STRUCTURAL CHARGE DENSITY AS INDICATED BY MONTMORILLONITE HYDRATION

by

EDWARD C. JONAS
The University of Texas, Austin

and

HERMAN E. ROBERSON
Harpur College, Binghamton, New York

ABSTRACT

A SODIUM-SATURATED Texas bentonite was fractionated into six particle-size ranges. The expansion of each fraction was observed by X-ray diffraction under controlled humidity conditions ranging from 0–100 per cent r.h. At all humidities, the fine fractions expanded more than the coarse. A single size fraction expands through a series 10 Å, 12.4 Å and 15.5 Å. The expansion from 10–12.4 Å occurs at progressively lower relative humidities for smaller size fractions in the same way as the expansion from 12.4–15.5 Å. The gradation from high resistance to expansion in the coarse fractions to low resistance to expansion in the fine fractions appears to be continuous.

Interlayer cation density, which controls the resistance to expansion, is dependent upon the structural charge density on the silicate layer. The continuous variation of resistance to expansion that is a function of particle size is interpreted to indicate a corresponding continuous variation in structural charge with particle size.

INTRODUCTION

STATEMENTS about the inhomogeneity of montmorillonite have appeared from time to time in the literature. Roth (1951), Byrne (1954), McAtee (1958), Johns and Tettenhorst (1959), and Roberson (1964) have cited definite indications that not all of the layers in bentonitic montmorillonite are identical. By particle size fractionation, McAtee (1958) succeeded in separating a coarse fraction that had mainly Ca-exchange ions from a fine fraction that had mainly Na-exchange ions. Because his size fractionation was made on a natural Ca-Na–bentonite he reserved judgement on exactly what he was separating. Both fractions could possibly consist of identical layers, some of which had Ca-exchange ions and therefore produced large flocs that made up the coarse fraction, and others with Na-exchange ions produced smaller flocs that made up the fine fraction. Because of the well-known flocculation effects of Ca it seemed reasonable that Ca should be concentrated in the coarse fraction—provided the particles being separated were flocs. On the other hand, McAtee felt that it was equally likely that he was separating silicate layers that differed in such a way as to make those in the coarse fraction prefer Ca and those in the fine fraction prefer Na.

A second suggestion of inhomogeneity in the silicate layers of montmorillonite appeared in Gillery's (1959) data on the expansion of homo-ionic clays. With increasing relative humidity (r.h.), his clays showed greater and greater hydration. Between two distinct hydration levels, there was an r.h. range through which mixed-layer diffraction occurred. At these r.h. values some of the layers were expanding to one hydration level and some to another. These layers all had the same exchange ion and therefore had to differ in their compositions. Differences in expansion of two silicate layers with the same exchange cation under the same hydration conditions have traditionally been considered to indicate differences in their compositions. For example, K-montmorillonite expands with ethylene glycol, whereas illite with interlayer potassium does not because of their differences in composition within the silicate layers. Gillery's (1959) mixed hydration levels suggest that inhomogeneities in the composition of the silicate layers of some expanding clays do exist. Layer composition differences can result in differences in surface charge density, and it is the surface charge density differences that produce the differences in expansion.

In this paper we are attempting to elaborate on the nature and distribution of these inhomogeneities in bentonitic montmorillonites.

TECHNIQUE

A bentonitic montmorillonite from Eocene sediments in Karnes County, Texas, was selected because it was suspected from preliminary tests of having a broad particle-size range. In the natural state, the exchange ions were predominately Ca and Mg. All of the layers expanded uniformly with ethylene glycol.

The interlayer cations were all changed to Na by suspending the sample in 2 N NaCl. The solution was renewed once, and the sample was washed with water until Cl^- free. A portion of the clay suspension was leached with 2 N NH_4Ac to extract the exchange ions. The NH_4Ac solution was analyzed by flame photometer and found to contain no detectable Ca or Mg. The main portion of the whole suspension was fractionated in a high-speed centrifuge into six fractions ranging from $>4\mu$–$<0.2\mu$. The two coarsest fractions were discarded because they contained crystalline impurities. Equivalent spherical diameter (e.s.u.) ranges were assigned to each fraction based on Hauser and Reed's (1939) modification of Stokes' law. No particular significance should be placed on the e.s.u. values. In addition to those factors of Stokes' law that are difficult to evaluate, fractionation of montmorillonite almost certainly involves variable flocculation, even when only one exchange cation is present. One can only be sure that the coarser size fractions contain particles (however they are constituted for settling) of larger size than smaller size fractions. The quantities of clay collected in the coarser fractions were compared with similar data from a standard pipette analysis and found to agree. The centrifuge technique does not seem to introduce any new uncontrollable factors that are not inherent in the pipette analysis.

Care was taken to collect only particles that belonged within the proper fractions. It should be remembered, however, that each fraction necessarily contains a range of particle sizes. The ranges of each fraction are considerably smaller than those of the entire sample, but they are still large enough to allow variations in the characteristics of particles collected in them.

From each fraction, oriented aggregates of equal weight of clay were prepared. The slides were stored in large desiccators for at least 24 hr over saturated salt solutions, which give the desired relative humidities. The slides were then transferred to an enclosed flat sample holder on the diffractometer (Messina, 1964). Air of the same relative humidity was being blown into the enclosure during the entire diffraction pattern registration. Patterns were registered several times in order to make sure that the clay was at equilibrium with the controlled atmosphere. Whenever changes in the controlled atmosphere occurred, the clay changed hydration levels quite rapidly.

RESULTS AND DISCUSSION

Grim (1953) has suggested that three factors control the expansion of montmorillonite layers:

1. Nature of the exchange cation.
2. Surface charge density at the interlayer site. It is this charge that will be referred to as the structural charge density to distinguish it from the total charge density which includes any edge charge.
3. Strength of the solvating or expanding forces.

Table 1 is a compilation of the periodicities of each fraction of the Texas bentonite equilibrated with each relative humidity. A single-size fraction, for instance C, expands progressively from the zero-layer hydrate up to the two-layer hydrate as the relative humidity increases. This is to be anticipated from Gillery's (1959) results. Each fraction has its own characteristic stability range of relative humidities for each hydrate. Fraction E shows some evidence

TABLE 1.—EXPANSION OF FRACTIONATED MONTMORILLONITE AT VARIOUS RELATIVE HUMIDITIES

Fraction	Size range e.s.u. in μ	% Relative humidity							
		100	90	80	60	40	20	10	0
B	1–2	15.5	14.8	13.2	12.4	12.4	12.4	11.8	9.7
C	0.5–1	15.5	15.0	14.0	13.2	12.4	12.4	11.8	9.7
D	0.2–0.5	15.5	15.5	15.0	13.2	12.4	12.4	12.4	9.7
E	<0.2	15.5	15.5	15.5	15.0	13.2	12.4	12.4	9.7

of the two-layer hydrate at 40 per cent r.h., whereas fraction B shows no tendency to expand to the two-layer hydrate even with the greater expanding force at 60 per cent r.h. The finer size fractions all tend to hydrate to a higher level than the coarser fractions under the same relative humidity conditions.

Fig. 1 is a plot of the approximate apparent basal spacings at each relative humidity for all four size fractions. The r.h. range over which fraction E maintains the two-layer hydrate is much greater than that for fraction C or B. This can probably be attributed to the fact that 100 per cent r.h. is the maximum expanding force available. Fraction B would probably remain at the two-layer hydrate under more forceful expanding conditions, whereas fraction E would tend to take a more expanded form. Similarly, the r.h. range for the one-layer hydrate shifts to lower values for finer size fractions.

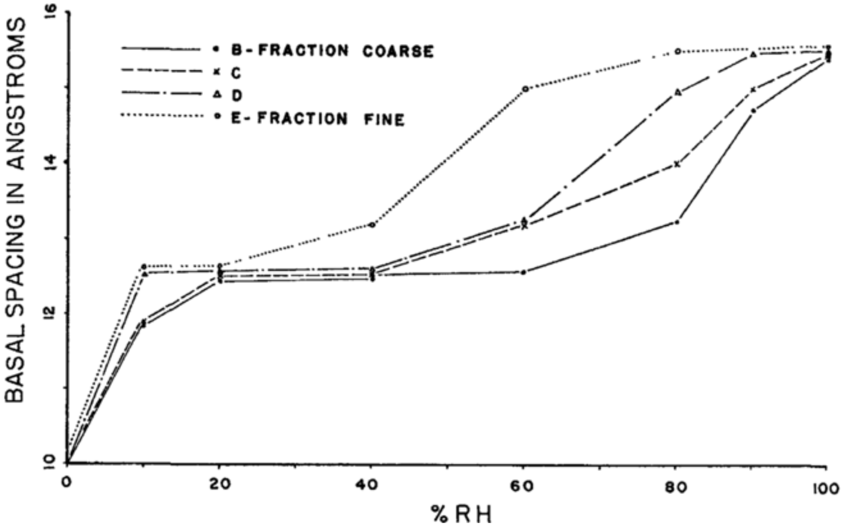

FIG. 1. Apparent basal spacing increase with increasing relative humidity for size fractions of a Texas bentonite.

The increasing relative humidity corresponds to a continuously increasing strength of the expanding force. Because the exchange ion is uniformly Na, at any one relative humidity, it can be considered that layers that do not expand have a higher structural charge density than those that do expand. Fortunately the range of 0–100 per cent r.h. is an ideal expansion force range to detect variations in montmorillonite structural charge. The expanding forces produced by some liquids are so strong as to expand all layers indiscriminately, e.g. ethylene glycol, which does discriminate in exactly the same way except at a much higher level of interlayer binding force between montmorillonite and illite. The higher level of binding force for illite is, of course, the result not only of its higher structural charge density but also of its interlayer K instead of Na.

Bradley, Weiss, and Rowland (1963) prepared a Na-saturated vermiculite for an X-ray diffraction analysis. They report a stable one-layer hydrate at about 40 per cent r.h. and a two-layer hydrate near 100 per cent r.h. Van Olphen (1963) shows the desorption isotherm for a large crystal of a Na-vermiculite with an extremely short intermediate r.h. range in the transition from the one-layer to the two-layer hydrate. This intermediate range is at approximately 40 to 50 per cent r.h., indicating that the vermiculite structural charge density is larger than that of the silicate layers in the fine fraction of the Texas bentonite but smaller than that of some of the layers in the coarse fractions. The inferior colloidal properties of Texas bentonites may be the result of a high structural charge density. On the other hand, comparison of the structural charge densities as indicated by the swelling properties of two vastly different minerals (montmorillonite and vermiculite) is much more tenuous, even when they both have the same exchange ion, than the comparison being drawn in this paper between two size fractions of the same mineral. Compositions of the individual layers within the bentonitic montmorillonite should be similar with only enough variation to result in a structural charge variation.

At critical r.h. values, some of the layers within a single size fraction will expand and some will not. However, the average expansion level expressed by the apparent basal spacing for the coarse fraction is always lower than for the fine fraction. Just as the particle size range is much more limited within a fraction than it is in the whole sample, so the structural charge density is more limited. The finest fraction, E, which contains particles with an e.s.u. less than 0.2μ, probably contains some particles that are very much smaller than the largest particle in the fraction. The range of relative humidities over which there is interlayer mixing of two periodicities is correspondingly wide. If sufficiently narrow-ranged particle size fractions could be separated, the intermediate (two periodicity) r.h. ranges would disappear. The layers of each fraction would either all expand or all not expand. The Na-saturated vermiculite studied by Van Olphen (1963) was all coarse-grained and showed very little tendency to develop stable hydration levels that were intermediate between the one-layer and two-layer hydrates.

Essentially, there appears to be a continuous variation in the structural charge density of layers within this bentonitic montmorillonite. The layers in the coarse fraction have a high structural charge density, whereas those in the fine fraction have a low structural charge density. This is essentially a continuation of the well-accepted trend set up by layer silicates that have a greater difference in composition and structural charge. Mica occurs in very large crystals and has a high structural charge density. Illite occurs as much smaller crystallites and has a lower structural charge density. Montmorillonites, in general, have still lower structural charges and are considerably finer grained.

The exact nature of the particles that are being separated is still unclear. If they were individual crystals and our Stoke's law calculations were valid, the larger fractions should contain easily recognized crystalline units in electron micrographs (1–2μ). These large crystals were not detected. The other obvious possibility is that the particles are flocs. The degree of flocculation is closely dependent upon the exchange ion composition, but because only Na ions are present in this experiment, all the flocs should be uniform in size unless there were silicate layer differences.

In another series of experiments conducted on this same fractionated montmorillonite, the quantities of Na and Ca exchanged on the various fractions when they were equilibrated with identical solutions containing both Na and Ca were measured. The details of this study will be reported elsewhere by Roberson, but it should be pointed out here that the coarse fraction adsorbed more Ca than did the fine fraction. This suggests that McAtee's (1958) fractionation of a Na–Ca montmorillonite was made on the basis of the same characteristic that controlled the fractionation of the Na-saturated Texas montmorillonite used here. Ca was associated with those layers that belong to the coarse fraction simply because those layers had the greater capacity to collect Ca than layers in the fine fraction. The layers of the fine fraction were left with the Na exchange. This is to say that layers with high structural charge density will develop larger flocs than layers with low structural charge density regardless of the exchange cation.

Jonas and Roberson (1960) have demonstrated that the reduction of size of a very coarse-grained layer silicate will reduce its ability to resist expansion. The size reduction was carried out by grinding in an effort to produce no change in structural charge density. The change in expansion properties was attributed to the reduction in the total number of interlayer ions binding adjacent silicate layers because of the reduction in flat-flake area. Individual crystallites that were large enough to be affected in size by grinding are in distinct contrast with the particles of the Texas bentonite that are being fractionated. The bentonitic montmorillonite particles being separated are almost certainly flocs of extremely small crystallites. The range of size of individual crystallites is probably not nearly so great as the range of size of crystallites produced by the grinding operation. In addition to this, the demonstration of a difference in exchange cation selectivity between size fractions strongly suggests a difference in the character of the exchanging surface.

Fig. 2 shows the variations in diffraction patterns of the several fractions at one relative humidity. The coarse fraction has only partially expanded to the two-layer hydrate, while the finest fraction has a completely developed 15.5 Å peak showing the full two-layer hydrate. A part of the difference in intensity in this sequence probably results from better orientation of the crystals in the fine fraction, but there is an over-riding tendency for the intensity from a single slide to increase whenever all the layers expand to the same level, and the peak becomes sharp. In other words, these fractions show

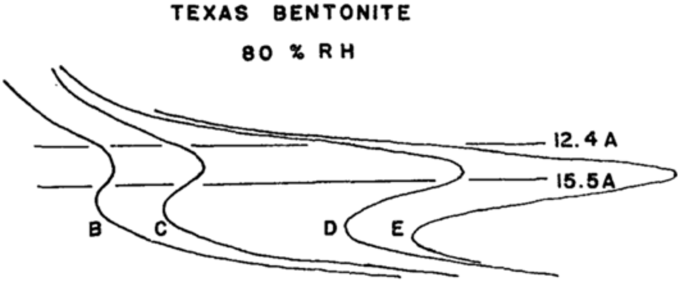

FIG. 2. First order basal reflections from the size fractions of a Texas bentonite showing less expansion in the coarse (B) fraction than in the fine (E) fraction. All fractions give diffraction typical of interlayer mixtures.

ideal characteristics of the random interlayer mixing of two periodicities. Each crystallite of this clay must be composed of layers that have different compositions.

This is to be compared with a pattern of an intermediate hydration level for Wyoming bentonite shown in Fig. 3. This curve indicates an ordinary mixture of two periodicities. The differences in composition of layers from this montmorillonite occur only in layers of different crystallites. All the layers of one crystallite have a relatively uniform composition.

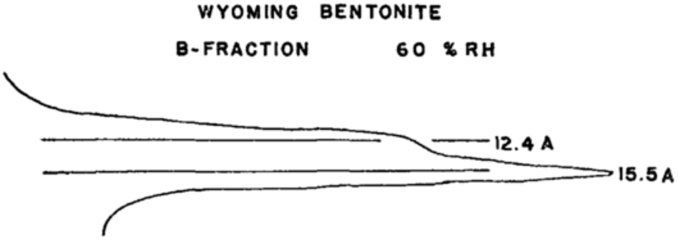

FIG. 3. First order basal reflection from a coarse size fraction of a Wyoming bentonite. Diffraction is typical of an ordinary mixture of particles expanding to two different hydration levels.

CONCLUSIONS

Size fractionation of bentonite suspensions separates silicate layers in the coarse fraction that expand less readily than those that are in the fine fraction. This reluctance to expand suggests that those layers in the coarse fraction have a high structural charge density. The high structural charge density results in their tendency to aggregate into large flocs. There appears to be a continuous variation in structural charge density in bentonitic montmorillonites. Layers of different structural charge density occur within a single crystallite of the Texas bentonitic montmorillonite. In the Wyoming bentonitic montmorillonite each crystallite consists of layers of only one structural charge density, but different particles have layers with different structural charge densities.

REFERENCES

BRADLEY, W. F., WEISS, E. J., and ROWLAND, R. A. (1963) A glycol-sodium vermiculite complex, *Clays and Clay Minerals*, 10th Conf. [1961], pp. 117–22, Pergamon Press, New York.

BYRNE, P. J. S. (1954) Some observations on montmorillonite organic complexes, *Clays and Clay Minerals*, Natl. Acad. Sci.—Natl. Res. Council, Publ. 327, pp. 241–53.

GILLERY, F. H. (1959) Adsorption–desorption characteristics of synthetic montmorillonoids in humid atmospheres, *Am. Mineralogist* **44,** 806–18.

GRIM, R. E. (1953) *Clay Mineralogy*, McGraw-Hill, New York.

HAUSER, E. A., and REED, C. E. (1939) Development of a new method for measuring particle size distribution in colloidal systems, *J. Phys. Chem.* **40,** 1169–73.

JOHNS, W. D., and TETTENHORST, R. T. (1959) Differences in montmorillonite solvating ability of polar liquids, *Am. Mineralogist* **44,** 894–6.

JONAS, E. C., and ROBERSON, H. E. (1960) Particle size as a factor influencing expansion of the three-layer clay minerals, *Am. Mineralogist* **45,** 828–38.

McATEE, J. L. (1958) Heterogeneity in montmorillonite, *Clays and Clay Minerals*, Nat. Acad. Sci.—Nat. Res. Council, Publ. 566, pp. 279–88.

MESSINA, M. L. (1964) Expansion of fractionated montmorillonites under various relative humidities, *Clays and Clay Minerals*, 12th Conf. [1963], pp. 617–32, Pergamon Press, New York.

ROBERSON, H. E. (1964) Petrology of tertiary bentonites of Texas, *J. Sediment. Petrol.* **34,** 401–11.

ROTH, R. S. (1951) The structure of montmorillonite in relation to the occurrence and properties of certain bentonites: Ph.D. Thesis, University of Illinois.

VAN OLPHEN, H. (1963) Compaction of clay sediments in the range of molecular particle distances, *Clay and Clay Minerals*, 11th Conf. [1962], pp. 178–87, Pergamon Press, New York.