

# HETEROGENEITY IN MONTMORILLONITE

*By*

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## ABSTRACT

X-ray diffraction patterns and cation-exchange data are presented for centrifuged Wyoming bentonite to demonstrate the heterogeneous nature of montmorillonite. It has been shown that in the bentonite samples studied, the montmorillonite can be separated into at least two fractions. One phase consists of essentially a sodium montmorillonite while the other consists of essentially a calcium-magnesium montmorillonite. It is postulated that these differences occur because of differences in the isomorphous substitutions within the montmorillonite crystal lattice.

## INTRODUCTION

The ability of montmorillonite to enter into the mechanism of ion exchange is one of its most important properties. In most cases, the use for which a given montmorillonite is employed depends on the particular exchangeable ions which are present. In montmorillonite, about 80 percent of the cation exchange is attributed to lattice substitutions, and this portion of the exchangeable cations is held to the basal plane surfaces. The remaining 20 percent of exchangeable cations are reputedly held to the edges as a result of broken bonds.

Naturally occurring montmorillonite contains as exchangeable cations various amounts of sodium, calcium, hydrogen, and magnesium, and lesser amounts of other cations. Some natural bentonites contain montmorillonite carrying mainly sodium ion, while others carry mainly calcium and/or magnesium ions. One of the best known examples of a naturally occurring sodium bentonite is the clay mined in the Black Hills region of Wyoming and South Dakota. This bentonite consists of about 85 percent montmorillonite and 15 percent non-clay minerals such as quartz, cristobalite, gypsum, calcite, and feldspar.

In a given deposit of bentonite, it might be expected that the montmorillonite phase would be fairly homogeneous. It could be visualized that the ratio of the different exchangeable cations would be almost the same for all of the montmorillonite particles in a given sample. Recently, however, Byrne (1954) proposed that every montmorillonite is actually a mixed layer sequence whose component unit sheets differ from one another in chemical composition or in the presence of some minor structural irregularity. Byrne based his conclusions on the lack of regular periodicity along the *c* axis upon treating various montmorillonites with piperidine and dodecylamine. Beavers and Larsen (1953) recently reported that Wyoming bentonite exhibits several discrete

mobilities, suggesting the presence of several different compounds in the seemingly homogeneous clay.

Further support of these ideas of heterogeneity in montmorillonite has been obtained by x-ray diffraction analysis of centrifuged bentonite. The experimental results indicate that, in general, the Wyoming bentonites contain at least two different kinds of montmorillonite. Apparently one type is predominantly a sodium montmorillonite and the other is predominantly a calcium montmorillonite. These results indicate that the exchangeable cations are not randomly distributed, but may be held preferentially to different types of montmorillonite. The hypothesis is presented that the types of montmorillonite differ primarily as to the isomorphous substitution within the tetrahedral and octahedral portions of the crystal lattice.

### MATERIALS AND EXPERIMENTAL DETAILS

The bentonite samples used in this investigation were taken from clay deposits near Colony and Osage, Wyoming, and Belle Fourche and Ardmore, South Dakota. Two samples from different geological horizons were taken near Colony, Wyoming. These were from the commercial bed or Mowry formation and from the Newcastle formation.

The centrifugation of the bentonite into its various fractions was achieved in a regular batch type laboratory centrifuge operating at about 1,850 or 2,500 rpm. A slurry consisting of 3 percent bentonite was employed as the original dispersion and this was centrifuged for a period up to one hour. The various fractions were removed by decantation or by means of a pipette and retained for x-ray diffraction and exchangeable ion analysis.

The preparation of the samples for x-ray analysis was as follows: The various clay suspensions were poured onto glass microscope slides and allowed to dry slowly at room temperature. The air dried samples were then placed in a desiccator maintained at a relative humidity of 52 percent, and allowed to come to equilibrium. These "oriented" samples were run on a North American Philips High Angle Spectrometer using Ni-filtered  $\text{CuK}\alpha$  x-radiation. The relative humidity of the room in which the x-ray diffraction was carried out was maintained at approximately 50 percent so that there was no change in the spacings during the x-ray examination.

The exchangeable ions on the various samples were determined by using a slightly modified ammonium acetate method. To 10 ml of each slurry, 20 ml of 5 *N* ammonium acetate was added. This mixture was shaken on a mechanical shaking device for one hour and then centrifuged for 20 minutes at 2,500 rpm. The extract was decanted into a 250 ml volumetric flask and two more extractions made using 1 *N* ammonium acetate. The extracts were made up to 250 ml with distilled water and the sodium, calcium, and magnesium ion concentrations determined. The sodium and calcium were determined by means of a Beckman Flame Spectrophotometer. Magnesium was obtained by determining the total hardness (combined calcium and magnesium) by the stand-

ard versenate (Cheng, 1951) analysis and calculating the amount of magnesium by difference.

## DISCUSSION

The results shown in the following figures of the x-ray diffraction patterns of centrifuged bentonite demonstrate the heterogeneity in montmorillonite. From a study of these x-ray patterns, it is reasoned that these bentonites consist of aggregates of essentially calcium montmorillonite and aggregates of essentially sodium montmorillonite.

Williams, Neznayko, and Weintritt (1953) and Roth (1951) have shown that ideally at room temperature and 50 percent relative humidity, a sodium montmorillonite has a "single water layer" giving a symmetrical 001 basal spacing of 12.4A, while calcium and/or magnesium montmorillonite has a "double water layer" and a corresponding symmetrical 001 basal spacing of 15.4A. Randomly interstratified mixtures of these two clays lead to intermediate 001 values and the peaks are asymmetrical. The higher-order spacings of sodium and calcium clay are integral while the higher-order spacings for mixed layer clays are nonintegral. In the following discussion, this interpretation of the x-ray patterns has been used.

A summary of the results obtained with the various bentonites is shown in Table I. The table gives the exchangeable ions, ratio of monovalent to divalent cations, and the 001 basal spacing and its asymmetry value. It will be noted that an asymmetry value less than 1.0 indicates that the peak is broader toward a lower spacing.

A comparison of the data given in Table 1 with Figures 1 through 5 will show that all the samples studied were separated into two montmorillonites. One type, found as the upper fraction in all samples, was a sodium type. The bottom fraction in all but the Osage sample was found to be a calcium type. (Note: calcium type will be used to denote all montmorillonites containing both calcium and magnesium.) It will be noticed that the Osage sample contains as its bottom and middle fractions, a mixture of sodium and calcium types as indicated by the double peak at 12.6 and 14A. From the asymmetry values given in Table 1, it is evident that the different montmorillonites do not consist of pure sodium or calcium clay, but it is apparent that the clay is fractionated.

Isomorphous substitution within the crystal lattice of montmorillonite is generally considered to be the principal cause for its cation-exchange capacity. Indeed, it has been reported that these substitutions contribute about 80 percent of the effect while broken edges contribute about 20 percent (Grim, 1953). The isomorphous substitutions usually consist of magnesium or divalent iron for aluminum in the octahedral layer, or of aluminum for silicon in the tetrahedral layer. This creates a net negative charge within the montmorillonite plate which is in turn balanced by the positively charged exchangeable cations.

TABLE 1.—EXCHANGEABLE IONS AND X-RAY DIFFRACTION RESULTS

	Exchangeable Ions mcg/100 g			Ratio of Cations Monovalent/Divalent	X-ray Diffraction	
	Na <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>		001	Asymmetry
<i>Mowry</i>						
Composite	60	26	21	1.3	12.2	0.6
Upper Fraction	—	—	—	—	12.3	0.9
Lower Fraction	—	—	—	—	13.2, v.b. <sup>1</sup>	0.8
<i>Newcastle</i>						
Composite	40	57	38	0.6	13.8, v.b.	1.1
Upper Fraction	—	—	—	—	12.4	0.3
Lower Fraction	—	—	—	—	14.2	1.7
<i>Osage</i>						
Composite	73	29	13	1.7	12.4	0.8
Upper Fraction	—	—	—	—	12.4	0.6
Middle Fraction	—	—	—	—	12.6, 13.8 <sup>2</sup>	1.0
Lower Fraction	—	—	—	—	12.8, 13.8 <sup>2</sup>	1.0
<i>Ardmore</i>						
Composite	—	—	—	—	15.0	1.0
Upper Fraction	—	—	—	—	13.8	1.3
Middle Fraction	—	—	—	—	15.0	1.0
Lower Fraction	—	—	—	—	15.0	1.0
<i>Blended Clay</i>						
Composite	68	63	8	1.0	12.6	0.3
Upper Fraction	96	51	9	1.7	12.6	0.8
Middle Fraction	41	60	10	0.6	14.9	1.8
Lower Fraction	34	51	10	0.5	15.0	1.2

<sup>1</sup> v.b.—very broad

<sup>2</sup> Double peak

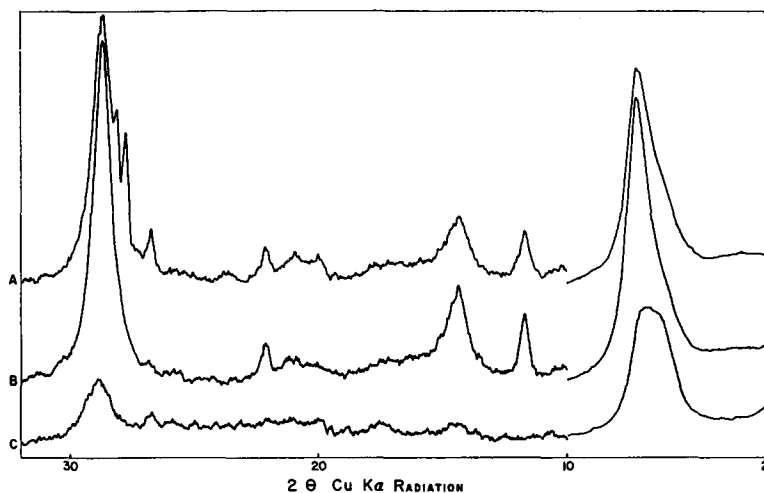


FIGURE 1.—X-ray diffraction patterns of Mowry bentonite.

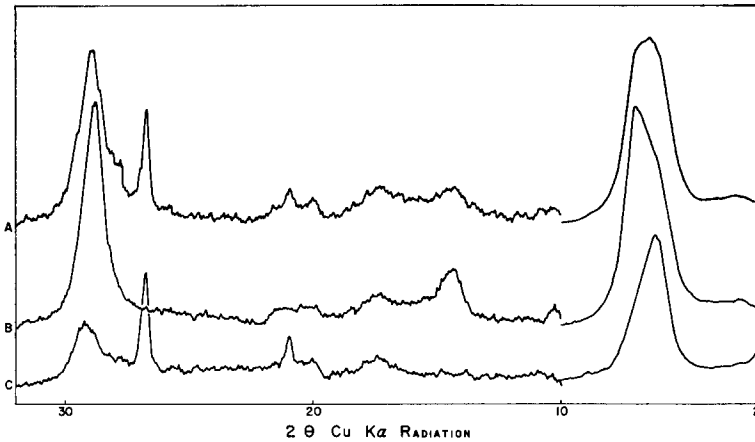


FIGURE 2.—X-ray diffraction patterns of Newcastle bentonite.

Base exchange charges resulting from substitution within the octahedral sheet of montmorillonite would have to act through a greater distance than for charges resulting from substitution within the tetrahedral sheet. It would be expected, therefore, that a given exchangeable ion would be held more tightly in the latter case.

The nonexchangeable character of potassium in the micas is an example of a stronger bond due to tetrahedral substitution of aluminum for silicon. Furthermore, Marshall (1949) has shown that, for alkali cations and for constant concentration of cations, montmorillonite has a higher degree of ionization than illite. The difference in these bonding energies is at least in part due to the fact that the base exchange charge in the illite is almost entirely associated with substitution in the tetrahedral layer while generally the charge in the montmorillonite results from substitution within the octahedral layer.

Many studies of the replaceability of exchangeable cations on montmorillonite (Grim, 1953) have shown that  $\text{Ca}^{2+}$  will more easily replace  $\text{Na}^+$  than  $\text{Na}^+$  will replace  $\text{Ca}^{2+}$ . In other words, for a given clay under given conditions, the base exchange bond between a montmorillonite plate and a calcium ion is stronger than that with a sodium ion. Again, considering the greater strength between a base exchange cation with a tetrahedrally substituted montmorillonite plate than with an octahedrally substituted montmorillonite plate, it is evident that one of the strongest base exchange bonds would be between a calcium ion and a tetrahedrally substituted montmorillonite. If, therefore, there occurred a mixture of montmorillonites, one fraction owing its base exchange mainly to octahedral substitution and the other to tetrahedral substitution, it would be expected that the calcium and magnesium ions would preferentially go to the tetrahedrally substituted fraction.

Williams, Neznayko, and Weintritt (1953) demonstrated that if there are excess ions present in a bentonite-water system, the divalent ions (calcium and

magnesium) would be associated with the clay base exchange spots while the sodium ions would be in the "free state" in the water phase. Upon drying this system, the divalent ions would be removed from the clay since the calcium and magnesium sulfate and carbonate salts are more insoluble than the corresponding sodium salts. Due to the removal of the divalent ions from the system, the sodium ions would become associated with the bentonite plates and the resulting clay would be a sodium montmorillonite. A further illustration of this monovalent-divalent equilibrium is demonstrated in Figure 6. The upper curve shows the x-ray pattern of a Wyoming bentonite which was dispersed in water and then dried at room temperature. The lower curve shows the same clay after filtering and washing it free of soluble salts with distilled water and then drying the clay at room temperature. It can be seen that the clay dried without removing the soluble salts, produced an x-ray pattern typical of a sodium-type clay, i.e., a basal spacing of 12.4A; while the washed clay gave a basal spacing of 14.9A for a calcium-type clay. The original exchangeable ion data for this particular clay are shown in Table 1 under "Blended Clay Composite." This clay has a base-exchange capacity of 82 meq/100 g clay; therefore, since there are only a total of 71 meq divalent ions present, it would be expected that the soluble salt-free clay would contain about 15 percent sodium ions; this compares very favorably with the basal spacing of 14.9A.

Recognizing the effect of the soluble salts on the interpretation of the x-ray diffraction patterns of the fractionated clays, all the samples taken for x-ray

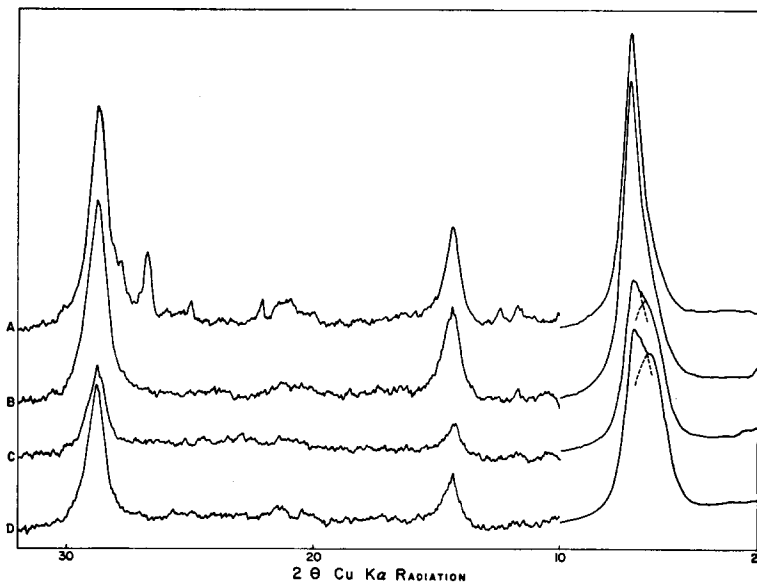


FIGURE 3.— X-ray diffraction patterns of Osage bentonite.

diffraction were of approximately equal volumes. By this means, the number of cations that were not associated with the clay but were "free" in the water phase were kept approximately equal for all fractions.

The x-ray diffraction patterns shown in Figures 1 through 5 and the data in Table 1 demonstrate that the exchangeable cations on these samples are preferentially situated on different clay particles.

Figure 1 shows the x-ray patterns for the several fractions obtained from a sample of clay from the Mowry formation near Colony, Wyoming. The principal component of this clay was an almost pure sodium clay (basal spacing of 12.3A) with a second montmorillonite which was removed by centrifugation and gave a very broad basal spacing of 13.2A, indicating about 50 percent sodium and 50 percent calcium ions on the dried clay.

The Newcastle bentonite mined from the Newcastle formation near Colony, Wyoming, also separated into two montmorillonites (Fig. 2). The major fraction yielded a basal spacing of 12.4A while the minor fraction gave a basal spacing of 14.2A.

Upon centrifugation of the Osage bentonite, it was found that the main fraction was a sodium type with a basal spacing of 12.4A (Fig. 3). The middle and lower fractions of this clay gave an oriented x-ray pattern indicating a mixture of two montmorillonites, one with a basal spacing of 12.6A and the other with a basal spacing of 13.8A. This may indicate that the sodium type (12.6A) material found in the middle and lower fractions of the centrifuge tube is of a larger particle size than that which remained in the upper fraction or it may be only an effect of the soluble salts.

The Ardmore clay (Fig. 4), a naturally occurring Wyoming calcium clay, was found to separate into a minor fraction which upon drying gave a basal spacing of 13.8A and a major fraction with a basal spacing of 15.0A.

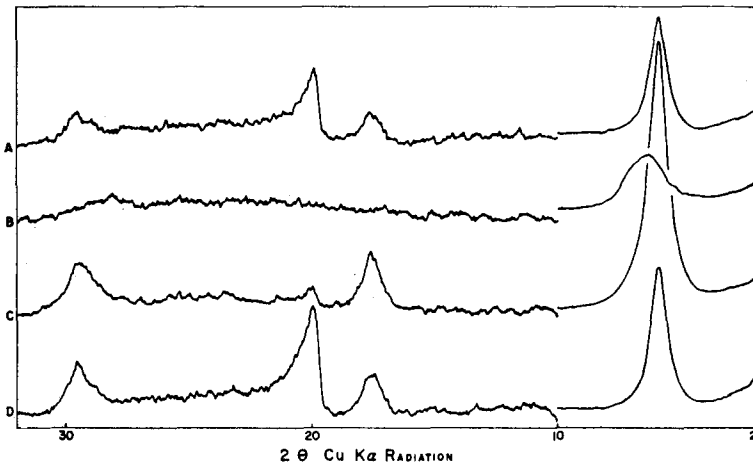


FIGURE 4. — X-ray diffraction patterns of Ardmore bentonite.

X-ray diffraction patterns (Fig. 5) obtained from the various fractions of the blended clay (approximately equal amounts of Mowry and Newcastle clay) showed basal spacings of 12.6Å and 15.0Å. The major fraction was found to give a basal spacing of 12.6Å. The exchangeable ion data given in Table 1 for the blended clay in general substantiate the x-ray data. It can be seen that the upper fraction is a sodium type, while the middle and lower portions are calcium types. Owing to the presence of soluble salts, the main consideration here must be based on the ratio of monovalent to divalent cations. Equal volumes of each fraction were used in the exchangeable ion determination so as to minimize the effect of the soluble salts.

Two different systems can be proposed to explain the x-ray diffraction data: The natural clay may be homogeneous or heterogeneous with respect to the cation distribution.

If the bentonite is a homogeneous material as it is mined, then a redistribution of the base-exchange cations takes place when the clay is dispersed in water. This redistribution possibly takes place as discussed previously, in that the calcium ions tend to go to plates that have their base-exchange charges originating from tetrahedral replacements, while the sodium will remain associated with plates that have their base-exchange charges originating from octahedral replacements. The predominantly calcium montmorillonite phase will then be separated from the "sodium clay" owing to its more highly flocculated condition and larger number of associated plates.

The second system which can be considered to explain the x-ray patterns

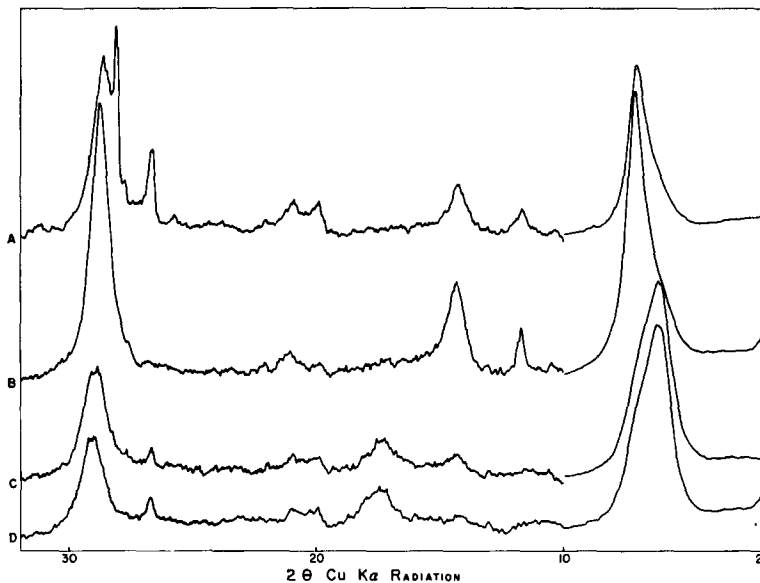


FIGURE 5.—X-ray diffraction patterns of blended clay sample.

is that the original clay is heterogeneous or contains discrete particles of essentially sodium montmorillonite and particles of essentially calcium montmorillonite. One way in which this can be visualized is that the cation distribution of the original clay was completely random and the clay was homogeneous. Upon weathering, the calcium ions that were associated with plates having octahedral base exchange positions would be removed from the clay to form insoluble carbonates at a much greater rate than the calcium ions associated with montmorillonite plates having tetrahedral base exchange positions. This would then result in a heterogeneous system.

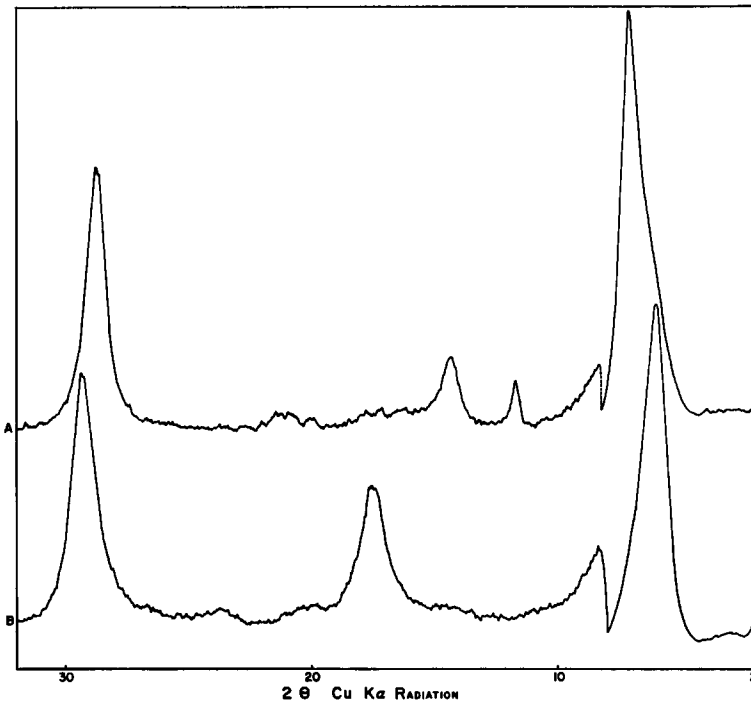


FIGURE 6. — X-ray diffraction patterns of dried “as received” bentonite (A) and “soluble salt free” bentonite (B).

It is believed that these examples demonstrate the heterogeneous nature of montmorillonite. This evidence, coupled with that of Byrne (1954) and Beavers and Larsen (1953), shows the necessity of carefully selecting the bentonite used for various studies on this clay mineral. Unless the bentonite is adequately cleaned by centrifugation or sedimentation, a heterogeneous material will be involved and invalidate much of the data obtained. Careful selection, treatment, and analysis of a starting bentonite will help one to explain logically the many different types of experimental results which can be obtained by

studying this valuable clay. The heterogeneous nature of the "as received" bentonite very likely can be used to explain many of the peculiar and unexpected results that have been obtained in bentonite experiments.

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