COLLAPSE OF POTASSIUM MONTMORILLONITE CLAYS UPON HEATING—"POTASSIUM FIXATION"

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ABSTRACT

THE lattice collapse and potassium fixation upon heating was studied for four expanding clay minerals in the potassium form by determining the change in X-ray patterns, and the decrease of both the cation exchange capacity and the total surface area derived from water vapour adsorption isotherms.

In the literature, two factors promoting collapse have been considered: a high degree of tetrahedral substitution and a high potassium ion population in the unit layer surface. For the four minerals studied these two factors varied between wide limits, and the ease and degree of collapse were indeed found to correlate with these two factors. A third factor which has been considered previously is the degree of crystallinity of the mineral, which is determined by the origin of the clay. For the two bentonites which were investigated, one shows poor crystallinity, indicating its volcanic origin, the other shows a higher degree of crystallinity with boundary conformity in stacks of layers, indicating its formation by weathering of a micaceous mineral. The latter shows a higher degree of collapse.

INTRODUCTION

Three-layer Clays and the Prototype Micas

IN THE literature, much attention has been paid to the processes of collapse and potassium fixation. These processes are of considerable interest in soil science, because they impair the availability of potassium ions for the plants. In geology, the possible conversion of montmorillonite clays into nonexpandable illite-type clays is of interest with regard to the detection of the source of the clay minerals in sedimentary rocks. Weaver (1958) has discussed the literature on collapse and potassium fixation of montmorillonites. Weaver has studied several specific examples of potassium fixation and has speculated on a possible relation between the tendency of a clay to collapse and the origin of the clay. He suggested that montmorillonites which collapse easily upon conversion to the potassium form are likely to be weathering products of the muscovite and biotite micas, "inheriting" from them the potential factors which make the micas nonexpandable. Montmorillonites which have little

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or no tendency to collapse and to fix potassium are likely to have different parent materials—for example, the montmorillonites of bentonite rock, which are weathering products of volcanic ashes.

Since the tendency to collapse varies appreciably for the different montmorillonites in the potassium form, a question has been raised as to which factors determine expansion and collapse. Generally speaking, three different interaction energies of unit layers should be considered—van der Waals attraction energy, repulsion energy due to hydration, and electrostatic interaction of the charged unit layers and the interlayer cations. For potassium clays, the electrostatic energy is a strong attractive energy because of the specific favorable geometry of the potassium ion–unit layer complex. If the van der Waals attraction and the hydration repulsion are assumed to be of the same order in different species of potassium clays, the tendency to collapse may be directly related to the strength of the potassium link between the unit layers per unit area of interacting surfaces.

Two factors which are likely to affect the strength of the potassium bond per unit area between the unit layers should be considered:

(a) The binding energy must be larger when there are more potassium ions per unit layer surface area. At the same time, it must be assumed that the hydration energy is largely due to surface hydration and not exclusively to ion hydration; otherwise, the hydration energy would also increase, and the net interaction energy would be independent of the amount of potassium ions per unit surface area.

(b) The binding energy may be larger for clays with a high degree of tetrahedral substitution, since the centres of negative lattice charge would be closer to the positive charge of the potassium ion than for clays with octahedral substitution.

In fact, in the mica minerals, muscovite and biotite, as well as in illite clays, a high potassium population of the surfaces and tetrahedral substitution both prevail. With respect to the potassium population, the following rough figures apply.

The number of milliequivalents of potassium which compensates the lattice charge deficiency in 100 g of clay amounts to about 250 for the prototype micas. For illites, a figure of 150 meq per 100 g is rather common, whereas values between 70 and 110 meq per 100 g are usually observed for montmorillonite clays, although some representatives of the group have much higher values, particularly the vermiculites.

In order to study the significance of the above mentioned factors, experiments on the collapse of clays upon heating have been carried out with four different montmorillonites in the potassium form. Wyoming bentonite, French bentonite, nontronite, and Llano vermiculite were chosen because of their wide variation in degree of tetrahedral substitution and potassium ion population, as derived from chemical analysis. In the first three clays, the contribution of tetrahedral substitution to the lattice charge increases from 16 to 100% in the given order, whereas the potassium ion population is within COLLAPSE OF POTASSIUM MONTMORILLONITE CLAYS UPON HEATING 395

the limits of 85-110 meq per 100 g, which is typical for montmorillonites. The potassium vermiculite combines a high tetrahedral substitution with a potassium content which is about twice as high as that of the other montmorillonites.

In the interpretation of the experimental data, it should be realized that the formula of the unit cell derived from chemical analysis only represents an average composition of the unit cell and the unit layer. Individual unit layers may have a composition that deviates from the average; therefore, for part of the unit layers, the conditions for collapse may be more favorable than for others. Actually, Weaver (1958) reports that clays which had been converted to the potassium form by treatment with KOH solutions show X-ray patterns indicating mixed layering of hydrated and collapsed layers together with packets of completely collapsed material.

COLLAPSE OF POTASSIUM FRENCH BENTONITE UPON HEATING

Origin of Clay

"French Bentonite" was obtained commercially. The clay is probably of Algerian origin.

Preparation of the Potassium Clay

The raw clay was suspended in water at a concentration of about 1%. Coarse impurities were allowed to settle for a day, after which the suspension was decanted. This suspension was converted into the potassium form by passing it through a column packed with Dowex-50 resin beads in the potassium form. The total exchange capacity of the resin in the column was about 150 times the total exchange capacity of the clay in the suspension. This operation was repeated 6 times. After every pass of the suspension through the column, the resin was regenerated by percolation of KCl solution through the column and then washed with distilled water.

The converted suspension was washed and concentrated in three cycles of sedimentation in the ultracentrifuge, of decanting of the supernatant liquid, and of redispersion of the clay in distilled water.

Chemical Analysis, Cation Exchange Capacity, and Formula of the Clay

The cation exchange capacity of the clay in the potassium form was determined by the conversion of the suspended clay to the ammonium form and the subsequent determination of ammonium in the washed and dried ammonium clay. The conversion to the ammonium form was carried out by repeatedly passing the potassium clay suspension through a column packed with Dowex-50 resin beads in the ammonium form. In an alternative procedure, the clay suspension was shaken with an excess of ammonium acetate. The ammonium clay was washed with 96% alcohol and dried at 105°C.

The ammonium content of the converted clay was determined by sulfuric acid digestion of the clay, followed by alkaline distillation of the ammonia into a known quantity of 0.1 N HCl and back titration of the acid.*

The cation exchange capacity of the clay was 110 meq per 100 g of dry ammonium clay. The same value was found from a flame-photometric determination of the potassium content of the clay.

Gravimetric analysis of the lattice constituents of the clay (after conversion to the potassium form) gave the following results:

$$SiO_{2}, 60.35\%; Al_{2}O_{3}, 23.25\%; Fe_{2}O_{3}, 2.57\%; MgO, 4.78\%$$

With the standard computation procedure, the following unit cell formula was derived from the analytical data:

$$\left\{\frac{(\mathrm{Si}_{3.79}\mathrm{Al}_{0.21})^{\mathrm{IV}}(\mathrm{Al}_{1.51}\mathrm{Fe}^{3}_{0.12}\mathrm{Mg}_{0.44})^{\mathrm{VIO}}_{10}(\mathrm{OH})_{2}}{X_{0.41}}\right\}_{2}$$

in which X stands for a monovalent exchange cation. According to this formula, about 50% of the lattice charge is due to substitution in the tetrahedral sheet.

Structural Change of the Clay upon Heating

In the study of the collapse of a clay upon heating, the temperature should be kept well below that at which "hydroxyl water" is lost from the interior of the lattice and the original clay structure is destroyed. Therefore, a differential thermal analysis (DTA) was run on the potassium clay. The rate of heating was 10° per minute. Figure 1 shows that loss of hydroxyl water takes



FIG. 1. DTA curve for potassium French bentonite.

place between about 450° and 750° C, in which region an endothermic reaction occurs. (A small endothermic peak is observed at about 540° C, and a stronger peak occurs around 690° C, indicating that the lattice hydroxyl groups occur in two distinctly different bonding states.)

After the clay was dried to constant weight at 400°C and at 900°C, a weight loss was observed of 1.12% and of 6.22%, respectively, based on the dry

^{*} The method of Mortland and Mellor (1954) for the determination of the CEC, which is based on the conversion of the clay to the barium form and the conductometric titration of the barium clay with magnesium sulfate, appeared to be unsuitable for the potassium clays. For potassium French bentonite, a CEC of 60 meq per 100 g was found with this method, and flame-photometric analysis of the barium clay showed that 43 meq per 100 g of potassium ions were still present in the barium clay.

weight of the clay at 105° C as the reference weight. The weight loss between 400° and 900° C, amounting to 5.10° , is a little higher than the theoretical weight loss due to "hydroxyl water", which is 4.7° , according to the chemical, formula of the clay. It seems safe, therefore, to assume that up to 400° C, primarily adsorbed water is lost by the clay.

Collapse of the Clay upon Heating

After some exploratory experiments, the degree of collapse of the clay was studied after it was heated for one month at 250°C. In a second experiment, the clay was heated for one month at 390°C, but essentially the same results were obtained as in the first experiment at the lower temperature.

A certain degree of collapse of the clay after heating was indicated by the X-ray patterns taken after exposure of the heated clay either to water or to ethylene glycol.

After the heated clay had been ground, wet with water, and dried under atmospheric conditions, a basal spacing of 9.8 Å was observed; a broadening of the peak indicated that some hydration to a larger spacings occurred. Under the same conditions, the original clay expands to 12.8 Å, and when dried first to 105° C, it expands to 11.8 Å.

When treated with ethylene glycol, the original clay expands to 17 Å, but the heated clay expanded to only 14.7 Å; the diffraction peak showed a shoulder at 10 Å.

Partial collapse of the clay upon heating is indicated by these X-ray observations, but no attempt was made to draw quantitative conclusions regarding the degree of collapse from the patterns. In order to obtain a quantitative measure of the degree of collapse, cation exchange capacities and water vapor BET areas were measured before and after heat treatment.

The cation exchange capacity of the heated clay was about 50 meq per 100 g. Since the exchange capacity of the original clay was about 110 meq per 100 g, 50-60% of the exchange cations were no longer available for exchange after the heat treatment at 250° or 390°C. This "fixation" of potassium ions indicates that 50-60% of the layers had collapsed.

The cation exchange capacity of the clay after drying at 105° C was only 87 meq per 100 g, which is about 20% lower than that of the original clay. (The CEC of the original clay was determined by conversion of the still-suspended potassium clay into the ammonium form and by drying the separated ammonium clay at 105° C.) Apparently, about 20% of the layers of the potassium clay collapsed merely by drying at 105° C.

Another estimate of the degree of collapse was derived from the change in BET surface area for water vapor before and after heating. For the original clay, dried at 105°C prior to measuring the adsorption-desorption isotherms at 25°C, a BET water vapor area of about 300 square meters per gram of clay was derived from the desorption branch. For the heated clay, this area was about 200 square meters per gram. The repetition of the adsorption-desorp-

tion isotherms on the same sample gave identical results for the desorption branch.

Apparently, 30-40% of the layer surfaces are no longer accessible to water vapor after exposure of the heated clay to saturated water vapor. Since the isotherms for the original clay were run on a sample which was previously dried at 105°C, the reduction of the surface area agrees with the reduction of the cation exchange capacity.

COLLAPSE OF POTASSIUM WYOMING BENTONITE Origin of Clay

This bentonite from Wyoming was taken from a homogenized 1000-pound batch supplied by Baroid Division, National Lead Company.

Preparation of the Potassium Clay

The potassium form of the Wyoming bentonite clay was prepared in the manner described for potassium French bentonite.

Chemical Analysis, Cation Exchange Capacity, and Formula of the Clay The cation exchange capacity, which was determined as described previously, was 85 meq per 100 grams of dry ammonium clay.

Gravimetric analysis of the lattice constituents of the Wyoming bentonite clay gave the following results:

SiO₂, 55.4%; Al₂O₃, 19.0%; Fe₂O₃, 3.6%; MgO, 2.5%

The following unit cell formula was derived from these results:

$$\left\{\frac{(\mathrm{Si}_{3.94}\mathrm{Al}_{0.06})^{\mathrm{IV}}(\mathrm{Al}_{1.53}\mathrm{Fe}^{3}_{0.19}\mathrm{Mg}_{0.27})^{\mathrm{VIO}}\mathrm{O}_{10}(\mathrm{OH})_{2}}{X_{0.32}}\right\}_{2}$$

According to this formula, about 16% of the lattice charge is due to substitution in the tetrahedral sheet.

Structural Change of the Clay upon Heating

The DTA curve is shown in Fig. 2. Loss of "hydroxyl water" takes place



FIG. 2. DTA curve for potassium Wyoming bentonite.

between about 600° and 750°C. A sharp minimum in the endothermic peak occurs at 700°C. An oscillating-heating X-ray pattern of the potassium clay was determined by Rowland, Weiss, and Bradley (1956), p. 90).

Collapse of the Clay upon Heating

The following exploratory heating experiments were run; the indications of collapse were obtained from X-ray analysis.

The original clay, when exposed to atmospheric conditions, showed a mixed hydration pattern. This pattern persisted after heating at 250° C for 18 days. After heating at 350° C for 22 days, a single hydration peak at about 15 Å was observed. After heating at 450° C for 2 months, the main diffraction peak stayed at 15–15.5 Å, but a shoulder developed at about 10 Å, indicating some degree of collapse.

The cation exchange capacity of the clay after heating at 450° C for 2 months was reduced from about 85 meq per 100 g for the original clay to about 65 meq per 100 g. Apparently, about 23% of the cations are no longer available for exchange. This degree of collapse did not change after heating at 450° C for 6 months.

Because of the relatively small amount of collapse, compared with that of potassium French bentonite, no adsorption isotherms were determined for the potassium Wyoming bentonite clay.

Essentially the same degree of collapse of potassium Wyoming bentonite was observed by Weaver (1958) when the original clay was allowed to stand in $1 \times \text{KOH}$ solution for 15 hr, washed with distilled water, and dried at room temperature. The degree of collapse was estimated from the analysis of the X-ray pattern.

COLLAPSE OF POTASSIUM NONTRONITE

Origin of Clay

The nontronite clay is from the Manito locality, Spokane County, Washington. The clay, which was obtained from Ward's, is described under No. 33-b, A.P.I. Reference Clay Minerals, Project 49.

Preparation of the Potassium Clay

The preparation of the potassium clay was carried out by the method described for French bentonite. About half the clay was rather coarse and could not be dispersed well in water. Although this fraction showed the same X-ray pattern as that which could permanently be dispersed, it was discarded prior to the conversion to the potassium form.

Chemical Analysis, Cation Exchange Capacity, and Formula of the Clay

The cation exchange capacity of the original clay was 112 meq per 100 g of dry ammonium clay. The original clay contained only a few milli-equivalents of potassium per 100 g.

Chemical analysis of the lattice constituents of the original clay, reported in A.P.I. report, Project 49, gave the following results:

$$SiO_2$$
, 40.54% ; Al_2O_3 , 5.19% ; Fe_2O_3 , 31.24% ; MgO, 0.06%

Neglecting the small amount of Mg, the following approximate formula was derived for the unit cell:

$$\left\{\frac{(\text{Si}_{3.45}\text{Al}_{0.55})^{\text{IV}}(\text{Fe}^{3}_{2.00})^{\text{VIO}}\text{I}_{0}(\text{OH})_{2}}{X_{0.55}}\right\}_{2}$$

According to this formula, practically the complete lattice charge is due to substitution in the tetrahedral layer.

Structural Change of the Clay upon Heating

The DTA curve of the original clay is shown in A.P.I. Project 49 report. Loss of hydroxyl water starts at 400°C, and the minimum in the endothermic peak occurs at 500°C. Figure 3 shows the DTA curve of the potassium form



FIG. 3. DTA curve for potassium nontronite.

of nontronite. Dehydroxylation starts at about 325° C, and two minima occur in the endothermic peak:—one at 450° C and one at 500° C. The relatively low temperature at which the lattice decomposes indicates that the OH groups are rather loosely bound.

Collapse of the Clay upon Heating

When the potassium nontronite samples were prepared for the heating experiments by drying the suspension at 105°C, changes appeared to have occurred in the clay, since it could no longer be suspended in water. With the alternative technique of freeze drying of the suspension, the dried clay could still be suspended in water, although with some difficulty. Therefore, the freeze-drying procedure was selected for the preparation of the samples for the heating runs.

Separate portions of the freeze-dried material were heated at different temperatures. The weight loss of the sample after heating was determined, as well as the cation exchange capacity. The basal spacing of the heated clay

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was observed after exposure to the atmosphere and to ethylene glycol. The results of these experiments are listed in Table 1.

Treatment	Weight, per cent of weight of freeze- dried clay		Basal spacing, A	
		CEC, meq/100 g	Water vapor exposure	Ethylene glycol
air-dried*		105†	12.5	13.8
freeze-dried	100	98	12.2	
30 days, 70°C	96.20	80	11.5	13.2-13.8
30 days, 100°C	96.20	80	10.9	12.8
30 days, 146°C	95.55	80	10.6	12.5-13.2
30 days, 245°C	95.70	80	10.5	12.3-13.6
30 days, 350°C	91.71	64	10.0	9.6-10.4
30 days, 450°C	89.77	46	10.0	9.8
24 hr. 800°C	89.84	5	no pattern	

TABLE 1.---COLLAPSE OF POTASSIUM NONTRONITE UPON HEATING

*Air-dried from the original suspension of the potassium clay.

†Determined by converting the original suspension of potassium clay with ammonium acetate and drying the separated ammonium clay.

Potassium nontronite appears to collapse very easily. Freeze drying alone causes a slight reduction of the cation exchange capacity from 105 meq per 100 g for the original potassium clay, converted in suspension, to 98 meq per 100 g. The CEC is further reduced by drying at 70°C to about 80 meq per 100 g, or about 25% compared with the CEC of the original suspended potassium clay. The clay thus dried swells less in water or in ethylene glycol than the original potassium clay, as shown by the basal spacings given in Table 1.

Further heating of the clay to 245°C has no additional consequences for the cation exchange capacity, which remains about 25% lower than that of the starting material. Only at 350°C and higher temperatures, a further reduction of the cation exchange capacity is observed; this reduction amounts to 40%at 350°C and to 55% at 450°C. A basal spacing which is typical of the dry clay is observed after heating at 350° and 450°C and no swelling takes place with water or with ethylene glycol. However, at these temperatures, structural changes in the clay due to loss of hydroxyl water might have already occurred, and hence, the reduction of the cation exchange capacity is probably no longer an accurate measure of the degree of collapse of the unaltered clay lattice. Figure 4 shows that the reduction of the exchange capacity actually parallels the loss of hydroxyl water. Up to about 300°C, the initial loss of adsorbed water remains constant. In this region, the cation exchange capacity is constant. Beyond 300°C, the increased loss of water must have been hydroxyl water, according to the DTA curve. The total loss of water between about 300° and 800°C is very close to the theoretical loss of 4.1% of hydroxyl water computed from the chemical formula of the clay.

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FIG. 4. Change in weight (per cent) and in cation exchange capacity of potassium nontronite upon heating.

Therefore, it can be concluded that potassium nontronite collapses about 25% under very mild conditions. A higher degree of collapse is indicated at higher, though still moderate, temperatures, but under these conditions, simultaneous structural changes in the lattice interior occur because of loss of hydroxyl water.

COLLAPSE OF POTASSIUM VERMICULITE

Origin of the Clay

The vermiculite clay used in this study occurs in Llano, Texas. The natural clay is in the magnesium form, and it is found together with its parent material phlogopite in a hydrothermal magnesite deposit.

Preparation of the Potassium Clay

Potassium vermiculite was prepared from the original clay by repeated washings with KCl solutions.

Chemical Analysis, Cation Exchange Capacity, and Formula of the Clay

The cation exchange capacity of the clay in the sodium form was 195 meq per 100 g of clay.

Chemical analysis of the lattice constituents gave the following results:

From these data, the following formula is computed:

$$\left\{\frac{(\mathrm{Si}_{2.64}\mathrm{Al}_{1.36})^{\mathrm{IV}}(\mathrm{Al}_{0.66}\mathrm{Mg}_{2.29})^{\mathrm{VIO}}_{10}(\mathrm{OH})_2}{X_{0.80}}\right\}_2$$

The deficiency of positive charge in the tetrahedral sheet is compensated by the sum of the exchange cation charge and the excess of positive charge in the octahedral sheet.

Collapse of the Clay

The mere conversion of the original clay into the potassium form caused an almost complete collapse of the layer lattice at room temperature. Apparently, the vermiculite was converted back into its parent material phlogopite. When the clay was contacted with water or with ethylene glycol, its basal spacing was 10.2 Å, which is typical for an unexpanded potassiummontmorillonite-type clay, although the diffraction peak showed a weak shoulder at a higher spacing, indicating partial swelling.

The cation exchange capacity of the potassium clay was 14 meq per 100 g, compared with 195 meq per 100 g for the unconverted clay. To establish whether such an exchange capacity was due to the exterior surfaces of the clay only, the argon surface area of the potassium clay was determined. This area was 13.2 square meters per gram of clay. Since the theoretical unit layer surface area computed from the unit cell weight and the unit cell dimensions is 718 square meters per gram of clay, $13.2/718 \times 195 = 3.6$ meq per 100 g of the exchange capacity is due to the exterior surfaces, and 9.6 meq per 100 g is still contributed by the interior surfaces. Hence, the reduction of the cation exchange capacity indicates a percentage of collapse of $100-9.6/(195-3.6) \times 100 = 95\%$.

From a water vapor desorption isotherm, the water vapor surface area was computed to be 60 square meters per gram of potassium clay, which is considerably higher than the argon surface area. The reduction of the accessibility of the interlayer surfaces to water vapor can be computed in the following manner: The total unit layer surface area of the clay is 718 square meters per gram; the exterior surface area, according to the argon isotherms, is 13.2 square meters per gram. Hence, the interior unit layer surface area is 718 - 13 = 705 square meters per gram, and the interior area of monolayer coverage is half this amount, or 352 square meters per gram. The accessible interlayer area is 60 - 13 square meters per gram, or 47 square meters per gram. Therefore, the per cent of collapse, according to the reduced water vapor area, is $100 - 47/352 \times 100 = 87\%$. This value is somewhat lower than that computed from the reduction of the cation exchange capacity. However, in the case of the vermiculite surface with the high density of potassium ions, there is some doubt regarding the structure of the water monolayer and the figure for the surface area per water molecule to be used in the computation of the surface areas.

The incomplete collapse of the potassium vermiculite was probably due to incomplete conversion to the potassium form; this is indicated by a somewhat low value for the flame-photometrically determined potassium content of the clay (approximately 165 meq per 100 g).

SUMMARY AND CONCLUSIONS

As mentioned in the Introduction, it has been suggested in the literature that a large proportion of substitution sites in the tetrahedral sheet and a high population of potassium ions on the unit layer surfaces promote lattice collapse and potassium fixation in montmorillonites. In these respects, the four clays that were studied rate as shown in Table 2.

Clay	Per cent of lattice charge due to tetrahedral substitution	Si–Al ratio in tetrahedral coordination	Potassium population expressed in meq/100 g of clay
1. Wyoming bentonite	16	3.94:0.06	
2. French bentonite	50	3.79:0.21	110
3. Nontronite	100	3.45:0.55	105
4. Llano vermiculite	100*	2.64:1.36	195

TABLE 2.—ANALYSIS OF FOUR CLAYS

* The negative tetrahedral charge is also partly compensated by a positive octahedral charge in this clay.

If an increasing degree of tetrahedral substitution and an increasing potassium population would indeed promote collapse and potassium fixation, the tendency of the clays to collapse should increase in the order given in Table 2. Such a trend certainly emerges from the observations described in the previous sections. In comparison with the potassium Wyoming bentonite, the potassium French bentonite collapses, upon heating, to a much higher degree. Although the potassium population is somewhat higher in the French bentonite, the considerably higher degree of tetrahedral substitution might be the major contributing factor. Potassium nontronite, which has a still higher degree of tetrahedral substitution but about the same potassium population as the French bentonite, collapses still more easily, i.e. at lower temperatures. However, the degree of collapse of the potassium nontronite is lower than for the potassium French bentonite at moderate temperatures. At the higher temperatures, where the degrees of collapse of the two clavs become comparable, the potassium nontronite already begins to lose lattice hydroxyl water, and therefore, the behavior of the two clavs is not strictly comparable in this region.

The spontaneous, almost complete collapse of potassium vermiculite at room temperature is certainly in agreement with both the high degree of tetrahedral substitution and the high potassium population in this clay.

It may be concluded from this work that both the degree of tetrahedral substitution and the degree of potassium population are contributing to collapse and potassium fixation in montmorillonite clays, but it is not possible to estimate the relative importance of the two factors. As long as such studies

are limited to natural clays, in which both factors are not varied independently with any other variables constant, only the observation of qualitative trends may be expected. When synthetic clays in which the degree of substitution and the potassium population can be varied systematically become available, a more quantitative study will be possible.

However, another factor which should be considered, but which may be difficult to study using synthetic clays, is the degree of crystallinity of the mineral specimen. As Weaver (1958) indicated, those minerals which inherit some degree of crystallinity from their parent micas after having been submitted to weathering are apt to collapse more easily upon exchange with potassium than the minerals of rather poor crystallinity which were created by the weathering of volcanic ash. In this respect, such differences in ease of collapse were indeed observed for the Wyoming bentonite which is of volcanic origin, and the French bentonite which has retained a higher degree of crystallinity from its probably micaceous parent material, as shown by boundary conformity in stacks of unit layers in electron micrographs. However, this single factor is again not completely isolated from other factors mentioned above in the comparison of the behaviour of the two clays.

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