

## PURIFICATION AND PROPERTIES OF MONTMORILLONITE

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### ABSTRACT

Descriptive mineralogical data have been obtained on ten montmorillonites from bentonite deposits located in the United States and Canada, using thermal,  $x$ -ray, electron, and chemical methods.

The montmorillonites were hand-picked and subsequently mechanically purified by settling and supercentrifugation. After purification cristobalite was detected in four of the ten samples. Lepidocrocite and hydrous mica were present in one sample. The differential thermal analysis curves show endothermic peaks at (140–160° C.), (650–715° C.), and (820–885° C.) followed by an exothermic reaction above 870° C.  $X$ -ray powder photographs show basal spacings up to the tenth order yielding  $d_{001} = 17.9$  to  $18.0$  Å for glycerol treated specimens. The electron micrographs reveal small, irregular thin plates. One sample showed some of the plates curled into tubes. The base-exchange capacity varies from 66 to 128 milliequivalents per 100 grams of sample depending on impurities and chemical composition of the montmorillonite, but independent of particle size. Formulae calculated from the chemical analyses show a fairly wide range of isomorphism. The peak temperatures of the thermal reactions, the “ $a$ ” and “ $b$ ” dimensions of the unit cell and base-exchange capacities are correlated with the substitution of magnesium and iron for aluminum in the octahedral layer and aluminum for silicon in the tetrahedral layer as determined from chemical analyses.

### INTRODUCTION

Many papers have been published on montmorillonite, but practically none of them give convincing evidence that the samples examined were free from impurities. Ross and Hendricks (1) pointed out that they used hand-picked samples checked for impurities with the petrographic microscope. As was noted by them, various kinds of impurities were present in many of the samples which they investigated. They reported that small amounts of impurities are difficult to detect; indeed, as much as one to two per cent of crystalline impurity may escape detection. They also stated that much larger amounts of amorphous silica as well as amorphous hydroxides of aluminum and iron cannot be detected with certainty by microscopic means. They further stated that one sample of montmorillonite was found, by chemical methods, to contain four per cent amorphous silica, and that cristobalite was present in several other samples. As was pointed out by Ross and Hendricks, silica is likely to be the most common impurity in montmorillonite from bentonites.

Kerr, et al (2) showed by microscopic study,  $x$ -ray diffraction, thermal analysis, and electron micrography that many of their samples were contaminated with several kinds of mineral impurities. Since impurities

of various kinds always affect the interpretation of analytical data, an attempt was made to remove impurities as completely as possible from ten montmorillonites from bentonite. This paper reports the results of a series of studies on at least partially purified montmorillonite from a number of widely distributed localities.

#### SOURCE OF SAMPLES

All but two of the montmorillonites used in this investigation were from the series of bentonites collected by Kerr, et al (2) as reported to the American Petroleum Institute (*A.P.I. Project 49*). Their report gives a description of the geological occurrence of these samples. Of the two other samples, one was a bentonite from Plymouth, Utah, collected by Dr. D. W. Thorne of the Agricultural Experiment Station, Logan, Utah. His description\* of this deposit follows:

"The bentonite occurs as outcroppings on the foothills along the Northern Utah and Western Idaho border. This sample was obtained about five miles north of Garland, Utah, and about three miles west of a small village called Plymouth on the side of a small ravine. There are large banks of volcanic ash about 100 yards to the west of this outcropping, made up of 90 to 95 per cent volcanic ash and five to ten per cent bentonite. The deposit occurs on top of what is known as Salt Lake Formation. The bentonite was formed through the period of the northwestern lava flow, probably late in Miocene time, by the hydrolysis of volcanic ash which fell into a prehistoric lake."

The other sample was obtained through Dr. H. S. Spence, Consulting Mineral Technologist, Ottawa, Canada. It occurs in a bentonite which outcrops at Quilchena near Merritt, British Columbia, and is described by Spence (3).

#### METHOD OF PURIFICATION

Hand selected lumps of the crude bentonites approximately air dry were first crushed in a mortar, then leached with 1.0 normal neutral sodium acetate or sodium chloride in order to convert the montmorillonite into the sodium saturated form and thereby bring about ready dispersion of the clay. Leaching with sodium salt solution was continued until a high percentage, but not quite all, of the natural exchangeable bases were replaced by sodium. As far as is known, the clay is affected in no other way by neutral salts. The naturally occurring soluble salts of all kinds, and calcium carbonate if not present in too high percentage, are completely removed by this treatment. The samples were then freed from occluded sodium salt by repeated leaching with 80 per cent neutral methyl alcohol. Distilled water was added, followed by dispersion in a Waring Blendor for ten minutes. Additional distilled water was

\* Private communication to Dr. Paul D. Foote from Dr. D. W. Thorne, June 20, 1949.

added, shaken by hand, and the dispersed clay, together with any other remaining substances, was poured into two-liter cylinders and allowed to settle. After standing ten minutes, the suspended clay was siphoned off and allowed to settle overnight. The material remaining in suspension was siphoned off the following day after which the suspensions were passed through a Sharples Super-centrifuge several times. After each centrifugation, the overflow solution was again passed through the centrifuge at a slower rate of throughput and at greater speed of revolution. By this means the sample was separated into a series of particle size fractions. The limit of particle size obtainable by this means is determined by the rate of flow of the suspensions and speed of revolution of the centrifuge. With most of the samples, particles less than  $50\text{ m}\mu$ , as calculated by Hauser's (4) modification of Stokes' law, were discarded.

By this method each fraction was at first thought to contain particles within a specified range of effective sizes. After the samples had been centrifuged as just outlined, a special study was made on the Santa Rita, New Mexico, bentonite by redispersing each fraction by vigorous shaking in distilled water, then passing the suspension through the centrifuge again. This was repeated ten times. By this means a very high percentage of the clay-like material less than  $500\text{ m}\mu$  was reduced to particles less than about  $50\text{ m}\mu$ . In view of these results, the actual range of particle sizes in each fraction discussed in the following pages is open to question. However, the purpose in this part of the work was to secure samples of the montmorillonite as free as possible from impurities. With the exceptions noted later it is believed that this objective was approached fairly closely.

#### ANALYTICAL RESULTS

*I. Differential Thermal Analysis.*—Differential thermal analysis was carried out using equipment described by McConnell and Earley (6). Since differential thermal analysis is a measure of the energy of reaction as a function of temperature, montmorillonite was compared with inert alumina which was ground to about 200-mesh. The temperatures of the montmorillonite and reference material were measured with platinum/platinum 10% rhodium thermocouples. The samples were heated from about  $70^\circ\text{ C.}$  to  $1000^\circ\text{ C.}$  at the rate of  $10^\circ\text{ C.}$  per minute. The  $300\text{--}200\text{ m}\mu$  fraction of montmorillonite was used for analysis since this fraction is sufficiently coarse to yield distinct reactions and does not contain enough impurities to seriously impair accurate interpretation of the thermograms. The samples were dried at  $65^\circ\text{ C.}$ , allowed to stand in stoppered bottles in contact with air, ground to about 200-mesh and packed in the sample holder using a tamping action (6).

TABLE 1. DIFFERENTIAL THERMAL ANALYSIS DATA

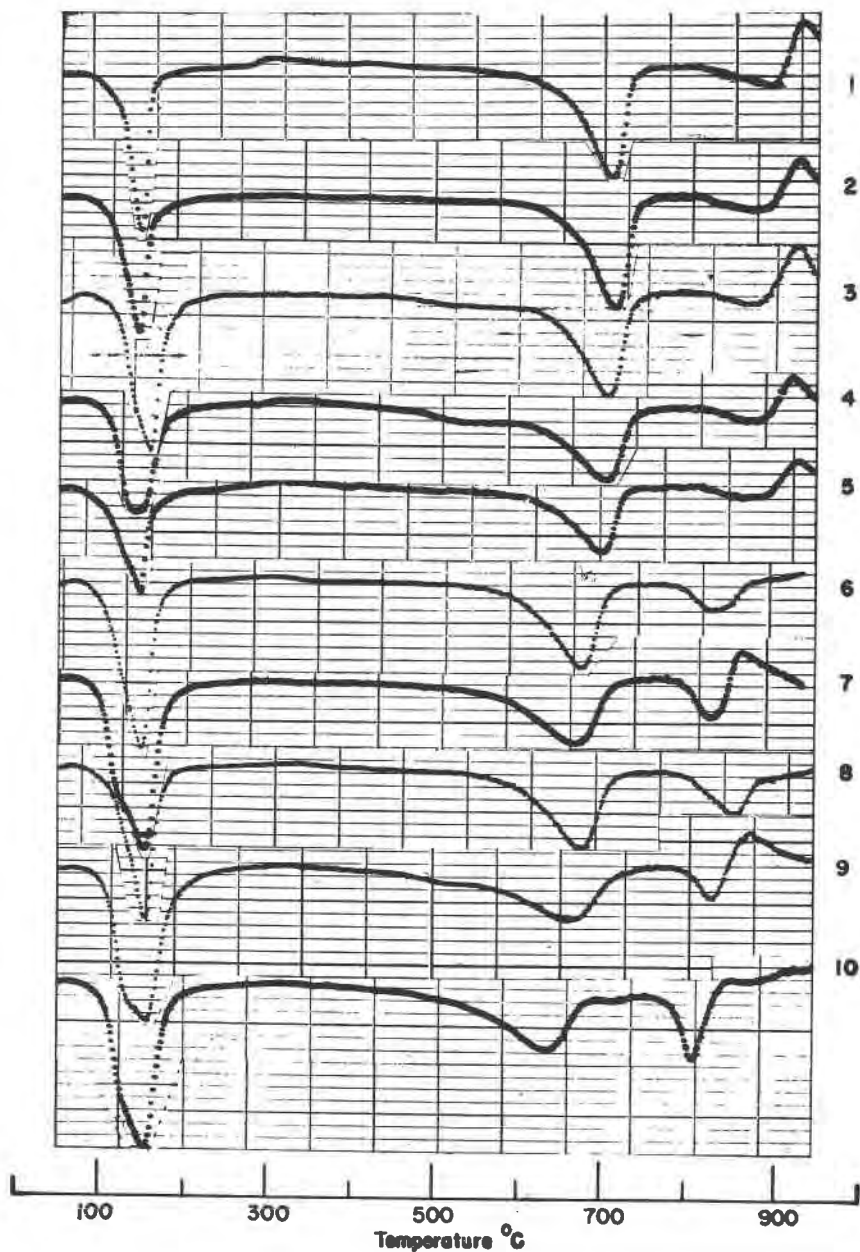
Sample	Peak Temperatures of Thermal Reaction— 300–200 m $\mu$ Fraction in ° C.						
	Endothermic					Exothermic	
Montmorillonite Belle Fourche, South Dakota		140		715		885	930
Montmorillonite Clay Spur, Wyoming		140		715		885	930
Montmorillonite Little Rock, Arkansas		150		710		880	925
Montmorillonite Amory, Mississippi		145	295 545	705		870	910
Montmorillonite Merritt, British Columbia		140		705		875	910
Montmorillonite Polkville, Mississippi		155		690		845	Exo. drift
Montmorillonite Chambers, Arizona		155		685		845	880
Montmorillonite Santa Rita, New Mexico	120	155		680	750	850	Exo. drift
Montmorillonite Plymouth, Utah	135	160	540	675		830	870
Montmorillonite Otay, California		155		650		820	Exo. drift

The differential thermal data shown in Table 1 and Figures 1–10 indicate that sodium-saturated montmorillonite is characterized by three distinct endothermic reactions at 140–160° C., 650–715° C., and 820–890° C. and an exothermic reaction at 880–935° C. or an exothermic drift of the baseline in this temperature range. Assuming the Hofmann-Endell-Wilm (5) structure for montmorillonite, the composite low temperature endotherm is interpreted as due to the removal of one or more sheets of water from the interlayer of the structure and incidental adsorbed water. Since sodium is only slightly hydrated, the water of cation hydration normally given off at about 200° C. is negligible. Some of the samples yield shoulder-type endothermic reactions at 120° C. to 135° C. suggest-

ing that these samples were not dried for sufficient time at 65° C. to remove excess adsorbed water. Thus, the configuration of the low temperature endotherm appears to be markedly affected by the state of hydration of the montmorillonite as pointed out by Hendricks, et al (7). The first high temperature endotherm which occurs at 650–715° C. is attributed to the removal of hydroxyl ions from the octahedral layer. The second high temperature endotherm, 820–890° C., may be accounted for by the release of hydroxyl ions which are held in the tetrahedral layer, or to the breakdown of the montmorillonite structure. The tetrahedral hydroxyl ions, if present, probably occur randomly distributed in the tetrahedral layer substituting for oxygen. It was proposed by Edelman and Favejee (8) that alternate tetrahedral groups have hydroxyl ions, although this explanation would not be compatible with the amount of water determined by Nutting (9) from dehydration experiments. This hypothesis was later modified by the proposal that only occasional tetrahedra have hydroxyl ions. McConnell (10) proposed that the second high temperature endotherm could be accounted for by (H<sub>4</sub>O<sub>4</sub>) groups in tetrahedral coordination and randomly substituting for (SiO<sub>4</sub>) groups. Although any of these explanations might account for the endotherm, none have been proven.

It should be noted that all three endotherms appear to be related. Those samples which yield the low temperature endotherm at the lowest temperature give correspondingly higher temperatures for the high temperature endotherms. This relationship can be accounted for on a basis of chemical composition since substitution of one ion for another results in bond energy changes and by perfection of crystal growth since rates of reaction are partly a function of crystal size. It is obvious in Figs. 1–10 that, as the peak temperature of the first high temperature endotherm decreases, the endotherm tends to become broader, supporting the idea that the rate of water removal is variable. This would not affect the total water but would merely be evidence for isomorphism and variation in the size of crystals.

The exothermic reaction at 870–930° C. is a result of the recombination of the elements in the structure to form oxides. It is doubtful that complete recrystallization takes place in this temperature range. Many of the oxides may remain in an amorphous state until higher temperatures are reached. The exothermic drift shown by some of the samples is probably due to delayed crystallization as suggested by Bradley and Grim (11) or possibly to contraction of the sample from the wall of the sample holder which would result in changes in thermal diffusivity. The temperature at which the exothermal reaction takes place is obviously related to the endothermal reactions suggesting that all of the thermal reactions



FIGS. 1-10. Thermograms of the 300-200  $m\mu$  fraction of sodium saturated montmorillonites ground to approximately 200-mesh; thermocouples Pt/Pt 10% Rh; sensitivity  $\pm 2.5$  microvolts per chart division.

as one would expect are dependent on chemical composition and crystal size. The endotherm at 295° C. for the sample from Amory, Mississippi, suggests the presence of a small amount of finely divided lepidocrocite. The endothermic reaction at 540° C. in the Plymouth, Utah, sample is probably due to a constituent which has not been identified since montmorillonite is not known to have thermal reactions at this temperature.

*II. X-Ray Diffraction.*—X-ray diffraction patterns of montmorillonite samples were obtained by means of a standard Norelco Unit equipped with Debeye-Scherrer type cameras of radius  $180/\pi$  mm. The patterns were all produced with FeK $\alpha$  radiation.

Powder samples were prepared from the 200–70  $\mu$  fraction of the sodium saturated montmorillonites which had been dried at 65° C. The samples were thoroughly mixed with glycerol and evaporated at 125° C. until the residue became thick and almost dry. At this point, sufficient glycerol remains to enable one to roll a specimen into a rod which can be mounted in the powder camera directly without the aid of any supporting material. All specimens were prepared in this manner and rolled into rods approximately 0.25 mm. in diameter. All photographs were taken in the same powder camera and exposed for 20 hours.

The powder patterns which are reproduced in Figures 11–20 inclusive all show a very strong diffraction line with  $d(001)=17.5$  to 17.9 Å. Higher orders of the basal spacing to (00.10) are present in some of the photographs. Calculation from (00 $l$ ) measurements yields  $d(001)=17.9$  to 18.0 Å. X-ray diffraction data for each of the samples are presented in Table 2.

Impurities are still evident in several of the samples. Cristobalite is present in large quantities in the Merritt, British Columbia, sample and in a somewhat lesser amount in the Santa Rita, New Mexico, material. It can be also detected in samples from Belle Fourche, South Dakota, and Little Rock, Arkansas, on the basis of the strongest line. The presence of a diffraction line at 3.30 Å suggests hydrous mica in the Amory, Mississippi, sample. This observation is consistent with the presence of about 0.60 per cent non-exchangeable K<sub>2</sub>O in this material. Except in the case of the cristobalite in the Santa Rita, New Mexico, and Merritt, British Columbia clays, these impurities probably do not constitute more than 5 per cent of the samples.

In addition to the (00 $l$ ) diffraction lines, the patterns all show ( $hk0$ )

FIG. 1. Belle Fourche, South Dakota.

FIG. 2. Clay Spur, Wyoming.

FIG. 3. Little Rock, Arkansas.

FIG. 4. Amory, Mississippi.

FIG. 5. Merritt, British Columbia.

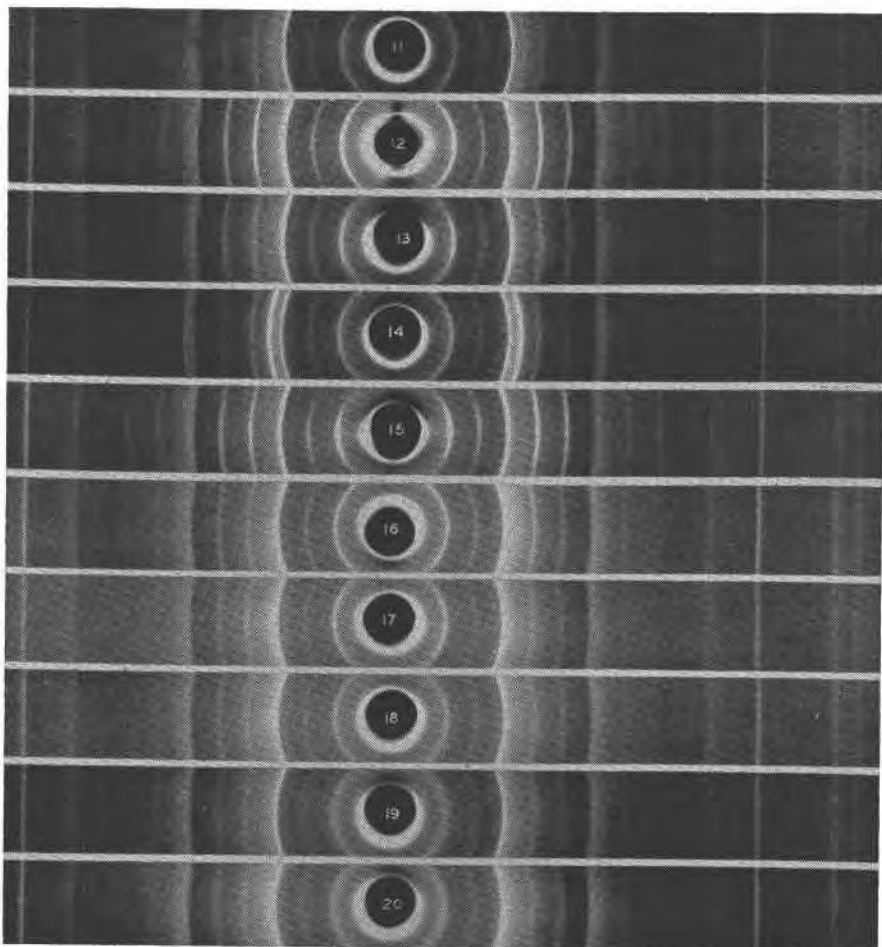
FIG. 6. Polkville, Mississippi.

FIG. 7. Chambers, Arizona.

FIG. 8. Santa Rita, New Mexico.

FIG. 9. Plymouth, Utah.

FIG. 10. Otay, California.



FIGS. 11-20. X-ray powder photographs with  $\text{FeK}\alpha$  radiation of the 200-70  $m\mu$  fractions of sodium-saturated, glycerol-treated montmorillonites; camera radius  $180/\pi$  mm.

FIG. 11. Santa Rita, New Mexico.

FIG. 12. Belle Fourche, South Dakota.

FIG. 13. Little Rock, Arkansas.

FIG. 14. Merritt, British Columbia.

FIG. 15. Clay Spur, Wyoming.

FIG. 16. Polkville, Mississippi.

FIG. 17. Amory, Mississippi.

FIG. 18. Chambers, Arizona.

FIG. 19. Plymouth, Utah.

FIG. 20. Otay, California.

lines which apparently do not differ in measurement beyond the expected experimental error. However, a separate careful measurement of the (330) (060) line on each of the films has shown that individual measurements can be reproduced within 0.001 Å and that there are appreciable differences in the spacing of (330) (060) between the various montmoril-



TABLE 2. MONTMORILLONITES X-RAY POWDER DIFFRACTION DATA  
200-70 m $\mu$  Fractions, Na-Saturated, Glycerol Saturated

Santa Rita, N. Mex.	Belle Fourche, S. Dak.	Little Rock, Ark.	Merritt, B. C.	Clay Spur, Wyo.	Polkville, Miss.	Amory, Miss.	Chambers, Ariz.	Plymouth, Utah	Olney, Calif.	Interpretation
<i>I</i>	<i>I</i>	<i>I</i>	<i>I</i>	<i>I</i>	<i>I</i>	<i>I</i>	<i>I</i>	<i>I</i>	<i>I</i>	
10 17.5	10b 17.6	10 17.8	10 17.6	10 17.9	10b 17.6	10b 17.7	10 17.6	10 17.6	10b 17.7	$dA$
6 9.00	7 9.04	6 8.98	6 9.01	7 9.03	5 8.97	5 9.01	5 9.00	5 9.04	5 9.04	(001)
4 5.98	4 5.98	2 5.98	3 5.99	4 6.02	3 5.93	1 5.96	1 5.99	2 5.95	2 5.95	(002)
1 4.97	1 4.94	1 4.95	1 4.94	1 4.98	1 4.93	1 4.98	1 4.95	1 4.97	1 4.93	(003)
9 4.48	8 4.49	7 4.51	7 4.50	8 4.51	8 4.48	8 4.50	8 4.49	8 4.50	8 4.48	$\beta$ (110) (020)
5 4.08	$\frac{1}{2}$ 4.13	$\frac{1}{2}$ 4.13	8 4.07	$\frac{1}{2}$ 3.95	1b 3.95	1b 3.94	1b 3.91	5 3.58	4 3.58	(110) (020) $\alpha$ Cristobalite $\beta$ (005)
6 3.58	6 3.58	5 3.58	5 3.58	7 3.60	4 3.58	4 3.57	4 3.58			Hydrous Mica $\alpha$ Cristobalite (006)
5 2.99	5 2.99	4 2.99	1 3.14	5 3.01	3 2.98	3 3.00	3 2.99	3 2.99	3 2.99	$\alpha$ Cristobalite (006)
5b 2.58	4b 2.58	4b 2.59	1 2.85	4b 2.59	4b 2.58	5b 2.58	4b 2.57	5b 2.58	5b 2.58	$\alpha$ Cristobalite (130) (200)
3 2.242	3 2.246	1 2.246	5 2.487	3 2.250	2 2.242	1 2.250	1 2.242	2 2.246	2 2.244	(220) (040) $\alpha$ Cristobalite (009)
1 1.993	2 1.995	1 1.989	$\frac{1}{2}$ 2.126	3 2.001	1 1.993	$\frac{1}{2}$ 1.981	$\frac{1}{2}$ 1.989	$\frac{1}{2}$ 1.976	$\frac{1}{2}$ 1.989	$\alpha$ Cristobalite (009)
$\frac{1}{2}$ 1.793	1 1.794		$\frac{1}{2}$ 2.038	$\frac{1}{2}$ 1.936						$\alpha$ Cristobalite (00.10)
5 1.700	3 1.703	3 1.706	2 1.699	3 1.701	2 1.705	2 1.702	2 1.699	2 1.704	4 1.705	(240) (310)
$\frac{1}{2}$ 1.658	1 1.658	$\frac{1}{2}$ 1.660	2 1.660	6 1.503	$\frac{1}{2}$ 1.655	$\frac{1}{2}$ 1.662	6 1.504	$\frac{1}{2}$ 1.656	$\frac{1}{2}$ 1.656	$\beta$ (330) (060)
7 1.501	5 1.501	5 1.502	6 1.501	6 1.503	6 1.504	6 1.505	6 1.504	6 1.504	7 1.504	(330) (060)
2b 1.296	2b 1.299	2 1.297	2b 1.298	2b 1.300	1b 1.298	1b 1.299	1b 1.294	1b 1.298	2b 1.299	(260) (400)
2 1.250	2 1.248	3 1.251	2 1.250	2 1.254	1 1.251	1 1.252	1 1.250	1 1.252	2 1.250	(250) (170) (420)

*b* = broad line.

lonites. The spacings for this line, which are given in Table 2, are those obtained by this separate measurement on the film. In order to further improve the accuracy of these measurements, specimens were examined with a Philips high angle Spectrometer ( $\text{CuK}\alpha$  radiation). The values obtained in this manner for the spacing of (330) (060) are as follows:

	$2\theta(330)(060)$	$d(330)(060)$
Montmorillonite, Santa Rita, New Mexico	61.90	1.4989 Å
Montmorillonite, Belle Fourche, South Dakota	61.90	1.4989
Montmorillonite, Little Rock, Arkansas	61.88	1.4993
Montmorillonite, Merritt, British Columbia	61.85	1.5000
Montmorillonite, Clay Spur, Wyoming	61.84	1.5002
Montmorillonite, Polkville, Mississippi	61.83	1.5004
Montmorillonite, Amory, Mississippi	61.82	1.5007
Montmorillonite, Chambers, Arizona	61.82	1.5007
Montmorillonite, Plymouth, Utah	61.77	1.5018
Montmorillonite, Otay, California	61.74	1.5024

It is considered that the  $2\theta$  measurements from the spectrometer traces are reproducible to  $\pm 0.01^\circ$  and consequently the  $d$  values are subject to a variation of  $\pm 0.0002$  Å.

*III. Electron Microscopy.*—Samples of the 200–70  $m\mu$  fraction of the ten montmorillonites were examined with the electron microscope. In all of the samples the clay particles appear as irregular flakes and masses. Montmorillonite from Clay Spur, Wyoming, shows well defined thin flakes in various stages of curling into tubes (Fig. 21) similar to the observations of Ardenne, et al (12) but which they interpret as crystals standing on edge. The appearance of the flakes suggests that the curling may be due to the process of drying during preparation of the sample or to the heating effect of the electron beam, rather than to an inherent structure. As a result of this curling, many flakes show straight edges, thus giving a false impression of crystal outline. Minor evidence of curling was seen in the electron micrograph of the Belle Fourche montmorillonite.

Curling, or development of tubes, has been observed with the mineral halloysite (13) and has been explained as the result of an imperfect fit in this two layer structure between the silicon-oxygen sheet and the hydroxyl sheet of the octahedral layer. A structural unit of the hydroxyl sheet normally has a smaller spacing than an equivalent unit of the silicon-oxygen sheet. With a water layer between two layer units, it seems possible that the next silicon-oxygen layer is unable to exert enough "stretching" force on the hydroxyl sheet to prevent a curling effect, which results in the development of tubes.

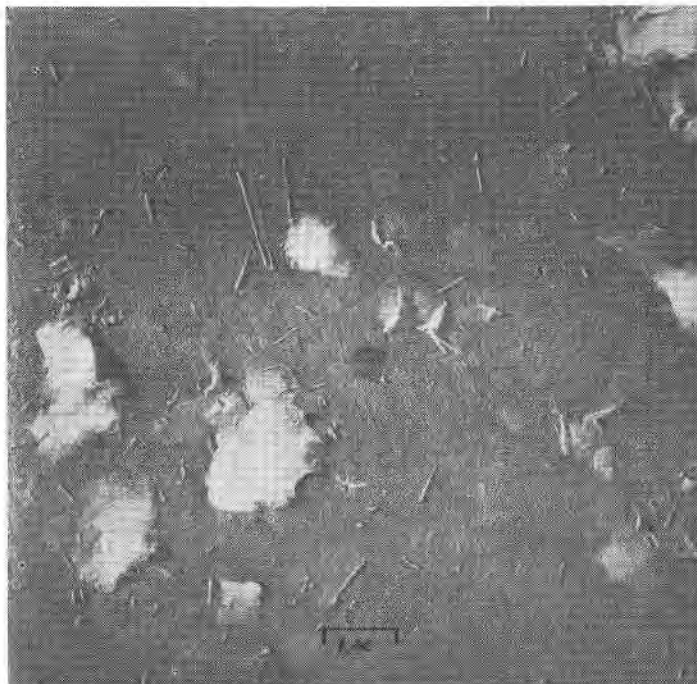


FIG. 21. Electron micrograph of the 200–70  $m\mu$  fraction of sodium saturated montmorillonite, Clay Spur, Wyoming, prepared from a water suspension which was evaporated onto a Formvar film supported on a standard screen, Pd—shadowed.

This explanation cannot be applied to montmorillonite since, in accordance with the Hofmann-Endell-Wilm structure, it has silicon-oxygen layers on both sides of an octahedral layer. Furthermore, there is not a continuous hydroxyl layer present. In this three layer structure, substitution in the tetrahedral or octahedral layers gives rise to equal forces on both sides of the “sandwich” and cannot produce curling. The curling which has been observed has always been in an upward direction and appears, therefore, to be due to drying effects during preparation and observation of the sample.

A more likely explanation involves the physical nature of the observed flakes and the actual size of clay crystals. It has already been suggested that the particle size attributed to the various clay fractions separated by centrifugation is that of aggregates rather than individual crystals. It has been concluded, therefore, that the curled flakes observed in the electron micrographs are aggregates formed during the preparation of the sample from a thin suspension. Since the crystals are presumably platy in nature, the aggregates will be composed of many overlapping

flakes along with entrapped water. Dehydration during evacuation of the electron microscope and by the heating effects of the electron beam, removes water from the upper portion of the aggregates most easily. This removal of water (not interlayer water) and the accompanying surface tension effects will draw the edges of flakes closer together, thereby causing the aggregate to curl upward. This phenomenon will be most apparent when the crystals occur as unusually large plates which should increase the differential drying effects between the top and bottom of the aggregates. It has been noted that those montmorillonites which show preferred orientation effects most readily in *x*-ray diffraction specimens and have the sharpest diffraction lines are the ones which exhibit the curling effect. This, in turn, suggests that crystal size and shape vary considerably in montmorillonites.

*IV. Base-Exchange Capacity and Chemical Analysis.*—The base-exchange capacities of these montmorillonites, both in their natural state and in various particle size fractions after sodium saturation have been reported by Osthaus (14). The data show a wide variation of the exchangeable cations present in the untreated montmorillonites. The base-exchange capacities of five particle size fractions of the purified sodium saturated montmorillonites show in some cases fairly constant values, while in others the base-exchange capacity increases markedly in the fractions less than 300  $m\mu$ . This increase in base-exchange capacity in the fine fractions is very likely due to concentration of impurities in the coarse fractions as suggested by Osthaus. However, the purity of a fine fraction cannot be inferred from the fact that the base-exchange capacity remains constant over a range of fine particle sizes. This is illustrated by the Merritt, British Columbia, and Santa Rita, New Mexico, samples which show a constancy of base-exchange capacity over the three finest particle size fractions but still contain large amounts of cristobalite.

Osthaus has suggested, on the basis of his data from specimens which appear to be relatively pure, that base-exchange capacity is independent of the particle size as calculated by Hauser's modification of Stoke's law. This could mean, of course, that the indicated particle size even in the finest fraction is that of aggregates of crystals, rather than individual crystals.

Chemical analyses and calculated structural formulae have been reported by Osthaus (14) for eight of the ten montmorillonites included in this paper. Additional analyses for montmorillonite from Little Rock, Arkansas, and from Amory, Mississippi, along with those already reported are given in Table 3. As outlined by Osthaus, a determination of soluble silica and alumina was made for each sample by means of an extraction with 0.5 normal sodium hydroxide.

TABLE 3. CHEMICAL ANALYSES AND BASE EXCHANGE CAPACITY OF MONTMORILLONITE (200-70 m $\mu$ ) After Sodium Saturation

	Belle Fourche, South Dakota	Clay Spur, Wyoming	Little Rock, Arkansas	Plymouth, Utah	Merritt, Br. Col.	Amory, Mississippi	Chambers, Arizona	Santa Rita, New Mexico	Polkville, Mississippi	Otay, California
SiO <sub>2</sub>	61.12	61.47	60.69	58.60	71.60	59.30	61.16	65.21	63.42	63.04
Al <sub>2</sub> O <sub>3</sub>	23.10	22.17	22.40	20.64	15.75	20.40	20.38	19.13	19.44	18.44
Fe <sub>2</sub> O <sub>3</sub>	4.37	4.32	5.67	4.89	3.78	7.74	3.66	1.07	1.87	1.20
TiO <sub>2</sub>	0.09	0.09	0.19	0.57	0.24	0.76	0.37	0.14	0.32	0.14
MnO	trace	trace	0.00	0.03	trace	0.07	0.03	0.03	0.00	0.01
P <sub>2</sub> O <sub>5</sub>	0.05	0.02	trace	0.02	0.04	0.14	0.03	trace	0.04	0.05
CaO	0.24	0.14	0.00	0.64	0.07	0.03	0.14	0.04	0.11	0.08
MgO	2.50	2.73	1.87	4.00	0.97	2.40	4.52	4.57	5.00	7.30
Na <sub>2</sub> O	2.90	3.18	2.50	3.00	1.88	2.52	3.70	3.90	3.46	3.40
K <sub>2</sub> O	0.04	0.03	0.13	0.07	0.09	0.66	0.04	0.14	0.08	0.02
H <sub>2</sub> O	5.84	6.02	6.61	7.63	5.34	6.25	6.40	5.83	6.15	6.47
Total	100.25	100.17	100.06	100.09	99.76	100.27	100.43	100.06	99.89	100.15
Sol.* SiO <sub>2</sub>	6.74	3.59	7.88	8.00	29.90†	6.59	5.80	8.00	8.40	3.92
Sol.* Al <sub>2</sub> O <sub>3</sub>	1.50	0.64	2.25	2.08	0.68	1.58	1.71	0.86	2.25	1.02
B.E.C.‡	94.2	103.0	86.8	118.4	65.9	84.7	124.0	117.0	121.0	128.3

\* Determined by sodium hydroxide extraction.

† Determination of uncombined silica by phosphoric acid method of Talvite (16) gave 37.65%.

‡ Base-exchange capacity in milliequivalents per 100 grams of clay dried at 85° C.

NOTE: Data for montmorillonites from Belle Fourche, South Dakota; Clay Spur, Wyoming; Plymouth, Utah; Merritt, British Columbia; Chambers, Arizona; Santa Rita, New Mexico; Polkville, Mississippi; and Otay, California from Osthaus (14).

TABLE 4. DISTRIBUTION OF CHARGES ON LATTICE LAYERS AND STRUCTURAL FORMULAE OF TEN SODIUM SATURATED MONTMORILLONITES AFTER DEDUCING SOLUBLE  $\text{SiO}_2$  AND  $\text{Al}_2\text{O}_3$ ; 200-70  $\mu$  FRACTION

	Belle Fourche, S. Dak.	Clay Spur, Wyo.	Little Rock, Ark.	Plymouth, Utah	Merritt, Br. Col.	Amory, Miss.	Chambers, Ariz.	Santa Rita, N. Mex.	Polkville, Miss.	Otay, Calif.
Tetrahedral	Si	7.539	7.671	7.597	7.465	7.552	7.692	7.930	7.886	7.899
	Al	0.461	0.329	0.403	0.535	0.692	0.308	0.070	0.117	0.101
	Total	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000
	Charge	-0.461	-0.329	-0.403	-0.535	-0.692	-0.308	-0.070	-0.114	-0.101
Octahedral	Al	3.068	3.033	3.013	2.692	3.131	2.748	2.912	2.789	2.642
	Fe	0.456	0.431	0.613	0.543	0.612	0.383	0.112	0.202	0.121
	Mg	0.516	0.559	0.401	0.864	0.311	0.512	0.929	0.943	1.419
Total	4.040	4.003	4.027	4.099	4.054	4.075	4.060	3.967	4.058	4.182
	Charge	-0.396	-0.530	-0.320	-0.567	-0.149	-0.287	-1.042	-0.893	-0.873
Layer Charge	-0.857	-0.859	-0.723	-1.102	-0.841	-0.735	-1.057	-1.112	-1.007	-0.974
Interlayer	Na	0.777	0.816	0.696	0.858	0.784	0.699	0.996	0.961	0.880
	K	0.007	0.005	0.024	0.013	0.023	0.023	0.007	0.014	0.003
	Ca	0.035	0.020	—	0.101	0.016	0.009	0.020	0.006	0.017
	Mg	—	—	—	0.015	—	—	0.007	0.014	—
Interlayer Charge	+0.854	+0.861	+0.720	+1.103	+0.840	+0.740	+1.057	+1.113	+1.009	+0.973

NOTE: Data for montmorillonites from Belle Fourche, South Dakota; Clay Spur, Wyoming; Plymouth, Utah; Merritt, British Columbia; Chambers, Arizona; Santa Rita, New Mexico; Polkville, Mississippi; and Otay, California from Osthaus (14).

The calculated structural formulae showing the distribution of lattice charges for the eight analyses reported by Osthaus and those for the Amory and Little Rock materials are given in Table 4. The analyses have been calculated according to the method of Kelley (15) after correcting for soluble silica and alumina. Osthaus has pointed out the uncertainty that the silica and alumina removed by sodium hydroxide are impurity or partial solution of the silicate. There is little doubt that the purity of the Santa Rita and Merritt samples is enhanced by this treatment since  $x$ -ray examination of the treated products shows no evidence of crystalline silica. On the other hand, samples which did not show crystalline impurities yielded appreciable silica and alumina upon extraction suggesting that these materials were admixed in an amorphous state or that some of the montmorillonite was dissolved. No attempt has been made to correct for iron that may be extraneous to the clay lattice although it seems likely that this element is present as an oxide or hydrate in the samples which contain five or more per cent  $\text{Fe}_2\text{O}_3$ .

#### DISCUSSION AND CONCLUSIONS

A necessary aim of a study of this kind is the correlation of the various sets of analytical data within our concepts of the crystal structure and properties of montmorillonite. The basis of such correlation must be chemical analysis but, unfortunately, this method of investigation is sensitive to errors because of impurities. Five of the ten purified samples which have been studied give  $x$ -ray diffraction evidence of crystalline impurities and it is considered that the remainder may contain more or less amorphous silica and alumina. Although attempts have been made to remove free silica and alumina by sodium hydroxide extractions, it is not certain that this method is completely reliable. No attempt has been made to remove hydrous mica from the Amory sample. Therefore, the chemical analyses and structural formulae can be accepted only as close approximations. Nevertheless, the structural formulae suggests a fairly wide range of isomorphism. The same criticism may be made of the base-exchange determinations which must be decreased by the presence of impurities which do not possess base-exchange properties. The  $x$ -ray and differential thermal analysis data are probably not altered greatly by small amounts of impurities. However, the temperatures of thermal reactions of layer silicates containing hydroxyl groups are decreased by decreasing particle size as indicated by the experimental results of Kelley, et al. (17) and Kulp and Trites (18). The thermal reactions must be controlled primarily by chemical composition but modified by particle size. It has already been suggested from electron micrographic

evidence that particle size varies considerably in this group of montmorillonites.

In Table 5 the spacing values of (330) (060) are given as measured by the  $x$ -ray spectrometer. These values are compared with the ratio of octahedral iron plus magnesium to total octahedral cations and it will be seen that, in general, increasing iron plus magnesium content is accompanied by an increase in the spacing of (330) (060). This is to be expected since the iron and magnesium atoms are larger than the aluminum atom. The relationship is not precise, particularly in the samples with a small ratio, but since some of these samples contained cristobalite

TABLE 5. COMPARISON OF PHYSICAL AND CHEMICAL PROPERTIES OF MONTMORILLONITES

Locality	Octahedral Fe+Mg	$d(330)(060)$	Peak Temp. First High Temp. Endotherm	Base- Exchange Capacity*
	Total Octahedral Cations			
Santa Rita, New Mexico	0.266	1.4989 Å	680° C.	128.4
Belle Fourche, South Dakota	0.240	1.4989	715° C.	102.7
Little Rock, Arkansas	0.252	1.4993	710° C.	96.6
Merritt, British Columbia	0.228	1.5000	705° C.	106.9
Clay Spur, Wyoming	0.243	1.5002	715° C.	107.5
Polkville, Mississippi	0.313	1.5004	690° C.	136.3
Amory, Mississippi	0.331	1.5007	705° C.	92.2
Chambers, Arizona	0.325	1.5007	685° C.	134.1
Plymouth, Utah	0.343	1.5018	675° C.	131.7
Otay, California	0.368	1.5024	650° C.	135.0

\* Milliequivalents per 100 grams; corrected for subtraction of soluble  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ .

it is likely that the ratio is somewhat unreliable. An additional factor, the isomorphous substitution of aluminum for silicon in the tetrahedral layer, which has not been taken into account in this comparison may have some effect on lattice dimensions. The temperatures of the first high temperature endotherm have been included in this table as well as the base-exchange values corrected for the removal of soluble silica and alumina. It will be seen that these two properties show some correlation, high base-exchange values being accompanied by low endotherm temperatures. From the ratios shown in Table 5 it is suggested that the substitution of iron and magnesium for aluminum in the octahedral layer of montmorillonite reduces the peak temperature of the first high temperature endotherm. There are important exceptions in the case of the Santa Rita and Amory samples which have lower and higher tempera-



tures respectively than would be expected from the apparent trend of the table. These exceptions indicate that an additional factor or factors other than chemical composition must be considered in interpreting these thermal reactions. It is suggested by the authors that the particle size of crystals may account for these anomalies. This would imply that the crystal size of the Santa Rita sample is small compared with the Belle Fourche sample which has almost the same octahedral ratio; in the case of the Amory montmorillonite, the higher temperature of its thermal reactions would indicate a crystal size larger than that of its neighbors in the table with similar octahedral ratios. In both of these cases, the base-exchange capacity also does not conform with the apparent trend of the table, that of the Santa Rita material being high while that of the Amory sample is low. These base-exchange capacities are adequately explained by isomorphous substitution, but some speculation on the apparent relationship between base-exchange capacity and thermal reaction temperatures appears to be justified. The obvious inference, in view of the arguments above, is that crystal size is directly related to base-exchange capacity. By this it is meant that the base-exchange capacity of montmorillonite may be indicative of structural factors which limit the maximum size of crystals and that a large base-exchange capacity is accompanied by small crystal size.

This study has indicated the need for improved methods of purification of montmorillonites in order to obtain accurate chemical data on this group of minerals. Improved purity and a more detailed knowledge of the shape and size of crystals will probably provide the answer to many of the anomalies which exist in analytical data.

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