead Co.)	75	83	
Montmorillonite Clay (F.C.B.)	116	133	

* Calculated from the formulae.

lower stability limit of a hydrate is reached. The Na curve (Fig. 1q) may show a similar effect, less pronounced, since the stability range of the hydrates is smaller.

DISCUSSION

Of the specimens examined it can be seen that the saturating cation has the predominant effect in determining the dehydration characteristics. The montmorillonoid layer composition and amount of substitution (x) have comparatively small effects.

The composition of the 2N synthetic saponite is approaching that of a natural vermiculite and it is instructive to compare this specimen with vermiculite studied by Walker (1955). The hydrates described by Walker for vermiculite are given in Table V. The third column indicates the difference between the first two and is about $+0.7$ Å. Walker describes

TABLE V. THE HYDRATES OF Mg-VERMICULITE (WALKER, 1955) COMPARED
WITH THOSE OF N AND NATURAL Ca SAPONITES

Mg-Vermiculite hydrates (Å)	Ca-Saponite hydrates (Å)	Difference
14.81	15.5	+0.7
14.36	15.0	+0.6
13.82	13.1	−0.7
11.59	12.4	+0.8
20.6	11.7	—
9.02	9.8	+0.8

the decrease between 14.81 and 14.36 Å as being continuous and this also is observed in the saponite which decreases from 15.5 to 15.0 Å in a continuous manner. The 15.5 Å spacing of the saponite is thought to be the 2-layer hydrate corresponding to the formula

$$(Mg_3)(Si_{3.66}Al_{0.33})O_{10}(OH_2) \cdot 6H_2O$$
$$\downarrow$$
$$Na_{0.33}$$
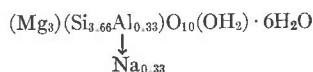
and the 15.0 Å spacing would correspond to the same formula containing $4H_2O$. The spacings 13.82 Å and 13.1 Å do not correspond but this may be because a *Mg* vermiculite is being compared with a *Ca* saponite, and according to Walker the transition between the 14.36 Å and 13.82 Å hydrate involves a movement of the cation from a position midway between the layers to a position adjacent to the layers. The 12.4 Å saponite hydrate corresponds closely in spacing to the 11.59 Å vermiculite hydrate and probably is the 1 water-layer hydrate ($3H_2O$) in the saponite as well as in the vermiculite. The 20.6 Å sequence in vermiculite is caused by regular mixed layering of the 11.59 and 9.02 Å hydrates, which is not the case with the saponite which gives a 11.7 Å spacing. Rowlands, Weiss and Bradley (1955) have also observed this hydrate in Ca montmorillonite and one of their explanations for it is that it corresponds to the same water content and structure as the 1 water-layer hydrate of vermiculite which is already accounted for herein. The other is that "inverted" Si-O tetrahedra eixist as in the Edelman-Favejee (1940) type montmorillonite structure. Insufficient work has been done in the present investigation either to confirm or to deny this supposition.

The variation of the 12.4 Å hydrate spacing of the sodium saturated specimens with the amount of substitution (x) is interesting. Since the N-synthetic and natural specimens appear to have the maximum spacing, this variation may be connected with the usual occurrence of natural montmorillonoids with near "normal" amounts of substitution. This

implies that a montmorillonoid with this amount of substitution is slightly more stable than montmorillonoids with either less or more substitution, that is, one with a lower free energy. Koizumi and Roy (1959) also indicated that the N specimens are more thermally stable than the N/2 and 2N specimens. If this is the case, then the maximum in the basal-spacing composition curve will correspond to a minimum in the free energy-composition curve. If we consider the number of interlayer cations increasing from zero, as in a pyrophyllite or talc type structure, the first few cations will probably expand the structure very little from the pyrophyllite or talc spacing, the layers being distorted around the cation positions. As more cations are introduced, more and more distortions will occur giving rise to poor crystallinity as is observed in the N/2 specimens examined. As the composition approaches "normal" a sufficient number of cations ($\frac{1}{3}$ of the number in a mica) and associated water molecules are present to extend the layers completely without appreciable distortion. This type of structure will presumably have a lower free energy than the distorted type of structure.

The addition of further cations causes an increase in the bonding between the layers and they are drawn closer together so decreasing the spacing. The increase in bonding will increase the difficulty of water penetrating between the layers and also increase the work necessary to produce hydration. This tendency can be seen in the higher humidity necessary to produce the second hydrate of the Na beidellites as the amount of substitution increases (Table III). The increase in the work required to obtain hydration would cause another increase in free energy of the specimens. Thus we have the minimum between this increase, and the increase due to the distortions introduced by too few interlayer cations which could account for the "normal" nature of natural montmorillonoids.

The spacing-humidity curves given by the Na-saturated and by the Ca-saturated specimens agree qualitatively with the % water absorbed-humidity curves. Due to the uncertainty of the absolute scale of the % water absorbed it is uncertain how much water is present in the different hydrates. It is possible however to state that the amount of water present (30% water corresponds to $9H_2O$/formula unit) in the 2-layer hydrates ($6H_2O$) of the Ca-saturated specimens at the higher humidities at which it is stable is more than can be accommodated between the layers having regard to the basal spacing. This gives rise to a consideration of the surface of the specimens. By measuring the x-ray reflection broadening of the montmorillonoid basal peaks an approximate crystal thickness can be obtained, assuming no other source of broadening. For the best crystallized specimens this is of the order of 100–200 Å or about 10 unit cell

heights. In such a crystal there will be 9 interlayers containing 2-water layers each and 2 outer surfaces with an unspecified number of absorbed water layers. This unspecified number would not have to become larger than about 3 or 4 before the adsorbed surface water becomes a very appreciable part of the total water measured by weight loss determinations. This effect could account for the surplus water apparently associated with the 2-layer Ca hydrate. It would also complicate any more accurate $\%$ water absorbed-humidity data.

The diffuse scattering band noticeable in most of the specimens, and corresponding to $2d_{001}$ can be explained only by supposing that there is some 2-layer nature in the stacking of the layers. This could be due either to a tendency to form two types of montmorillonite layers which then alternate, or (what is more likely) to hydration tending to take place in alternate layers.

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