

THE EFFECT OF THE INTERLAYER CATIONS ON THE EXPANSION OF THE MICA TYPE OF CRYSTAL LATTICE

ISAAC BARSHAD, *University of California, Berkeley, California.*

ABSTRACT

The ionic radii, the valency, and the total charge of the interlayered cations, as well as the nature of the interlayered substance seem to determine the extent of the interlayer expansion of the mica type of crystal lattice.

Recent investigation of the base exchange properties of vermiculite (2) together with results reported herein, shed considerable light on the factors other than degree of hydration which affect the expansion along the *c* axis of the mica type of a crystal lattice. One of these of special importance is the interlayer cations. The mica type minerals with which this effect has been noted by others or studied experimentally include vermiculite, biotite, montmorillonite, paragonite, muscovite, glauconite, celadonite, hydrous mica clay minerals, and margarite.

STUDIES WITH VERMICULITE

The effect of the exchangeable ion on the expansion of air dry vermiculite is shown in Table 1. It is seen that the expansion of the lattice saturated with Ba, Li, or Na ions is equivalent to the thickness of a monomolecular layer of water; whereas when saturated with Mg, Ca, or H ions the expansion is equivalent to the thickness of two layers of water molecules. In contrast is the lattice saturated with K, NH₄, Rb, or Cs which is only slightly expanded, the amount being caused apparently by the size of the exchangeable ion (2).

TABLE 1. BASAL REFLECTIONS* *d*(002) FOR VERMICULITE SATURATED WITH VARIOUS CATIONS AS RELATED TO IONIC RADIUS AND CHARGE OF ION

Saturating cation	Mg	Ca	Ba	H	Li	Na	K	NH ₄	Rb	Cs
Ionic Radius (13) Å	0.65	0.99	1.35	0.30†	0.60	0.95	1.33	1.48	1.48	1.69
Charge of Ion	2	2	2	1	1	1	1	1	1	1
Basal Reflection <i>d</i> (002) Å	14.33	15.07	12.56	14.33	12.56	12.56	10.42	11.24	11.24	11.97

* This interlayer spacing is usually designated as the *d*(002) spacing for vermiculite and the micas and as the *d*(001) spacing for montmorillonite.

† Covalent radius.

It is important to note that although the crystal lattice of Li, Na, or Ba vermiculite expands the equivalent of a monomolecular layer of water when immersed in water (Table 2), the total interlayer expansion of these forms and also of the Mg or Ca forms does not exceed two monomolecular

layers of water. The contracted nature of the crystal lattice of K, NH₄, Rb, or Cs vermiculite is further indicated by the fact that no change in the interlayer spacing takes place when immersed in water.

TABLE 2. BASAL REFLECTION $d(002)$ FOR VERMICULITE* SATURATED WITH VARIOUS CATIONS WHEN IMMERSSED IN WATER†

Saturating cation	Mg	Ca	Ba	Li	Na	K	NH ₄	Rb	Cs
Basal Reflection $d(002)$ Å	14.47	15.41	15.41	15.07	14.76	10.57	11.22	11.22	11.97

* Vermiculite no. 2 (2).

† To obtain x -ray diagrams of material immersed in water, the sealed ends of capillary tubes packed with air dry material were broken off and immersed in water. After the samples became saturated with water by capillarity the two ends of the tubes were sealed with De Khotinsky cement to prevent water loss during exposure to x -rays.

STUDIES WITH MONTMORILLONITE

The effect of the exchangeable ion on expansion of montmorillonite in water has been investigated by Hendricks *et al.* (8) and by Hofmann and Bilke (10). The effect appears in the following manner:

(1) At relatively low states of hydration Mg, Ca, Sr, or H saturated montmorillonite expands to a thickness equivalent to two monomolecular layers of water, whereas Ba, Li, Na, or K saturated forms expand to a thickness equivalent to only one monomolecular layer of water.

(2) Mg, Ca, Sr, or H montmorillonite expands from a thickness of one molecular layer of water to a thickness of two molecular layers of water, at very low states of hydration (3), but Ba, Li, or Na montmorillonite does not expand similarly until the water content is relatively high and sufficient to form a continuous monomolecular layer of water consisting of hexagonal rings of at least two water molecules per half unit cell (3).

(3) The lattice of K or Cs montmorillonite apparently does not expand beyond the equivalent of a monomolecular layer of water even at very high relative humidities.

The effect of the exchangeable ion on expansion of montmorillonite determined in the present investigation is shown in Table 3. It is interesting to note that the interlayer spacing of the air dry samples of Mg, Ca, Ba, H, Li, or Na montmorillonite is approximately the same as with air dry vermiculite saturated with the same ion. However, montmorillonite saturated with K, NH₄, Rb, or Cs ions differs from vermiculite saturated with these ions in that the former have an expanded lattice the equivalent of a monomolecular layer of water, whereas the latter have a non-expanded lattice.

Upon immersion in water, under the conditions specified, montmorillonite saturated with Mg, Ca, Ba, H, Li, or Na ions assumes interlayer

TABLE 3. BASAL REFLECTIONS $d(001)$ FOR AIR DRIED MONTMORILLONITE SATURATED WITH VARIOUS CATIONS AND WHEN IMMERSÉD* IN WATER

Saturating cation		Mg	Ca	Ba	H	Li	Na	K	NH ₄	Rb	Cs
Bentonite† No. 2	Air Dry‡	14.8	15.1	12.9	14.5	13.4	11.9	12.0	12.1	12.3	12.9
	Immersed in Water	20.7	17.9	18.5	19.3	23-18†	24-18†	13.2	13.2	12.3	
Bentonite† No. 5	Air Dry		15.2				12.1	11.9			
	Immersed in Water		19.6				24-18	13.2			
Bentonite† No. 7	Air Dry	15.1	15.1	12.6			12.6	12.3	12.4		
	Immersed in Water	19.4	19.6	19.6			24-18	13.2	13.7		

* To obtain x-ray diagrams of materials immersed in water, thick pastes were prepared and then packed in capillary tubes. The tubes were sealed with De Khotinsky cement to prevent water loss during exposure to x-rays.

† Li and Na montmorillonites form gels upon wetting; it was found that the expansion varied with the concentration of the gel. The reflection lines were broad, diffused, and very weak in dilute gels; in more concentrated gels the lines were somewhat narrower and with somewhat stronger intensities but still diffused.

‡ See note † Table 4.

§ The relative intensity of the reflection lines according to cation is as follows: Ca=Mg>Na>Ba=Li=NH₄>H=K>Rb>Cs. The intensity of the lines of the last two cations are very weak and diffused.

|| The relative intensity of the reflection lines according to cation is as follows: Mg=Ca=Ba>H=NH₄>K>Na=Li>Rb>Cs. The lines of Mg, Ca, Ba, and H ions are narrow and with sharp edges, those of NH₄ and K ions are a little broader and with edges which are not as sharp, but the lines of Li, Na, Rb, and Cs ions are very diffused.

spacings equivalent to three, four, or more (possibly in suspensions) monomolecular layers of water (3) (Table 3), whereas the similarly saturated vermiculite samples, do not expand beyond the equivalent of two monomolecular layers of water. K, NH₄, Rb, or Cs montmorillonite, upon immersion in water shows only a relatively small change in the interlayer spacing amounting possibly to an expansion equivalent to one layer of water molecules.

The similarity as well as the difference between montmorillonite and vermiculite saturated with like ions is also clearly demonstrated by the differential thermal curves of the air dried samples (see Figs. 1, 2, and 3, and also the differential thermal curves of the vermiculites previously published (2)). The significant portion of the curves is represented by the first endothermic trough at low temperatures. It is seen that two types of troughs are present, namely, that of the Mg, Ca, Ba, H, or Li montmorillonite and that of Na, K, NH₄, Rb, or Cs montmorillonite. Whereas the bottom of the trough of Na, K, NH₄, Rb, or Cs montmorillonite has one sharp point, the bottom of the trough of Mg, Ca, Ba, H, or Li montmorillonite has two sharp points. The two sharp points suggest, possibly, that these are points of two endothermic troughs, as in the differential thermal curves of the Ca or Mg vermiculite, but which overlapped on account of their close proximity. This is apparently also true of H vermiculites (Fig. 3). The most striking dissimilarity between mont-

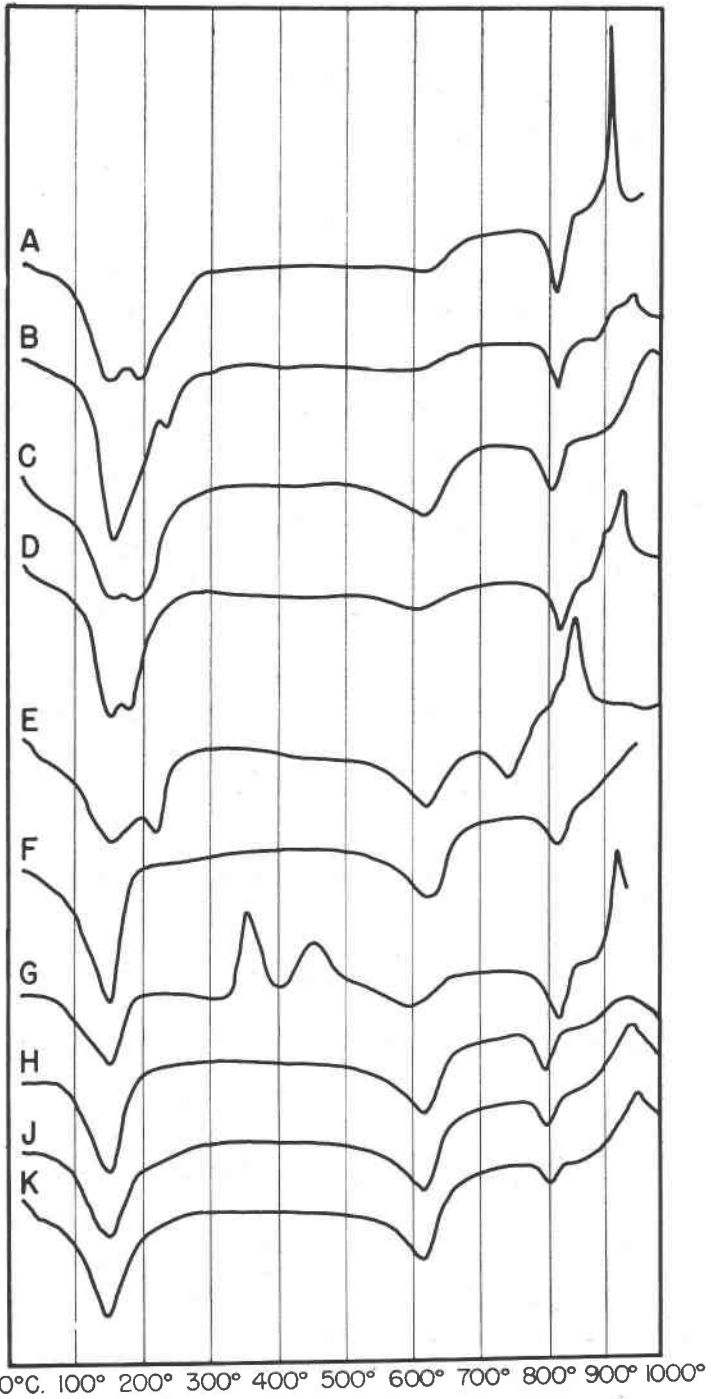


Fig. 1. Differential thermal curves of montmorillonite from bentonite No. 2.

- | | |
|-----------------|------------------------------|
| A. Mg saturated | F. Na saturated |
| B. Ca saturated | G. NH ₄ saturated |
| C. Ba saturated | H. K saturated |
| D. H saturated | J. Rb saturated |
| E. Li saturated | K. Cs saturated |

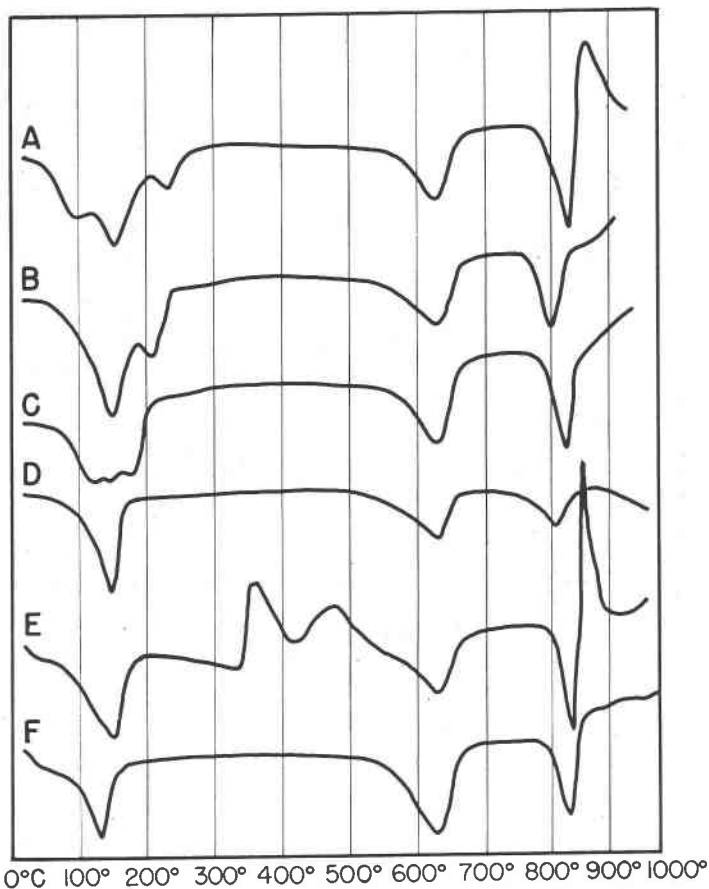


FIG. 2. Differential thermal curves of montmorillonite from bentonite No. 7.

- | | |
|-----------------|----------------------------|
| A. Mg saturated | D. Na saturated |
| B. Ca saturated | E. NH_4 saturated |
| C. Ba saturated | F. K saturated |

morillonite and vermiculite appears in the NH_4 , K, Rb, and Cs saturated forms. The former have an endothermic trough at the low temperatures whereas the latter do not. As with vermiculites, the exchangeable (adsorbed) ion influences somewhat the exothermic reaction at ignition temperatures (Figs. 1 and 2).

The differential thermal curve of NH_4 montmorillonite is of special interest, for it has two exothermic breaks, the peaks of which are at 360°C . and 470°C ., and these are absent in the curves of the other montmorillonites. These two breaks are apparently associated with the loss of NH_3 , for they correspond to the temperatures at which NH_3 is lost as reported by Cornet (6).

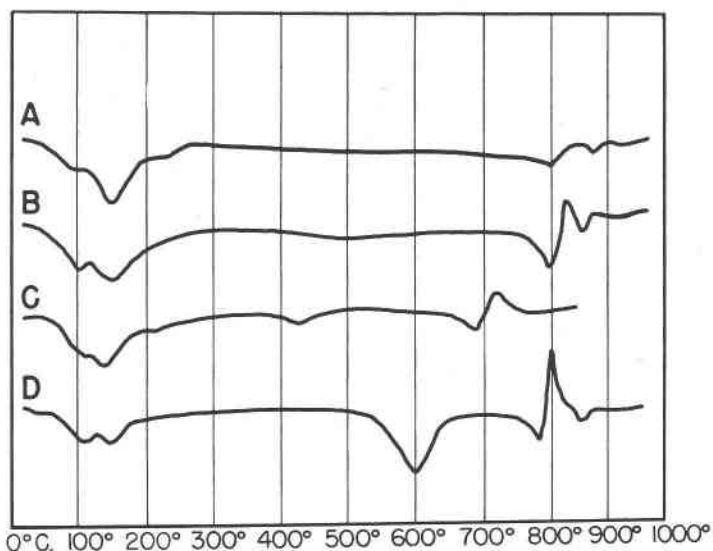


FIG. 3. Differential thermal curves of hydrogen saturated vermiculites (2).

A. Vermiculite No. 1.

C. Vermiculite No. 3.

B. Vermiculite No. 2.

D. Vermiculite No. 5.

EXPANSION IN GLYCEROL

To clarify further the effect of the interlayer ions on lattice expansion, the interlayer spacing of vermiculites and montmorillonites were determined when immersed in glycerol. MacEwan (11, 12) and Bradley (4) have shown that montmorillonite saturated with either H, Na, NH_4 , Ca, or Pb^{++} ions forms a complex with glycerol whereby two monomolecular layers of glycerol occupy the interlayer space. This results in an interlayer spacing of 17.7 Å. However, MacEwan reported that vermiculite does not form a glycerol complex.

In the present study the method employed to saturate vermiculite and montmorillonite with glycerol was as follows: Air dry powdered samples were packed in glass capillary tubes. The sealed end of the tubes were broken off and held in hot (110° C.) water-free glycerol until glycerol rose by capillarity to the top of the sample. Samples of vermiculite #2 (2) and several montmorillonite samples saturated with various ions were thus treated. The results are reported in Table 4.

It is seen that the glycerol treated vermiculite saturated with Mg, Ca, Ba, H, Li, or Na have an identical interlayer spacing of about 14.33 Å. Apparently wetting the Mg saturated form (the natural vermiculite) with glycerol caused no visible change in the interlayer spacing, but the

TABLE 4. BASAL REFLECTIONS FOR VERMICULITE* AND MONTMORILLONITE† SATURATED WITH VARIOUS CATIONS WHEN IMMERSSED IN GLYCEROL

Saturation cation	Mg	Ca	Ba	H	Li	Na	K	NH ₄	Rb	Cs
Sample										
Vermiculite	14.33	14.18	14.33	14.33	14.33	14.33	10.64	11.22	11.22	11.97
Bentonite no. 2‡	17.7	17.7	17.7	17.7	17.7	17.7	14.2	14.5	14.4	15.4
Bentonite no. 1		17.8					14.2	14.5		
Bentonite no. 4		17.8					14.2	17.8		
Bentonite no. 5		18.0					14.4	17.7		
Bentonite no. 7	17.7	17.7	17.7			17.7	14.1	17.7		
Bentonite no. 14		17.7					14.1	17.2		
Bentonite no. 15		17.8					14.1	17.7		
Bentonite no. 16A		17.7					14.1	17.7		
Bentonite no. 16B		17.7					14.1	17.7		
Bentonite no. 17		18.0					14.1	17.7		

* Vermiculite described as no. 2 (2).

† Montmorillonite samples consisting of fractions of $<1\mu$ particles were obtained by sedimentation from the following bentonites:

Bentonite no. 1 from Death Valley, California.

Bentonite no. 2 also called Otaylite from Otay (near San Diego), California.

Bentonite no. 4 from Merrit, British Columbia, Canada.

Bentonite no. 5 from Rosedale, Alberta, Canada.

Bentonite no. 7 from Goldfield, Nevada.

Bentonite no. 14 from Newell, South Dakota.

Bentonite no. 15 from Death Valley, Junction, California.

Bentonite no. 16A from Newberry, California (white colored).

Bentonite no. 16B from Newberry, California (red colored).

Bentonite no. 17 also called Saponite and Hectorite from Hector, California.

‡ The intensity of the reflection is affected by the cation; the relative intensity of the lines according to cations is as follows: $Ca = Mg = Na = H > Ba = NH_4 > K > Li > Rb > Cs$. The intensity of the Rb line is very weak and that of Cs is very very weak; the lines are quite diffused. The basal reflection lines of glycerol wet material are narrower and with sharper edges than those of air dry or water saturated material.

change in the other forms was very marked (compare Tables 1 and 4). Thus the Ca form showed a small contraction of the lattice as compared to that of the water treated material while the Ba, Li, or Na forms showed an expansion. These changes indicate that a complex was formed between the vermiculite and glycerol similar to the montmorillonite-glycerol complex but with one monomolecular layer of glycerol instead of two.* It should be noted that a monomolecular layer of glycerol has approximately the same thickness as two layers of water molecules organized in the manner indicated (3). This, perhaps, is the reason for MacEwan's failure to observe the formation of a glycerol complex in the case of vermiculite. K, NH₄, Rb, or Cs vermiculite showed no change in the interlayer spacing when wetted with glycerol. This again confirms the

* This was verified by a study in which vermiculite samples were dehydrated at 250° C. before treating with hot anhydrous glycerol. The vermiculite glycerol complex formed had nearly the same interlayer spacing as reported in Table 3. Details of this study will be reported at a later date.

results previously observed that the lattice of these minerals is contracted and consequently glycerol is unable to enter the interlayer space of the lattice to bring about expansion.

The results with montmorillonite confirm those reported by MacEwan. An interlayer spacing of 17.7 Å was obtained not only for H, Na, or Ca saturated montmorillonite but also with Mg, Ba, and Li forms. The interlayer spacing of NH₄ saturated montmorillonites was not consistent; out of ten samples from different sources eight gave the 17.7 Å while two gave a 14.5 Å spacing. These two expanded the equivalent of one layer of glycerol molecules instead of two as in the case of the other forms. The interlayer spacing of all ten of the K saturated montmorillonites was 14.1–14.2 Å. This again is the equivalent of only one layer of glycerol molecules. Although Rb and Cs saturated montmorillonite from Otay, California, gave very weak and diffused lines, the position of the 001 line was approximately that of the K montmorillonite.

The results obtained with glycerol treated NH₄ montmorillonite seem somewhat anomalous. From the similarity of NH₄ and K montmorillonite in their air dry and wet states it would be expected that this similarity might hold true in glycerol. Instead only two out of ten NH₄ montmorillonite samples studied gave spacings similar to that of K montmorillonite. The reason for this is not known.

From the foregoing it may be concluded that when montmorillonite and vermiculite are saturated with like ions, the former expands to a greater extent than the latter in glycerol or water.†

The difference in expansion between vermiculite and montmorillonite is of particular significance when K, NH₄, Rb, or Cs are the adsorbed ions. Vermiculites with these adsorbed cations have contracted lattices whereas montmorillonites have expanded lattices. This difference possibly may explain the near absence of K fixation in montmorillonite and the large fixation exhibited by vermiculite.

As previously indicated (2) fixation or irreversibility of the base exchange reaction in vermiculite occurs between ions which produce a contracted lattice and since no such phenomenon takes place in montmorillonite with the ions studied, irreversibility is also absent.

THE EFFECT OF PARTICLE SIZE ON EXPANSION IN VERMICULITE

To eliminate the possibility that the observed smaller interlayer expansion of vermiculite as compared with that of montmorillonite was due to the larger dimensions of the vermiculite particles, the expansion of small particles (<0.25μ) was studied. The small particles were obtained

† A similar study with many other organic substances led essentially to the same conclusion. This study will be reported separately.

by grinding and sedimentation. The results showed that the expansion of these particles whether air dry, immersed in water, or in glycerol was the same as that of larger particles.

STUDIES WITH PARAGONITE AND MUSCOVITE

Additional evidence for the effect of the interlayer cation on lattice expansion was obtained with paragonite—a mineral similar to muscovite in its composition but with Na as the dominating interlayer ion.

Paragonite samples #1 and #2 studied by Schaller and Stevens (15) were kindly furnished by R. E. Stevens for the present investigation.

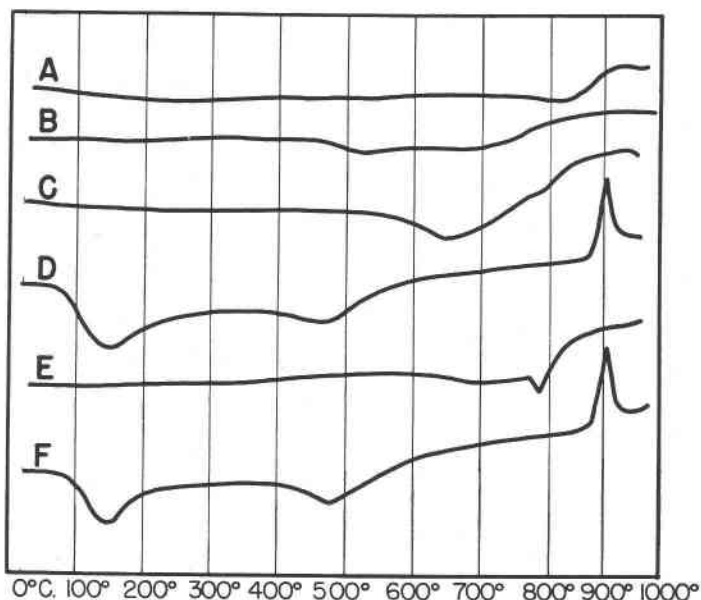


Fig. 4. Differential thermal curves of muscovite and paragonite.

- | | |
|--|--|
| A. Muscovite 5-50 μ particles. | D. Paragonite #1 <0.5 μ particles. |
| B. Muscovite <0.5 μ particles | E. Paragonite #2 5-50 μ particles. |
| C. Paragonite #1 5-50 μ particles. | F. Paragonite #2 <0.5 μ particles. |

Since paragonite is a true mica formed under high temperatures and pressures, it would be expected to be dehydrated and contracted in its natural form. This was verified by the differential thermal curve (Fig. 4) and the x -ray diagrams of these samples (Table 5). The x -ray diagrams were identical to those of muscovite with the exception that the basal spacing $d(002)$ is at 9.7 Å instead of 10.0 as for muscovite.

From the results reported herein it was anticipated that if the parag-

TABLE 5. BASAL REFLECTIONS $d(002)$ FOR PARAGONITE* AND MUSCOVITE† FOR COARSE ($5-50\mu$) AND FINE ($<0.5\mu$) PARTICLES‡ WHEN AIR DRY, IMMERSSED IN WATER, OR IMMERSSED IN GLYCEROL

		Air dry	Immersed in water	Immersed in glycerol
Muscovite	5-50 μ	10.06	10.06	10.06
	<0.5 μ	10.06	10.06	10.06
Paragonite No. 1	5-50 μ	9.7	9.7	9.7
	<0.5 μ	12.9	14.3	14.3
		9.7	9.7	9.7
Paragonite No. 2	5-50 μ	9.7	9.7	9.7
	<0.5 μ	12.9	14.3	14.3
		9.7	9.7	9.7

* Paragonite No. 1 from Fenestrella, Italy. Paragonite No. 2 from Monte Campiani, Switzerland. These samples were kindly furnished by R. E. Stevens (15).

† Muscovite from Pennington County, South Dakota.

‡ The samples were ground in an agate mortar and fractionated by sedimentation.

onite samples should be ground to extreme fineness, i.e., to less than 0.5μ , they would hydrate or form the glycerol complex and thereby expand. Muscovite, however, receiving the same treatment, i.e., grinding, should show no such change.

The results of this treatment are shown in Table 5 and Fig. 4. It is seen that the grinding brought about expansion and hydration in the case of paragonite but not with muscovite. These results leave no doubt that the Na ion imparts to the paragonite, when in extreme fineness, the ability to hydrate and expand. It is to be expected that even coarser fractions would hydrate if given enough time.

GLAUCONITE AND CELADONITE

The relation between H_2O content and K_2O , Na_2O and CaO of glauconite and celadonite, reported by Hendricks and Ross (9), indicates that the hydration of these micaceous minerals is also affected by the nature of the interlayer cation. In nearly all the samples the water content found was greater than the theoretical OH^- ions of the framework, namely, about 5 per cent. Nearly all the samples contain some Na_2O and CaO but those samples which contain the largest amounts of Na_2O and CaO and the least amounts of K_2O contain also the largest amounts of water.

STUDIES WITH HYDROUS MICA

The clay minerals resulting from the weathering of micas are known by a variety of names such as "illite," "hydrous mica," etc. (14). All

contain water of hydration. It was not realized until the present study that the hydration of the micas upon weathering was mainly the consequence of the replacement of the K by Ca, Mg, and H ions. Hendricks and Alexander (7) state, "In particular, montmorillonite and hydrous micas probably occur together." Similarly Aldrich *et al.* (1) state, "Some soil clays which earlier had been characterized as being principally hydrous mica were shown under these conditions of preparation to consist largely of montmorillonite." The criteria for montmorillonite used by these investigators was based solely on the expansion of the crystal lattice.

The results, however, of the present investigation have shown that interlayer lattice expansion is not confined to montmorillonite but it is a property of the mica type of a crystal lattice and is dependent upon the interlayer cation. For this reason the clay mineral with the expanded lattice reported to be associated with the "hydrous mica" is not necessarily montmorillonite as such, but is probably the result of alteration of mica by replacement of K with Ca, Mg, and H ions, as was shown to take place when biotite is leached with a $MgCl_2$ solution (2). A more detailed discussion of the nature of hydrous mica and its relation to vermiculite and montmorillonite will be presented elsewhere.

DISCUSSION

The conversion of a contracted lattice, like biotite, to an expanded lattice, like vermiculite, by merely exchanging the K ions with Mg ions (2) warrant a closer examination of the relation between expansion and the exchangeable ions.

It is well known that the interlayer K ions in the contracted mica lattice occupy the cavities formed by the hexagonal rings of oxygens on the bases of the linked silica tetrahedra of opposite lattice layers (5). It is probable that in the contracted lattice found when the interlayer cation is K, NH_4 , Rb, or Cs and when Li, Na, Mg, Ca, and Ba vermiculite lattices are dehydrated, the interlayer cations also occupy similar positions.

Calculations show that the radius of a sphere that just equals the size of the cavity within the hexagonal network of O ions is 1.35 Å. Comparison of the radius of a sphere of this size and the radii of the interlayer ions indicates that the radius of the interlayer cations may have an important bearing on the expansion of the lattice. In vermiculite when the interlayer positions are occupied by monovalent ions having a radius much smaller than 1.35 Å, namely, Li and Na ions, the lattice is expanded equivalent to a thickness of a monomolecular layer of water, whereas those ions with either an equal or a larger radius, namely, K, NH_4 , Rb, and Cs ions are associated with an essentially contracted

lattice. Furthermore when the radius of the exchangeable ion is at a minimum, for example the H ion, the expansion of the lattice becomes still greater and is equivalent to a thickness of two monomolecular layers of water. Among the divalent ions, those having radii substantially less than 1.35 Å cause expansion of the lattices about twice that of the Ba ion which is equal to 1.35 Å.

A comparison of the expansion of the crystal lattices with interlayer ions of equal size but different in charge, namely, monovalent versus divalent ions, suggests that the charge of the ions is an important factor in lattice expansion. Thus Mg or Ca ions cause about twice the expansion resulting from Li or Na ions. On the other hand, Ba ions bring about expansion equivalent to a monomolecular layer of water, whereas the K ions cause no expansion whatever.

Another factor appears when a comparison is made between the total interlayer charge and the degree of expansion of margarite, vermiculite, and montmorillonite. The essential difference between these three minerals, of significance in the present discussion, lies in the total negative charge neutralized by the interlayer cations. This charge per half unit cell is approximately 2 in margarite, from 1.0 to 0.7 in vermiculite, and from 0.5 to 0.3 in montmorillonite (14). Thus when the total charge is at a minimum, as in Ca montmorillonite, the lattice may expand to a width greater than that of two monomolecular layers of water; when the charge is at a maximum, as in margarite, there is no expansion at all (5); but when the charge is of an intermediate value, as in Ca vermiculite, expansion is limited to a thickness equivalent to two monomolecular layers of water.

A comparison of expansion of vermiculite and montmorillonite in glycerol and in water in terms of number of monomolecular layers of the interlayered substance rather than in terms of Å units reveals a very significant difference in expansion. Thus the total interlayer expansion of the vermiculites when immersed in water is equal to two monomolecular layers but when immersed in glycerol it is only equal to one layer. Similarly the total interlayer expansion of montmorillonites when immersed in water is equal to four or more monomolecular layers but when immersed in glycerol it is only equal to two layers. Therefore it may be concluded that expansion of these minerals in glycerol is considerably less than in water and that the similarity in expansion when expressed in Å is the result of differences in size or shape of the molecules of the interlayered substance.*

* An extensive study of the effect of the nature of the interlayered substance on expansion of vermiculites and montmorillonites is nearly complete. The results indicate that the dipole moment, the dielectric constant, and in some instances the form of the molecules are all factors in the expansion of dehydrated and contracted vermiculites and montmorillonites.

Therefore, it seems probable that: (1) the size of the interlayered ion, (2) the charge of the interlayered ion, (3) the total excess negative charge per unit cell of the mineral, and (4) the nature of the interlayered substance, are all factors in expansion.

In a separate discussion it will be suggested that the cause for these factors in expansion is related to their effect upon the interlayer attractive forces which hold the mica sheets together.

SUMMARY

1. The interlayer expansion was determined for air dry, water saturated, or glycerol saturated, vermiculite and montmorillonite containing any one of the following interlayer cations: Mg, Ca, Ba, H, Li, Na, K, NH_4 , Rb, or Cs.

2. The interlayer expansion of air dry vermiculite and montmorillonite saturated with Mg, Ca, or H ions is equal to two monomolecular layers of water, but those saturated with Ba, Li, or Na ions are equal to only one molecular layer of water.

3. Air dry vermiculite saturated with K, NH_4 , Rb, or Cs ions shows no expansion in terms of a monomolecular layer of water, whereas montmorillonite saturated with the respective ions shows an expansion of one molecular layer of water.

4. When immersed in water vermiculite saturated with Mg, Ca, Ba, H, Li, or Na shows a total expansion of only two monomolecular layers of water, but montmorillonite saturated with the respective ions shows an expansion of four or more monomolecular layers of water.

5. When immersed in water, K, NH_4 , Rb, or Cs vermiculite shows no expansion, but the respective montmorillonite shows an expansion of one molecular layer of water.

6. When immersed in hot anhydrous glycerol, Mg, Ca, Ba, H, Li, or Na vermiculite shows an expansion of one layer of glycerol molecules whereas the respective montmorillonite shows an expansion of two layers of glycerol molecules. This results in an interlayer spacing of 14.3 Å for vermiculite and 17.7 Å for montmorillonite.

7. When immersed in hot anhydrous glycerol, K, Rb, or Cs vermiculite remains contracted, but the respective montmorillonite expands to a thickness of one molecular layer of glycerol.

8. NH_4 vermiculite remains contracted in hot glycerol but NH_4 montmorillonites expand to a thickness of either one or two layers of glycerol molecules.

9. Finely ground paragonite hydrates and expands.

10. The nature of hydrous mica clay minerals is discussed briefly.

11. Interlayer expansion of the mica type of a crystal structure was found to depend upon the size, the valency, and the total number of the interlayer cations as well as the nature of the expanding substance.

REFERENCES

1. ALDRICH, D. G., HELLMAN, M. N., AND JACKSON, M. L., Hydration control of montmorillonite as required for its identification and estimation by *x*-ray diffraction methods: *Soil Sci.*, **57**, 215-231 (1944).
2. BARSHAD, I., Vermiculite and its relation to biotite as revealed by base exchange reactions, *x*-ray analyses, differential thermal curves, and water content: *Am. Mineral.*, **33**, 655-678 (1948).
3. BARSHAD, I., The nature of lattice expansion and its relation to hydration in montmorillonite and vermiculite: *Am. Mineral.*, **34**, 675-684 (1949).
4. BRADLEY, W. F., Molecular associations between montmorillonite and some polyfunctional organic liquids: *J. Am. Chem. Soc.*, **67**, 975-981 (1945).
5. BRAGG, W. L., Atomic structure of minerals. Cornell University Press, Ithaca, New York (1937).
6. CORNET, I., Sorption of NH₃ on montmorillonite clay: *J. Chem. Phys.*, **11**, 217-226 (1943).
7. HENDRICKS, S. B., AND ALEXANDER, L. T., Minerals present in soil colloids: *Soil Sci.*, **48**, 257-267 (1939).
8. HENDRICKS, S. B., NELSON, R. H., AND ALEXANDER, L. T., Hydration mechanism of the clay mineral montmorillonite, saturated with various cations: *Am. Chem. Soc. Jour.*, **62**, 1457-1464 (1940).
9. HENDRICKS, S. B., AND ROSS, C. S., Chemical composition and genesis of glauconite and celadonite: *Am. Mineral.*, **26**, 683-708 (1941).
10. HOFMANN, U., AND BILKE, W., Über die innerkristalline Quellung und das Basenaustauschvermögen des montmorillonits: *Kolloid-Zeit.*, **77**, 238-251 (1936).
11. MACEWAN, D. M. C., The identification and estimation of the montmorillonite group of minerals, with special reference to soil clays: *Jour. Soc. Chem. Indus.*, **65**, 298-304 (1946).
12. MACEWAN, D. M. C., Complex formation between montmorillonite and halloysite and certain organic liquids: *Trans. Faraday Soc.*, **46**, 349-367 (1948).
13. PAULING, L., The nature of the chemical bond, Cornell University Press, Ithaca, New York (1940).
14. ROSS, C. S., AND HENDRICKS, S. B., Minerals of the montmorillonite group: *U. S. Geol. Survey, Prof. Paper 205-B* (1945).
15. SCHALLER, W. T., AND STEVENS, R. E., The validity of paragonite as a mineral species: *Am. Mineral.*, **26**, 541-545 (1941).