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X-Ray Diffraction Aspects of Montmorillonites

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Abstract

The breadth and position of the basal X-ray diffraction maxima were analyzed for nine montmorillonites and hectorite. Some samples were size-fractionated and all were subsequently treated with ethylene glycol and/or heated to 450°C. None of the samples gave a rational series of orders, a result believed to be due to the thinness of the particles among other factors. The apparent particle thicknesses decreased with sedimentation size fraction and decreased following treatment of the clay suspensions with an ultrasonic probe. The identity of the interlayer cation made no change in the particle thicknesses. Wyoming montmorillonites contained on the average more silicate layers per particle (N) than did the others. Surface glycol appeared to contribute less to the diffraction pattern than the glycol bounded on both sides by silicate layers. With one exception the glycol-treated clays gave N values smaller than those obtained from the same clays that had been heat-treated. This result may be caused by incomplete penetration of the glycol molecules between silicate layers and consequent interstratification, or to some other factor that resulted in relatively broad reflections from the glycol-treated clays. The heat-treated clays are believed, therefore, to provide a more reliable estimate of N than the organic-treated clays.

Theoretical analyses were made of the extent of irrationality of the basal orders of diffraction as a function of particle thinness and layer structure factor. The overall agreement of the experimental and theoretical data was not impressive. The apparent lack of agreement was partially due to the chemical variations among the clays and may reflect individual differences which were not accounted for in the theoretical computations, *e.g.*, size distribution or interstratification.

Introduction

Ross (1968) and Reynolds (1968) have shown theoretically that the apparent spacings of finite particles deviate from the true values as the particles become thin. The true spacings are those that would be exhibited by a large crystal containing many unit cells. The variations in spacing are such that a sequence of basal reflections may be irrational owing to particle thinness. The direction of the spacing shift and its magnitude depends on the nature of the crystal surface (Tettenhorst and Reynolds, 1971) among other factors.

Ross (1968) compared experimental data with theoretical predictions for graphite, and Reynolds (1968) did likewise for illite. The comparisons showed that spacing deviations could be reasonably accounted for by thin particles. These investigators reiterated that irrational spacings could result from factors other than particle thinness such as layer disorder or interstratification.

The main objective of this study was to determine if a relationship existed between particle thickness and basal X-ray spacings for montmorillonites, and to provide an overall view of the group which might suggest future lines of investigation. Montmorillonites were chosen for the following reasons: (1) A series of size-fractionated samples that were characterized by other methods were available (Roberson, Weir and Woods, 1968). (2) Montmorillonites likely were composed of particles containing fewer layers (unit cells) than the substances studied previously. Smaller particles would provide larger spacing shifts which might prove easier to measure experimentally. (3) Montmorillonites have large repeat distances especially when complexed with organic compounds and, therefore, basal spacings that occur at small diffraction angles. Spacing shifts are relatively more

TABLE 1. MONTMORILLONITES STUDIED

Name	Size fraction (μ)	Designation	Reference*
Fayette (Na)	0.1-0.5	F_3	RWW
"	0.05-0.1	F_2	RWW
"	< 0.05	F_1	RWW
Fayette (Ca)	< 0.05	CaF_1	RWW
Upton (Na)	0.1-0.5	U_3	RWW
"	0.05-0.1	U_2	RWW
"	< 0.05	U_1	RWW
Chambers (Na)	< 0.1	C	RWW
Mowry (Na)	0.1-0.5	M	RWW
Camp Berteaux (Na)	< 2	CB	W
Otay	< 2	O	GK
Polkville	< 2	P	GK
Hector	< 2	H	GK
Santa Rita	< 2	SR	API
Volclay	< 2	V	---

* Chemical analyses, structural formulas and other details may be found in the following: (RWW) Roberson, Weir and Woods (1968); (W) Weir (1965); (GK) Grim and Kulbicki (1961); (API) American Petroleum Institute Project 49 (1950).

pronounced at small diffraction angles. (4) No large-scale study of particle thickness of montmorillonites appears to have been carried out.

The montmorillonites investigated are listed in Table 1 along with the designations used in this report. The main interlayer cation is indicated for those clays subjected to ion exchange prior to this X-ray study. All of the clays are dioctahedral aluminous montmorillonites except hectorite. The Hector, Volclay, Mowry, Upton, and Fayette clays have relatively low layer charges, the Otay and Chambers clays have relatively high layer charges, and the remaining montmorillonites (Camp Berteaux, Polkville, and Santa Rita) have medium layer charges. The Mowry clay is the same as that named "Crook" by Roberson, Weir and Woods (1968). The Otay, Hector, Polkville and Santa Rita clays were obtained from Wards, Inc., and none of these was subjected to an ion exchange pretreatment. Otay, Hector and Volclay are presumed to be mainly sodium-saturated naturally. The Polkville and Santa Rita clays are presumed to be mainly calcium-saturated. The size fractions indicated in Table 1 for Otay, Polkville, Hector, Santa Rita, and Volclay are approximate. The fraction used for these X-ray studies was obtained by taking the material that remained in suspension following settling in water for 24 hours.

TABLE 2. ABSOLUTE MAXIMUM AND AVERAGE DEVIATIONS FROM MEAN POSITION AND BREADTH VALUES FROM REPLICATE EXPERIMENTS IN DEGREES TWO THETA

	GLYCOL-TREATED	
Order	Positions	Breadths
001	0.03 (M, F_2)	0.05 (F_2)
002	.03 (M, F_2)	.03 (F_2, H, SR)
003	.04 (M)	.04 (F_3, H, P)
005	.06 (F_2)	.04 (O)
Average	0.012	0.015
	HEATED TO 450°C	
Order	Positions	Breadths
001	0.04 (CaF_1)	0.06 (SR)
002	.06 (CaF_1)	.07 (H)
003	.05 (CaF_1)	.06 (H, P)
Average	0.015	0.021

Experimental

X-ray

The X-ray data were taken on a Philips high-angle diffractometer equipped with a geiger detector. The goniometer was aligned carefully and calibrated with a sample of powdered semi-conductor-pure silicon metal. The positions of the (001) reflections from a permanently-mounted small muscovite flake were calibrated with the silicon reflections. The low angle peaks from the muscovite were used as an external standard to calibrate the positions of the clay maxima throughout the diffraction analyses. The clay maxima were scanned automatically at a rate of one-quarter degree 2θ/min. A significant portion of the background was included on either side of the peaks. A correction suggested by Warren and Bodenstein (1965) was made for steeply sloping background on non-Wyoming montmorillonites to determine the position of the (002) peak of the ethylene glycol-treated clays and the (001) peak of the samples heated to 450°C. The correction was never more than 0.03° two theta.

Other X-ray conditions were: Ni-filtered CuKα radiation, 1° divergence and anti-scatter slits, 0.006″ receiving slit, 30 inches per hour chart speed, and a time constant of 4. Peak positions and breadths were measured to the nearest 0.01° two theta. A strip of scotch tape was placed over the slot in the scatter shield to provide an enclosed chamber. The linear range of the detector was determined to be about 480 cps for the lowest tube potential used so the scale factor settings were fixed to provide a maximum on-scale reading of 400 cps. The power settings (Kv and ma) were adjusted for all maxima to keep them on scale but as large as possible, in order to reduce errors in measurement.

Clays

The diffraction conditions and the clay specimen dimensions were designed to minimize errors in positions and breadths of X-ray maxima inherent in the method of analysis. Montmorillonite specimens were prepared by evaporating dilute suspensions onto glass slides. The mounts were made as thin as possible to avoid errors caused by sample transparency with specimens whose absorption coefficient is low. Most mounts were about 0.001" thick or less as measured by a micrometer. The length of the samples parallel to the X-ray beam was about 25 mm. A specimen length of 25 mm allows for an error in line positions owing to the flat specimen aberration of not more than about 0.02°2θ over the entire range of diffraction angles we studied. The length and thickness were sufficient to provide data that were reasonably reproducible (Table 2) within the limits of the power settings for the X-ray tube.

One set of slides was treated with excess liquid ethylene glycol and maintained in an enclosed chamber containing additional free liquid glycol, all of which was placed in an oven at 60°C. for at least several days. An initial attempt to obtain montmorillonite-glycol data by employing the vapor pressure complexing method gave non-reproducible results and was discontinued. The first, second, third, and fifth order basal reflections were scanned. The first order reflection was then rescanned as a check on any possible deterioration of the complexes during X-ray analysis. Some specimens were X-rayed periodically up to two months after the initial complex was made with no apparent change in the diffraction patterns. Ocassionally higher orders of diffraction were scanned for the well-oriented samples, usually the Wyoming clays and the very fine-grained fractions of the others. The samples were scanned while they were slightly moist with glycol.

Another set of slides was heated overnight to 450°C. Drierite was placed in the X-ray chamber to deter rehydration during the scan. The first, second and third basal orders were scanned and the first order was rerun as a check. It was hoped to use the same slides for the heating experiments that were glycol-treated. This was not possible as these slides when heated gave non-reproducible results probably because of retention of variable amounts of glycol. This was so regardless of many attempts to rid the clay of the sorbed glycol by such means as standing under ambient conditions for long periods, passing dry air over them, or preheating to modest temperatures prior to firing at 450°C. Heating to temperatures below 450°C. gave poorer reproducibility probably because of incomplete dehydration. One such specimen (hectorite heated to 200°C.) is included for comparison in Figure 4. Heating to temperatures greater than 450°C. was not investigated because of possible dehydroxylation and the consequent expansion perpendicular to the layers (Bradley and Grim, 1951) which would complicate interpretation of the results. Unfortunately some of the fractionated clays which were glycol-treated were not available for the heating studies.

Results

Experimental

The breadths of all maxima were measured at half-maximum intensity and the two theta positions were determined as the midpoint of the chord drawn at half-maximum intensity. The fractionated Upton and Fayette glycol-treated clay data represent the mean taken on three separate specimens. All other data represent the average of two runs on separate mounts. Maximum individual and overall average deviations from the final mean position and breadth values from the replicate analyses are in Table 2. The average deviations from the mean values were about the same as the experimental error in estab-

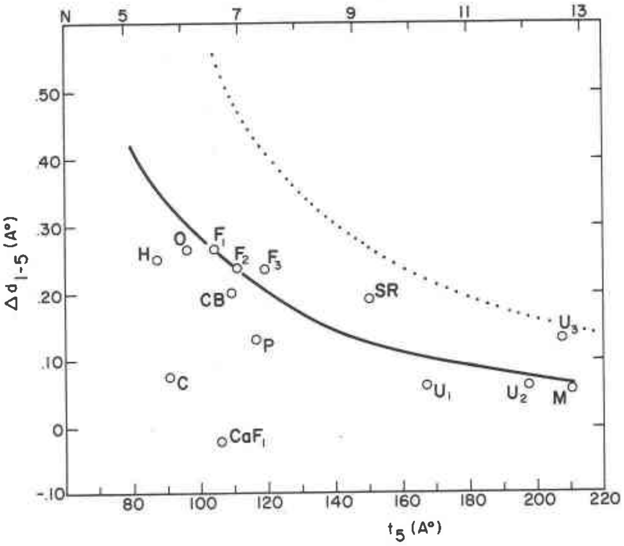

FIG. 1. Apparent spacings of (001) for montmorillonite-ethylene glycol complexes versus particle thickness. Open circles represent experimental data, curves represent computed data. Solid curve is for particles terminating on basal oxygen clay surfaces; dotted curve is for particles terminating on glycol molecules.

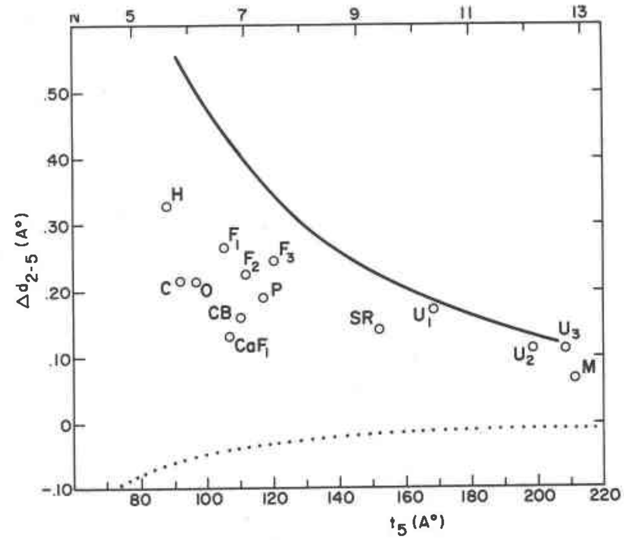

FIG. 2. Apparent spacings of (002) for montmorillonite ethylene glycol complexes versus particle thickness.

lishing the two theta values. The glycol-treated clays gave somewhat more reproducible results. The method chosen to represent the data in the figures was based on the following considerations.

Three facts were apparent in the data: (1) Regardless of pretreatment *none* of the montmorillonites showed an integral or rational series of basal reflections. (Complexes with other organic compounds, *e.g.*, tetraethylene glycol dimethyl ether, also gave irrational series of orders with these montmorillonites.) (2) The basal repeat distances were not identical from clay to clay. (3) The widths of the maxima were not identical from clay to clay, nor were they identical for a given clay. With respect to the last observation no consistent relationship was found between breadths and diffraction angle, *i.e.*, cos θ or tan θ.

The layer structure factor is rather constant in the region of the (005) montmorillonite-glycol maximum and the (003) collapsed montmorillonite maximum. This suggested that these two reflections were best suited among those studied to serve the following dual purpose: (1) The *breadths* of these reflections were a measure of the particle thickness, *i.e.*, the mean distance perpendicular to the layers and, thereby, the number of layers per particle (N). (2) The *positions* of these maxima were relatively unaffected by the thinness of the particles, overall chemical composition, or the specific nature of the particle's surface and, therefore, were a measure of the thickness of the unit layer. The extent of the irrationality of the basal reflections was determined by subtracting these latter unit layer thickness values from those apparent layer thicknesses determined from other reflections whose positions were affected by the number of layers per particle.

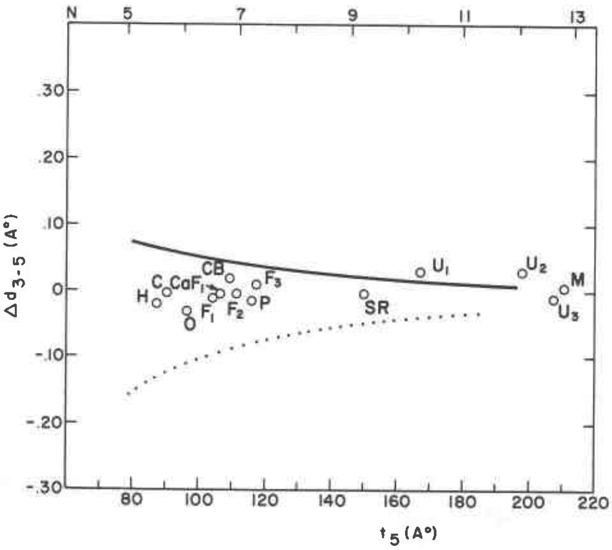

FIG. 3. Apparent spacings of (003) for montmorillonite-ethylene glycol complexes versus particle thickness.

The experimental data are plotted as open circles in Figures 1–4. Figures 1–3 represent a summary of the clay-glycol data and Figure 4 represents the data from the heating experiments. The ordinate in the figures represents a d-spacing difference, *e.g.*, in Figure 2

$$\Delta d_{2-5} = 2 \times d(002) - 5 \times d(005).$$

The horizontal coordinate of the data points in the figures is particle thickness derived from the Scherrer equation using a constant of 0.9. The widths of the diffraction maxima from a small muscovite flake were used as a measure of the instrumental broadening (b). The observed diffraction widths (B) were converted into pure diffraction breadths (β) by means of the relationship $\beta^2 = B^2 - b^2$. The particle thicknesses for the clay-glycol data (t_5) were obtained from the measured breadths of (005), the particle thicknesses of the fired clays (t_3) were derived from (003).

The basal repeat distances of the glycol-treated clays ranged from 16.72 Å for Otay to 17.03 Å for Mowry. The basal spacings were somewhat less for the high layer-charge clays complexed with ethylene glycol. The Ca-Fayette clay gave a basal repeat of 16.88 Å which is close to that determined for a Ca-Wyoming clay (16.86 Å) by Reynolds (1965). The effect of the layer charge was not evident on the heated clays. All of the Na-clays had collapsed spacings of about 9.6 Å.

Larger-valence interlayer cations decreased the basal spacings of both the glycol-treated and heated clays. For example, the glycol-treated Na-Fayette and Ca–Fayette clays in the same size fraction had spacings of 16.95 and 16.88 Å respectively. The Fayette montmorillonites heated to 450°C had spacings of 9.60 Å for Na–clay and 9.47 Å for the Ca–clay.

Additional observations from the experimental data were made. (1) The particle thicknesses of the fractionated Upton and Fayette clays (*e.g.*, Fig. 1) decreased with sedimentation size fraction. A larger difference was indicated between the particle thicknesses of very fine and fine Upton (U_1 and U_2) than between very fine and fine Fayette (F_1 and F_2).

(2) The particle thickness of the very fine Na- and Ca-Fayette clays were virtually identical. (3) The medium size fractions of Fayette and Upton (F_3 and U_3) were additionally pretreated for 5–10 minutes with an ultrasonic probe. The Δd and breadth values obtained from the probe-treated samples, both heated and glycol-treated, were similar to those values obtained from the non-probe-treated very fine size fractions, F_1 and U_1, respectively. (4) The data from the glycol-treated clays was more scattered than that from the heated clays. (5) All of the heated clays except Santa Rita had larger N values than their glycol-treated counterparts. (6) The particle thicknesses of the heated clays fell into two groups. The Wyoming clays were thicker and had about 13–14 layers per particle, all others had $N = 8$ except Camp Berteaux ($N = 10$). Mering (1946) deduced the same N for this latter clay.

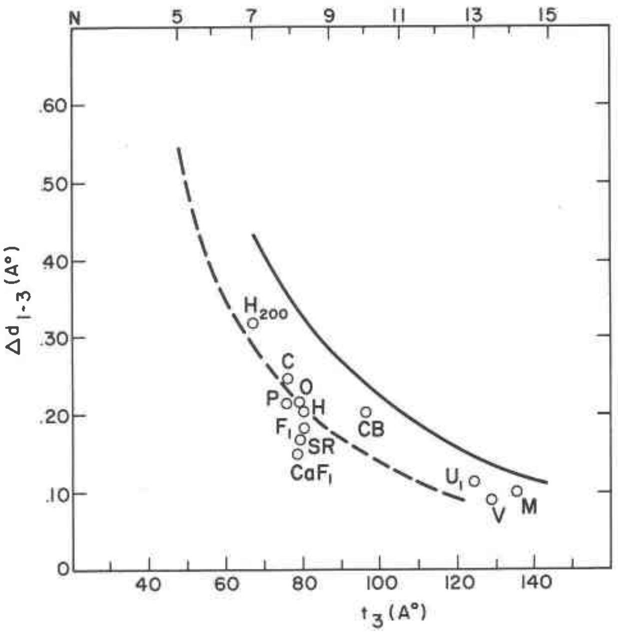

FIG. 4. Apparent spacings of (001) for montmorillonites heated to 450°C versus particle thickness. Solid curve is for an all-aluminum octahedral composition; dashed curve is for an all-iron octahedral composition.

Theoretical

Known variations in chemical composition of the clays plus the scatter in the diffraction data, as shown in Figures 1–4, precluded an attempt to account for all of the experimental data points by means of a single theoretical curve. Nevertheless, it seemed desirable to compute and plot a theoretical relationship (irrationality of basal orders versus N) based on a minimum number of assumptions to which the experimental data could be referred and discussed. A computer program was written to calculate the X-ray diffracted intensity from montmorillonites along the c^* direction. The program allowed for variations in layer structure factor (true d-spacing, chemical composition, atomic positions, temperature factors) and N. Computations were made for CuKα radiation and ranged from 4–32° 2θ in 0.01° 2θ increments. The powder Lorentz-polarization factor was used throughout and the origin of all of the layer repeat units was the octahedral sheet. The powder Lp factor was employed to be consistent with the findings of other investigators (*e.g.*, Reynolds, 1965). However, use of the single crystal Lp factor did not change the positions of computed maxima by more than 0.01° 2θ. The breadths and positions of maxima were determined from computed patterns in the same manner as was done for the experimental data.

The structures and temperature factors assumed for the clay-glycol complexes were those proposed by Reynolds (1965), with the following exceptions: The true d-spacing was 16.90 Å, the silicate layer was dioctahedral with aluminum as the cation and the interlayer cation was sodium and its position was fixed midway between adjacent silicate layers. The model used to compute the theoretical relationship for the heated clays was identical to that just described except that water and glycol molecules were omitted from the interlayer region and the true d-spacing was taken as 9.60 Å. Two models were used for the clay-glycol system; one model represented by the dotted curves (Figures 1–3) assumed double layers of glycol molecules (plus water and cations) between adjacent silicate layers with a single layer of glycol (plus water and cations) at the ends of the particles; the second model represented by the solid curves in Figures 1–3 was identical to the first model except that the single glycol layer and water molecules at the ends of the particles were eliminated. We wish to thank Dr. R. C. Reynolds, Jr., for suggesting the latter model to us.

Less glycol overall for the case where surface glycol was present shifted the dotted curves toward the solid curves but had the undesirable effect of changing the structure factors considerably from those given by Reynolds (1965). The model with no surface glycol did not produce this latter effect.

Several parameters were varied to ascertain their effect on computed positions and breadths of maxima. (1) Large variations in the scattering power of the atoms caused discernible effects in the Δd vs t plots. To illustrate, a dashed curve is plotted in Figure 4 for the heated clays, which represents the results obtained from an all–Fe octahedral composition rather than an all–Al octahedral composition. These two compositions represent extremes in the scattering efficiency of the octahedral sheet and approximately bracket any composition from a naturally occurring clay. The position of the dashed curve in Figure 4 indicated that the first-order reflection from the collapsed clays was more nearly rational (for a given N) with more scattering matter in the octahedral sites. The identity or position of the interlayer cation or the Si to Al ratio in the tetrahedral sites caused no measurable differences. The effect of an all-Fe octahedral composition on the clay-glycol complexes was also computed but the results were omitted from Figures 1–3 for clarity. Regardless of the clay-glycol model, the effect of an all-Fe composition made the first and second orders more rational and the third order more irrational. Compared with the effect of this substitution on Δd_{1-3} for the collapsed clays, the shift in the theoretical Δd vs t curves was smaller for the first and third order clay-glycol reflections and larger for the second order clay-glycol reflection. (2) The temperature factor of all of the atoms in the outer half (including the octahedral atom) of the surface silicate layers on both ends of the particles was increased. To illustrate this effect, a temperature factor of 100.0 for the outer half of the end silicate layers had about the same result as changing the octahedral composition from all-Al to all-Fe, *i.e.*, from the solid to the dashed line in Figure 4. This temperature factor increase also caused the computed breadths to increase, more for small N values. (3) Additional scattering matter in the interlayer or on the surfaces of the "collapsed" silicate particles, *e.g.*, water molecules, suggested by the hectorite heated to 200°C., raised the computed curve, *i.e.*, increased Δd_{1-3}. (4) The orientation of the glycol molecules made little difference in the computed Δd and breadth values.

Discussion

An objective of this study was to determine whether or not the apparent basal spacings of montmorillonites were affected by particle thickness. Although the results indicate a particle size effect, there is a lack of impressive agreement of the experimental data, which in some cases are highly scattered and show no trend (*e.g.*, Figure 1), with the theoretical curves. The theory was based on an analysis of two factors only, the layer structure factor and N. Some of the disagreement is apparent since the curves were drawn for an "ideal dioctahedral aluminum montmorillonite" and none of the clays analyzed has that composition precisely. Nevertheless, other factors not included in the theoretical analysis, such as size distribution, interstratification, and detailed structural aspects (*e.g.*, inverted silica tetrahedra) are likely to be more or less important than particle thickness in determining the breadths and irrationality of basal reflections of a given montmorillonite.

None of the montmorillonites studied, organic-treated or heated, gave a rational sequence of basal orders. This result is likely due to the thinness of the particles, among other factors. A "particle size effect" was clearly indicated by the results of the fractionated Upton and Fayette clays whose breadths increased and thicknesses decreased with a decrease in size fraction.

Roberson, Weir and Woods (1968) showed that clay suspensions subjected to a concentrated energy input with an ultrasonic probe exhibited thinner particles than before such treatment. A 5–10 minute treatment of the medium Fayette and Upton samples (F_3 and U_3) gave increased breadths of diffraction maxima and reduced particle thicknesses which were similar to the non-probe-treated very fine fractions of these clays (F_1 and U_1) for both the glycol-treated and heated specimens. The probe-treated and very fine fractions always gave enhanced intensities for the basal orders compared to the intensities obtained from coarser fractions, a result noted by Roberson, Weir and Woods (1968) and attributed by these investigators to better particle orientation in the former. The better oriented specimens produced the broader reflections, a result likely due to thinner particles.

Non-rigorous chemical treatment or different methods of sample preparation did not affect the experimental breadths and consequent N values. A change in the identity of the interlayer cation, *i.e.*, Ca for Na, did not change N for the Fayette clay. Roberson, Weir and Woods (1968) and others have shown, however, that the microaggregate morphology of such clays was definitely affected by this exchange, and other studies have shown that rheological properties are affected by a change in the cation composition. The breadths of the reflections used herein are a measure of the thickness of the "X-ray particles" and this thickness appears to be unaffected by cation exchange. Different methods of sample preparation other than that described above, *e.g.,* powder mounts from freeze-dried clays, gave the same N values as those reported here if the mounts were thin. Since cation exchange (Ca for Na) or powder mounts prepared from freeze-dried clays produced more random orientation of the clay particles, we conclude that orientation did not affect the breadths of the reflections.

Comparison of the experimental and theoretical clay-glycol data suggests that the surface glycol may make a rather small contribution to the diffraction effects. This conclusion implies that glycol molecules must be sandwiched by two silicate layers to contribute significantly to the diffraction pattern. While this conclusion is by no means definite, the model with no surface glycol should be considered in future studies of this system.

The data in Figure 2 are pertinent with respect to surface condition. We first attributed the non-integral orders of the organic-treated clays to interstratification which was a result of the partial glycol contents of various interlayer regions. This explanation proved insufficient, by itself, to account for the experimental data. Computations of expected diffraction effects were made for interstratified systems composed of abundant two-layer glycol spacings with a small percentage of zero and/or one layer glycol spacings and which allowed for variations in the scattering efficiency of the interlayer material. The calculations predicted negative Δd_{2-5} which was contrary to the positive values observed experimentally for all of the clays. The model with no surface glycol, without any extra assumptions concerning interstratification, provided positive Δd_{2-5} values and showed somewhat better agreement with the other data.

The sample of hectorite heated to 200°C retained more water (as evidenced by its higher *d*-spacing) than did the hectorite heated to 450°C and the former gave broader reflections. A smaller N value was therefore computed for this sample which is not real (Figure 4). The increased breadth of the reflections was due to the presence of randomly intercalated water molecules and consequent interstratification. This example serves to show the relative, though in this case rather small, effect of interstratification in reducing the apparent N values and it is likely that none of the samples regardless of pretreatment was completely free of this effect. The ordinate of the hectorite heated to 200°C (Figure 4) relative to the theoretical curve is similar to those of the other clays. Whether this result is significant or fortuitous is unknown.

The experimental $\beta(005)$ values for the glycol clays were slightly larger than the calculated values, more so for smaller N values, while the $\beta(003)$ values for the heated clays were about equal to those computed. The experimental (001) and (002) breadths from the glycol treated clays were definitely larger than those computed, *e.g.,* 0.10° 2θ for $N = 5$ for (001), while the experimental breadths of the low orders from the heated clays were slightly less than the computed values. Also, the experimental N values for the glycol-treated clays were smaller than those for the comparable heated clays with one exception (Santa Rita). These results might be due to the glycol-treated clays having larger amount of interstratification, or they could be caused by some other reflection-broadening factor that affected the experimental glycol-clay results that was not accounted for in the theoretical computations. It is suggested, therefore, that the N values obtained from the heated clays may be a somewhat more reliable estimate than those obtained from the organic-treated clays. However, it is possible that thicker particles are created during the heating process.

Electron microscope observations (Roberson, Weir and Woods, 1968) on the ultrasonically treated clays reveal a significant number of apparently very thin particles, presumably one layer thick. We wonder, therefore, why the X-ray maxima from the sonic-treated clays were not broader than what we observed. Could it be that, although the sonic-treated clays contain a large number of exceedingly thin particles, the preponderance of the X-ray intensity is due to the presence of a relatively small number of thicker particles? Or are the breadths of the basal reflections of montmorillonites not a measure of "mean particle thickness" but determined by the amount of order obtained by piling layers in a quasi-parallel fashion? The latter conclusion, if true, might preclude a relationship of apparent basal spacing and particle thickness.

Acknowledgments

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