PARTICLE SIZE AS A FACTOR INFLUENCING EXPANSION OF THE THREE-LAYER CLAY MINERALS

Edward C. Jonas, *The University of Texas, Austin, Texas,* and Herman E. Roberson, *Harpur College, Endicott, New York.*

Abstract

Expansion properties of three-layer clay minerals are the result of an interaction between a binding force, which acts from particle to particle through interlayer cations, and an expansion force created by the adsorption of liquid molecules on interlayer surfaces. The binding force between two particles is a function of the charge density on the interlayer surfaces and the areal extent of the particles. The influence of areal extent of the particles on expansion properties is studied in a comparison between two size fractions of a single sample and between two samples before and after grinding. Fine fractions always contain more expanding layers than coarse fractions. Ground samples always expand more completely than unground samples. It was concluded that mica layers with a high surface charge density can expand provided they have a sufficiently small particle size. There is no simple correlation that can be made between charge density (or silicate composition) and expansion properties.

Introduction

Expansion is a property of the three-layer clay minerals which may be easily measured with diffraction techniques. Expansion in response to a prescribed treatment has commonly been used to make a distinction between two clay mineral groups, the illites and the montmorillonites. It has been generally accepted that minerals of the montmorillonite group are characterized by lower Al^{+3} for Si^{+4} tetrahedral substitution and/or lower octahedral substitution than are minerals of the illite group. A two-fold classification of these clay minerals has resulted: illites having highly charged silicate layers that do not expand when soaked in ethylene glycol, and montmorillonites having relatively low-charged silicate layers that do expand under this treatment. This classification is thought to be based on compositional variations in the silicate layers.

There is no reason to believe that the degree of isomorphous substitution is not a continuous variable in the clay minerals, ranging from a minimum in the clay equivalent of the talc-pyrophyllite minerals to a maximum in the clay muscovite-biotite minerals. If expansion is truly related to the charge on the silicate layer and the charge is controlled by isomorphism, then expansion properties should be viewed as a continuous variable. With this concept of the three-layer clay minerals in mind, the wisdom of basing a two-fold classification on expansion properties becomes doubtful. It has become apparent (Walker, 1957; Weaver, 1958b) that this two-fold classification *is* artificial and that the three-

layer clay minerals actually do exist as a continuous series of silicate layer charges. Furthermore, Walker (1958) has shown that a single specimen varies markedly in its expansion depending on the manner in which this property is tested. It is therefore important to understand all fundamental attributes of a clay layer which will control its tendency to enter into expansion.

FUNDAMENTALS OF CLAY EXPANSION

Expansion in three-layer clay minerals is an interaction between two forces. On the one hand, liquid molecules adsorbed onto the oxygen surface of the silicate layer require space between the layers and act through their adsorption forces as a lever to pry the layers apart. Their effectiveness in separating the silicate layers is determined by the strength of this adsorption force. On the other hand, this tendency of the adsorbed liquid molecules to separate the silicate layers is resisted by binding forces exerted through whatever charged interlayer material is present. Expansion occurs when the adsorbed liquid molecules exert a separating force which exceeds the binding force acting through the interlayer material between the silicate layers. The layers remain unexpanded when the binding force exceeds the separating force.

At this point it should be mentioned that the liquids commonly used to expand the clay minerals vary widely in the strength of their adsorption onto the silicate surface. Walker (1958) and Johns and Tettenhorst (1959) have shown that some clay layers that cannot be expanded with glycerol will expand when soaked in ethylene glycol. In the authors' laboratory, diethylene glycol monoethyl ether has been placed in the solvation strength series below ethylene glycol and above water by the observation that clay layers not expanded by water can be expanded by either diethylene glycol monoethyl ether or ethylene glycol, and those not expanding with either ether or water can be expanded by ethylene glycol.

The binding force between silicate layers is a result of a coulombic attraction between the negatively charged silicate layer and the positively charged interlayer ions. The negative charge on the silicate layer originates with isomorphism. Assuming that each negative charge on the silicate layer is neutralized by a singly charged interlayer cation, the binding force should be proportional to the number of interlayer cations per layer. This number of interlayer cations would be, in turn, equal to the product of the charge per unit area of surface (charge density) and the areal extent of each particle. Figure 1 is a graph showing a possible relationship among these three variables. The binding force is an increasing function of charge density. When charge density is low,

the effect of particle size on the binding force is small. For silicate layers that are more highly charged, the particle size exerts a strong control over the binding force acting between two silicate layers.

Assuming that there is a possible continuously varying charge on the silicate layer, hence a continuously varying number of cations between layers of a given size, it seems reasonable to consider that there would be natural clays with all possible interlayer binding strengths. For particles of uniform surface charge density, the binding force would vary directly with surface area of the particle.
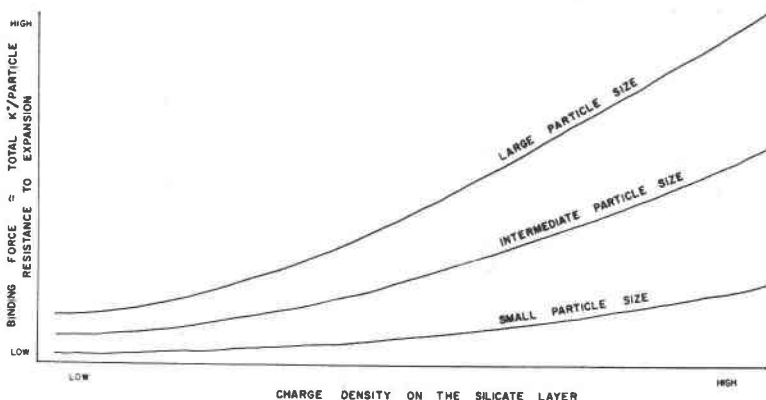

FIG. 1. A proposed relationship between resistance to expansion in three-layer clay minerals and charge density for varying particle size layers.

Besides being dependent on the number of interlayer ions, the binding force also depends on the *character* of the interlayer ions. There are in the literature numerous references to expanding three-layer clay minerals which will exchange potassium, contract to a 10 Å spacing, and resist expansion with water and ethylene glycol (Weaver, 1958a; Walker, 1950). The fact that many micaceous clay minerals will expand with Ca^{+2}, Mg^{+2}, or Na^{+1} as the interlayer ion but become non-expanding when K^{+1} occupies the interlayer position suggests that the binding force through potassium ions is much stronger than that through these other ions. Other clays can be supplied with an excess of K^{+1} to neutralize all of the charge sites and still never gather enough binding strength to develop a force sufficiently strong to prevent expansion with water. For these clays it has been assumed that the particles have a low charge density resulting from a low degree of isomorphous substitution, and therefore the number of potassium ions necessary to neutralize the charge deficiency on the clay particles would be so small as to preclude a

binding force of sufficient strength to render the layers non-expanding. However, it might also be argued that particles with high charge densities having very small areal dimensions would exhibit identical expansion properties after potassium saturation as particles with low charge densities. (See authors' scheme in Fig. 1.)

It may also be proper to assume that in any one natural sample there is a wide distribution of particle sizes. If this be the case, it is expected that particles in spite of having a uniform charge density would exhibit various expansion characteristics.

In dealing experimentally with a system in which there are many variables, the effects of one of the variables can only be viewed under conditions designed to hold the remainder of the variables constant. The variables which determine the expansion of a clay layer are (1) charge density on the silicate, (2) character of the interlayer ion, (3) the adsorbed liquid, and (4) the areal extent of the layer.

Charge density on the silicate layer can be eliminated as a variable if expansion properties are compared only on samples of a single clay mineral that has been variously treated in the laboratory. It must be assumed that the silicate layers are not altered in composition by the mild chemical laboratory treatments and therefore are not changed in charge density. The interlayer ion can be kept from varying by saturating all of the samples with K^{+1} before expansion properties are measured. If expansion properties among the variously treated samples are compared with only one solvating liquid, the effects of non-uniform adsorption forces can be avoided. These were the conditions selected to study the effect of particle size variation on the expansion of three-layer clay minerals, in the belief that they effectively held all the other controlling variables constant.

Procedure

The samples examined in this study were selected because their physical properties and chemical compositions were such that an induced change in particle size would possibly result in strikingly different expansion characteristics. It can be seen from Fig. 1 that only the relatively small particle size material is expanding when the layer charge has a high density; therefore, it would be of little value to grind a coarse-grained, well-crystallized mica or illite in an effort to produce an expanding material. The severe grinding necessary to reduce large particles to particles small enough to expand would have a tendency to damage the structure. Likewise, there would be little value in reducing the particle size of material with a low charge density. The resistance to expansion would already be low and would vary little with particle size. Size reduction would be unlikely to yield observable differences in expansion properties.

The authors have been particularly fortunate in having available for study two samples which are thought to have none of the undesirable properties just described. One sample (0–13) was selected because it was discovered that a great deal of the $<2\mu$ fraction is composed of a three-layer 15 Å clay mineral which will expand to 17 Å after ethylene glycol solvation and will also contract to a non-expanding 10 Å spacing after being treated with a 1 N KCl solution. It was reasoned that this expanding mineral could be characterized by a high charge density and a relatively large particle size. However, it should be pointed out that the expanding material in the 0–13 sample differs from illite (10 Å, non-expanding, K^{+1} irreversibly held in the interlayer position under normal laboratory ion exchange experiments) in that the 0–13 sample probably consists of particles which are smaller and/or possess a somewhat lower charge density. This may be suggested in view of the fact that the 15 Å material in the 0–13 sample, after having been rendered non-expanding by potassium saturation, may be re-converted into the expanding form by exchanging Ca^{+2} for K^{+2} in the interlayer position. This suggests a lower binding force through potassium for the material in the 0–13 sample than for normal illite. Material in the 0–13 sample could be ground while still in the expanded state as highly charged single layers of considerable areal extent. It is thought that size reduction by short-time grinding can be accomplished without severe damage to the silicate layer structure.

The other sample selected for study was an Ordovician metabentonite (8-ONY) of which the $<2\mu$ fraction is composed of approximately 80 to 90 per cent non-expanding layers and 10 to 20 per cent interstratified expanded layers. It was anticipated that short-time grinding of this sample would reduce the size of some of the particles to such an extent that they would no longer remain non-expanding after potassium saturation.

Recognizing that the individual particles of the 0–13 sample must cover a wide range of sizes, they therefore must possess varying total charges and binding forces. It was reasoned that separation of fine particles from relatively coarser ones might enable one to observe differences in expansion qualities. Following Hathaway's (1956) formula for centrifugal size separation, two size fractions ($1–2\mu$ and $<.5\mu$) were obtained. Separation of the natural sample into various size grades appeared to be a direct experimental approach to study the effect of particle size on expansion properties. Three problems detract from the utility of the data gathered from a size fractionation sequence and, in the authors' opinion, make the conclusions drawn from the data only tentative. These three problems are: (1) It is highly probable that all particles of a

specimen are never completely dispersed and that the size fractionation may be only a measure of the aggregate size instead of the size of the individual particle; (2) the composition of the particles may not remain constant through all the size grades, thus introducing a new uncontrolled variable; and (3) the character of the adsorbed ions, which have been shown to vary with the particle size fraction (McAtee, 1955; Roberson, 1959), would undoubtedly influence the expansion characteristics of the particles. With these difficulties in mind, it was decided that careful grinding over a short period of time would introduce fewer complications than size separations and would provide greater confidence in the experimental relationships observed.

Several attempts have been made to determine changes in physical properties which may be brought about by grinding clay minerals. Most of these investigations have been concentrated on measuring changes in the ion exchange capacity of clays after severe grinding. Kelley and Jenny (1936) have shown that the ion exchange capacities of muscovite, biotite, kaolinite, and montmorillonite may be greatly increased by grinding from 48 to 72 hours. Others (Laws and Page, 1946; Perkins, 1948; MacKenzie and Milne, 1953) have shown not only that the ion exchange capacities can be increased by grinding but also that long-time grinding seriously damages the structure of muscovite and kaolinite. The great increase in ion exchange capacity is attributed to the fact that grinding causes a decrease in particle size, an increase in surface area, and an increase in the number of broken bonds at particle edges. There appears to have been little attention directed toward detecting changes in the expansion properties of micaceous clays caused by short-time grinding.

Specimens weighing 0.50 grams were dispersed in a small volume of water and ground in a Bakelite capsule of a Wig-L-Bug. Wet grinding was preferred over day grinding because it was reasoned that particles in a disaggregated state would be thinner and more effectively reduced in size than thick packets of layers in the dry state. It also is possible to maintain a low temperature during wet grinding. The Wig-L-Bug was thought to be the best means of reducing the particle size without damaging the structure because grinding is effected by impact instead of shear, as produced by grinding with a mortar and pestle. The only apparent disadvantage of this grinding technique is the dilution of the clay by the addition of the fine particles of Bakelite from the cylinder.

The potassium treatments were carried out by suspending 0.50-gm. portions of the samples in 50 ml. of a 1 N KCl solution. The samples were allowed to stand overnight, concentrated after decantation, and washed three times with a total of 150 ml. of distilled water.

Ethylene glycol solvation was carried out in vapor at 60° C. overnight.

Heating to remove molecular interlayer water was carried out at 300° C. for one hour in an electric muffle furnace. The samples were then air-quenched and analyzed immediately.

Diffraction tracings show only the 00l peaks because oriented slides were prepared for analysis. Diffraction was registered with a GE XRD-3 with filtered CuKα radiation.

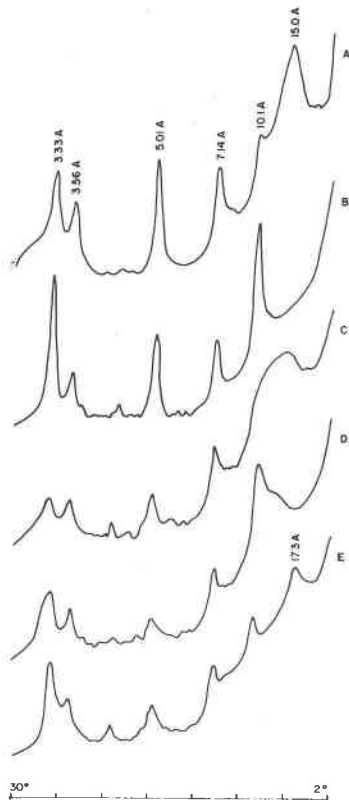FIG. 2. Diffraction traces showing variable expansion properties for two size fractions of the three-layer clay mica (0–13).

A. 1–2 μ natural sample, hydrated at 50 per cent RH.

B. 1–2 μ potassium treated, expanded with ethylene glycol.

C. 0.1–0.3 μ natural sample, hydrated at 50 per cent RH.

D. 0.1–0.3 μ potassium treated, hydrated at 50 per cent RH.

E. 0.1–0.3 μ potassium treated, expanded with ethylene glycol.

RESULTS

Figure 2 shows clearly that the diffraction characteristics of material in the 1–2μ fraction of the 0–13 sample are quite different from those of

material in the 0.1–0.3μ fraction. The 1–2μ fraction of the sample is mainly composed of particles with a 15 Å spacing which expands to 17 Å after glycolation, non-expanding particles with a 10 Å spacing (illite), and kaolinite particles. The 0.1–0.5μ fraction contains less illite than does the 1–2μ fraction, indicating that many of the illite particles are relatively large. The diffraction tracing of the 0.1–0.3μ fraction also shows that the 15 Å peak is broad and asymmetrical, whereas the diffraction tracing of the 1–2μ fraction exhibits a rather sharp, symmetrical peak. The broadening and the asymmetry of the peak may be caused by an interlayering of Na^{+1} particles with Ca^{+2} particles. It has been shown that particles in the fine fractions of bentonites often carry a higher percentage of sodium ions as the exchange cation (McAtee, 1955; Roberson, 1959).

The most striking difference between coarse and fine fractions is shown after potassium treatment. After the particles in the 1–2μ fraction are treated with potassium their spacing is contracted to 10 Å, and expansion cannot be effected even with ethylene glycol. However, it can be seen that after potassium treatment of the particles in the fine fraction, there is still present some material which will expand with water and ethylene glycol. If it can be assumed that the composition does not change with particle size (*i.e.*, charge density remains constant), then it follows that the difference in expansion properties is directly related to variation in particle size. However, because of the difficulties inherent in size fractionation experiments which have been discussed previously, careful grinding of the 1–2μ fraction was undertaken to determine if size reduction by this means would produce the same results.

The diffraction patterns shown in Fig. 3 illustrate the effect of particle size reduction produced by short-time grinding of the 1–2μ fraction of sample 0–13. By comparing the patterns labeled 3A and 3B with the pattern labeled 2B, it can be readily observed that a considerable proportion of the particles in the 1–2μ fraction, which were initially non-expanding after potassium saturation, cannot be bound together strongly enough by interlayer potassium ions to resist expansion with water or ethylene glycol after being ground for one hour in the Wig-L-Bug. Because of the gentle conditions under which the grinding was performed, it is assumed that little or no composition change was brought about, and therefore the sole factor controlling expansion under these conditions is thought to be the size of the particles.

Figure 4 shows the effect of particle size reduction on the expansion properties of an Ordovician metabentonite (8-ONY). As can be seen from the tracings labeled 4A and 4B, the <2μ fraction of the natural sample consists of non-expanding layers randomly interstratified with expanding layers. After grinding for 1½ hours, diffraction from two sep-
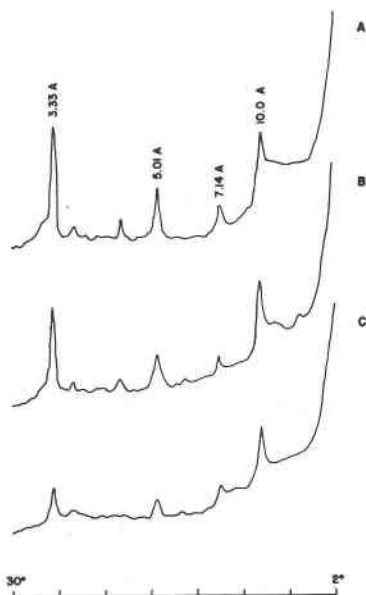
FIG. 3. Diffraction traces showing the expansion properties of the three-layer clay mica (0-13) after grinding 1 hour and potassium treatment.
A. Hydrated at 50 per cent RH.
B. Expanded with ethylene glycol.
C. Heated to 300° C.

arate phases—discrete non-expanding material and material which expands with water—is recorded. The expanding phase cannot be made non-expanding by potassium treatment. The ground material was heated to 300° C. to determine if the expanding material could be contracted to 10 Å. As can be seen from 4D, most of the expanding material collapsed to a 10 Å spacing.

SUMMARY

Jonas and Thomas (1959) have shown that as the effective surface charge density decreases in a series of clay micas of uniform particle size distribution, the interlayer binding force decreases. Those clay micas with effective high surface charge densities resist the expansion forces of even the strongest solvating agents. Clay micas with progressively lower effective surface charge densities yield to the expansion forces of strong solvating agents and continue to resist those of the weaker solvating agents. The clay micas with relatively low effective surface charge densities yield to the expansion forces of even weak solvating agents.
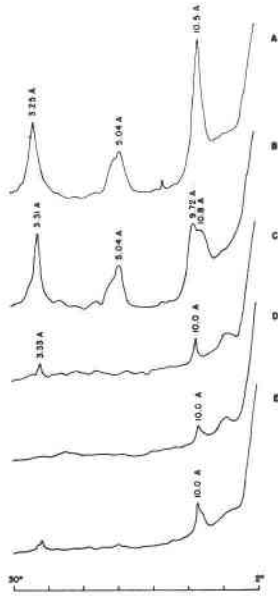
Fig. 4. Diffraction traces showing the effect of grinding on expansion properties of an Ordovician metabentonite (8-ONY).
  A. Natural sample, hydrated at 50 per cent RH.
  B. Natural sample, expanded with ethylene glycol.
  C. 1½ hours grinding, hydrated at 50 per cent RH.
  D. 1½ hours grinding, potassium treated, and hydrated at 50 per cent RH.
  E. 1½ hours grinding, heated to 300° C.

Expansion properties of micas are also determined by particle size. The actual forces involved in separating the silicate layers during expansion cannot be measured directly. It is therefore not possible to write a specific formula for the relationship between interlayer binding force, surface charge density, and particle area. The relative strengths of the forces are clearly demonstrated by the expansion or lack of expansion. Effects of the two controlling factors are studied here and in the experiment by Jonas and Thomas outlined in the preceding paragraph.

In spite of the qualitative nature of the data, at present it is still possible to state that mica layers with a high surface charge density can expand provided they have a sufficiently small particle size. The belief that expanding clay micas are all of a lower surface charge density than non-expanding micas is, in the light of the foregoing reasoning, not well founded. There are undoubtedly many expanding clay micas whose surface charge density is erroneously judged to be low because of this property. With a fundamental relation between surface charge and isomor-

phism, any assumptions (based on expansion properties) concerning the composition should be only tentative.

Experimental observations of the effect of particle size on expansion properties of other clay mineral groups, such as vermiculite-chlorite, montmorillonite-chlorite, and vermiculite-montmorillonite, might be fruitful in light of the data reported herein.

ACKNOWLEDGMENTS

REFERENCES

HATHAWAY, J. C. (1956), Procedure for clay mineral analyses used in the sedimentary petrology laboratory of the U. S. Geological Survey: *Clay Minerals Bulletin*, **3,** 8–13.

JOHNS, W. D., AND TETTENHORST, R. T. (1959), Differences in the montmorillonite solvating ability of polar liquids: *Am. Mineral.*, **44,** 894–896.

JONAS, E. C., AND THOMAS, G. L. (1959), Hydration properties of potassium deficient micas: *Seventh National Conference on Clays and Clay Minerals, Norman, Oklahoma* (abstract).

KELLEY, W. P., AND JENNY, H. (1936), The relation of crystal structure to base-exchange and its bearing on base-exchange in soils: *Soil Sci.*, **41,** 367–382.

LAWS, W. C., AND PAGE, J. B. (1946), Changes produced in kaolinite by dry grinding: *Soil Sci.*, **62,** 319–336.

MACKENZIE, R. C., AND MILNE, A. A. (1953), The effect of grinding on micas. I. Muscovite: *Mineralogical Mag.*, **30,** 178–185.

MCATEE, J. L. (1955), Heterogeneity in montmorillonite: *Proc. of the Fifth National Conference on Clays and Clay Minerals, National Academy of Science-National Research Council Pub.* **566,** 277–288.

PERKINS, A. T. (1948), Kaolin and treated kaolins and their reactions: *Soil Sci.*, **65,** 185–192.

ROBERSON, H. E. (1959), Petrology of Tertiary bentonites of Texas: Ph.D. Thesis, University of Illinois.

WALKER, G. F. (1950), Trioctahedral minerals in the soil clays of northeast Scotland: *Mineralogical Mag.*, **29,** 72–84.

——— (1957), On the differentiation of vermiculites and smectites in clays: *Clay Minerals Bulletin*, **3,** 154–163.

——— (1958), Reactions of expanding lattice clay minerals with glycerol and ethylene glycol: *Clay Minerals Bulletin*, **3,** 302–313.

WEAVER, C. E. (1958a), The effects and geologic significance of potassium "fixation" by expandable clay minerals derived from muscovite, biotite, chlorite, and volcanic material: *Am. Mineral.*, **43,** 839–861.

——— (1958b), A discussion on the origin of clay minerals in sedimentary rocks: *Proc. of the Fifth National Conference on Clays and Clay Minerals, National Academy of Science-National Research Council Pub.* **566,** 159–173.