VERMICULITE AND ITS RELATION TO BIOTITE AS REVEALED BY BASE EXCHANGE REACTIONS, X-RAY ANALYSES, DIFFERENTIAL THERMAL CURVES, AND WATER CONTENT

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ABSTRACT

Vermiculite is a base-exchange mineral with a high base exchange capacity. The exchangeable bases are Mg exclusively, or Mg and Ca. Base exchange takes place readily without grinding the material. Upon replacing the naturally occurring exchangeable bases of vermiculite with Li, Na, K, NH₄, Rb, Cs, Mg, Ca and Ba, the resulting samples were subjected to x-ray and differential thermal analysis and water loss was determined at various temperatures. The results showed that the kind of adsorbed cation determines the expansion of the lattice, its hydration properties and the shape of the differential thermal curve. The properties of K saturated vermiculite closely approximate those of biotite.

By leaching Gruner's hydrobiotite with MgCl₂ solution, K ions are replaced by Mg ions with the resulting conversion of hydrobiotite into vermiculite, and by prolonged treatment of biotite with MgCl₂ solution, it was converted into a material closely resembling vermiculite.

The results of this investigation seem to justify the conclusion that the exchangeable bases of vermiculite occupy interlayer positions as do K ions in biotite, and that vermiculite is essentially a Mg or Mg plus Ca mica. A new formula for vermiculite with the exchangeable bases in interlayer positions is proposed.

INTRODUCTION

In a study of the colloids of California prairie soils, a vermiculite-like substance, or possibly Gruner's hydrobiotite, was found (1). The similarity to vermiculite lay chiefly in the x-ray diffraction pattern and the differential thermal curve. At the time, the soil colloids were thought to differ from vermiculite in that the former had pronounced base exchange property. The structural formula for vermiculite, as given by Gruner (2), does not provide for exchangeable cations. Accordingly, it was decided to investigate the base exchange property of vermiculite. As this work proceeded, other aspects of the subject seemed to need further study. This paper reports the results of this work.

MATERIAL USED

(1) Vermiculite from Union of South Africa. Large, pale yellow transluscent sheets.

(2) Vermiculite called culsageeite or jefferisite from Culsagee Mine, Macon County, North Carolina. Bronze in color and in large flakes.

(3) Protovermiculite from Magnet Cove, Arkansas. Large golden yellow scales. (This apparently comes from the same source as Gruner's vermiculite no. 2.)

(4) Vermiculite from Libby, Montana. Dark greenish brown scales. (From the same source as Gruner's vermiculite no. 10.)

(5) Vermiculite from Lenni, Delaware County, Pennsylvania. Apple green, compact, and in small scales.

(6) Biotite (source unknown).

(7) Prochlorite from Chester, Vermont.

(8) Chlorite from Chester, Vermont.

(9) Ripidolite from West Chester, Pennsylvania.

BASE EXCHANGE STUDIES

The experimental work is based on the idea that base exchange is represented by the equation:

$$AX + B^+ \rightleftharpoons BX + A^+$$
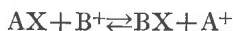
where A^+ and B^+ represent solution cations of equal charge, and AX and BX represent the exchange material saturated with A^+ and B^+, respectively. When the exchange material has only one kind of exchangeable cation, the material is said to be saturated with that ion. The total

amount of exchangeable cations is usually expressed as milliequivalents per 100 grams and this quantity is called base exchange capacity.

To demonstrate that a material possesses base exchange property, it is necessary to show that the material will undergo the above reaction. If one starts the reaction with an AX material and B^+ in solution and carries the reaction to completion, it should then be possible to demonstrate the presence of BX and of A^+ in the solution. If the reaction is reversible, it will be possible to reconvert BX into AX by means of a solution of A^+.

The method of effecting base exchange was as follows: A small amount of material (0.5–2.0 grams)—either unground or lightly ground by hand to pass a 100 mesh sieve—was placed in a small beaker containing a neutral normal solution of the desired cation and heated to about 70° C. for several hours. The material was then transferred to a sintered glass bottom crucible under suction. After the solution had passed through the filter completely, the material was transferred back to the beaker with fresh salt solution and the process was repeated two or three times daily for about 10 days. The filtered solutions were analyzed for bases. At the end of this treatment the material was washed free of the salt solution with neutral methanol and dried in the air.

Standard methods of analysis were used for determining the bases replaced from the sample and the bases adsorbed by the material from the solution.

NH_4 Exchange Capacity and the Exchangeable Bases in Natural Vermiculites

The results of leaching vermiculites 1, 2, 3, and 5 with N neutral NH_4Ac, the salt commonly used in the determination of replaceable bases, are given in Table 1. NH_4^+ taken up by exchange was determined by distillation in the presence of NaOH.

It is seen (Table 1) that the NH_4 exchange capacity of vermiculites 1, 2 and 3 is very high but that of vermiculite 5 is considerably smaller. The reason for this difference will appear later.

In the light of the structural formula of vermiculite, as given by Gruner, these results were difficult to explain, for the formula does not show any exchangeable bases. At first an explanation for the large exchange capacity was sought by an early theory for the cause of the base exchange property, which states that adsorbed water molecules dissociate into OH^- and H^+; the OH^- remains on the exchange material and H^+ exchanges for an NH_4^+ or any other cation. Since vermiculite is highly hydrated, this reaction was thought possible, and it was reasoned that if this reaction should take place, a large amount of acidity would de-

TABLE 1. BASES EXCHANGED FOR NH₄⁺ BY UNGROUND AND LIGHTLY GROUND VERMICULITES WHEN LEACHED WITH N NEUTRAL NH₄Ac SOLUTION

Milliequivalents per 100 grams air dry material

Vermiculite	Exchangeable Bases					NH₄⁺ Adsorbed
	Mg^{++}	Ca^{++}	Na^+	K^+	Σ	
1. Lightly ground	128.3	13.7	0.0	0.0	142.0	141.3
2. Lightly ground	146.0	0	0.0	0.0	146.0	145.5
3. Unground	144.5	0	0.0	0.0	144.5	145.9
4. Lightly ground	40.0	93.0	0.0	0.0	133.0	134.5
5. Lightly ground	65.5	0	0.0	0.0	65.5	64.8

velop in the leaching solution. The vermiculites were therefore leached with N neutral NaCl solution and the pH of the leachate was determined. It was found that the pH of the NaCl solution did not change by passing it through the samples. This led to the conclusion that H⁺ was not replaced, and hence the foregoing explanation of the exchange is not acceptable. That the exchange property of the vermiculite was not due to the presence of water, was also shown by the fact that the exchange capacity did not change materially when the material was dehydrated to the extent of losing all the free water as seen in Table 2.

TABLE 2. NH₄⁺ ADSORBED BY LIGHTLY GROUND VERMICULITES TREATED WITH H₂O₂ OR HEATED TO VARIOUS TEMPERATURES

Milliequivalents per 100 grams air dry material

Vermiculite	Treatment		
	H_2O_2	110° C.	255° C.
1	146.5	141.0	135.2
2	144.0	143.7	139.0
3	131.0	127.6	88.5
5	65.5	62.4	60.8

That the Mg^{++} and Ca^{++} found in the leachates were actually replaced by NH₄⁺ is shown by the fact that Mg^{++}, or $Mg^{++}+Ca^{++}$ found in solution closely approximates NH₄⁺ adsorbed. The exchangeable base of samples 2 and 5 is exclusively Mg^{++} whereas samples 1 and 3 contain exchangeable Mg^{++} and Ca^{++}; in sample 1, the base is chiefly Mg^{++}, but in no. 3 the Ca^{++} is more than twice the Mg^{++}.

The Effect of Particle Size on Base Exchange Capacity

To determine whether or not light grinding has any effect on the base exchange capacity of the vermiculites, the base exchange capacity and the exchangeable bases of an unground vermiculite (no. 2) were determined. The results reported in Table 1 show that the exchange capacity and the exchangeable bases were not affected by lightly grinding the material.

As the solution acted on the unground material, a visual picture was presented of the path the ions take in passing in and out of the crystal lattice. Vermiculite no. 2 upon exchanging its Mg^{++} for NH_4^+ changed color from bronze to dark gold. This color change was observed to proceed from the edges towards the center of the plates or sheets, indicating that the ions enter and leave by the edges, and travel in a plane parallel to the tetrahedral layers.

The effect of particle size on base exchange was further studied by treating the hand ground samples with hydrogen peroxide, which, as Gruner (3) showed, produces exfoliation, and this reduces the particles to extreme fineness. As shown by comparing Tables 1 and 2, base exchange capacity was not affected by treating the sample with H_2O_2. The conclusion seems to be warranted that particle size has no effect on the base exchange capacity of vermiculite.

The Reversibility of the Base Exchange Reaction

The reversibility of the base exchange reaction with the vermiculites is readily demonstrated in various ways: (1) by converting the NH_4 vermiculite to Na and Ca vermiculites and reconverting them back to the NH_4 vermiculite without any change in exchange capacity (Table 4); (2) by reconverting the NH_4 vermiculite, Na vermiculite and K vermiculite back to the original Mg vermiculite. These reconversions can best be observed by the use of the differential thermal curves and the x-ray diffraction patterns. In Figures 1 and 2 the differential thermal curves of the original Mg saturated vermiculites are given, as well as those of the Na, NH_4 and K forms and also those of the reconverted Mg vermiculites. These curves show that the original Mg vermiculites were reobtained by treating the sample with $MgCl_2$. The x-ray diffraction pattern of these vermiculites also give a clear picture of the changes which take place. These changes are most clearly brought out by the basal spacing ($d002$), as may be seen in Table 8. These results verify those of the differential thermal curves in showing that the original vermiculite was reobtained.

Vermiculites saturated with Na^+, K^+ and Ca^{++} were also prepared and the total content of these ions adsorbed was determined by the HF

method for total analysis of silicates (Table 3). Similar determination on the original vermiculites showed that none of these ions were present in sample 2, and only Ca in sample 1, the amount of which just equalled exchangeable Ca^{++}. It is seen in Table 3 that the amount of K^+ adsorbed is higher than Na^+, and Na^+ higher than Ca^{++}. These differences are due chiefly, as will be seen later, to different degrees of hydration of the K, Na, and Ca vermiculites and also, to a smaller extent, to the different molecular weight of these ions.

TABLE 3. TOTAL Na^+, K^+, AND Ca^{++} ADSORBED BY LEACHING LIGHTLY GROUND VERMICULITES WITH N NaCl, KAc, AND CaAc

Milliequivalents per 100 grams air dry material

Vermiculite	Na^+	K^+	Ca^{++}
1	155.6	180.0	143.0
2	154.5	177.5	145.0
5		68.0	

TABLE 4. BASES EXCHANGED FOR NH_4 BY VERMICULITES SATURATED WITH VARIOUS CATIONS WHEN LEACHED WITH N NEUTRAL NH_4Ac SOLUTION

Milliequivalents per 100 gram air dry material

Vermiculite	Saturated With	Base Replaced	NH_4 Adsorbed
1	K	K 49.4	50.8
	Mg	Mg 142.0	141.5
2	K	K 28.5	31.0
	Na	Na 146.5	147.0
	Mg	Mg 145.5	146.0
	Ca	Ca 143.0	145.5

The Nature of "K+ Fixation"

The results given in Tables 3 and 4 show that only part of the K^+ taken up by exchange, was replaced by HN_4^+, whereas Na^+, Mg^{++} and Ca^{++} exchanged completely. The taking up of K^+ in excess of the amount replaceable by NH_4^+ has long been observed with soil colloids (6), and is known as K^+ fixation. The amount thus fixed by soil colloids is much less than by the vermiculites.

The nature of K^+ fixation by vermiculite was investigated (1) by thoroughly leaching K vermiculite with NaCl, $MgCl_2$ and NH_4Ac solu-

tions, and (2) by distillation of the NH_4 vermiculites with various bases until no further NH_3 appeared in the distillate. The results of the leaching experiment (Table 5) show clearly that the fixed K^+ is replaceable by Na^+ or Mg^{++} but to a limited extent only by the NH_4 ion. The distillation experiment (Table 6) shows that adsorbed NH_4^+ is likewise only partially replaceable by K^+ and to a lesser extent by Rb^+ and Cs^+, whereas NH_4^+ is readily replaced by Li^+, Na^+, Mg^{++}, Ca^{++}, and Ba^{++}. It is interesting to note that the amount of NH_4^+ replaced by K^+ is approximately equal to K^+ replaced by NH_4^+ (compare Tables 5 and 6).

TABLE 5. AMOUNTS OF K^+ REPLACED FROM K-SATURATED VERMICULITES BY
PROLONGED LEACHING WITH N NEUTRAL NH_4Ac, NaCl, AND $MgCl_2$

Milliequivalents per 100 grams air dry material

Vermiculite	Replaced By		
	NH_4Ac	NaCl	$MgCl_2$
1	49.4	170.9	
2	28.5	166.9	170.5

TABLE 6. AMOUNTS OF NH_4^+ REPLACED FROM NH_4-SATURATED VERMICULITES
BY DISTILLATION WITH DIFFERENT BASES

Milliequivalents per 100 grams air dry material

Vermiculite	LiOH	NaOH	KOH	RbOH	CsOH	$Mg(OH)_2$	$Ca(OH)_2$	$Ba(OH)_2$
1		163.2	45.3			164.0		
2	164.4	165.0	31.7	25.4	7.5	165.3	163.5	165.9

Having found that vermiculite has pronounced base exchange property, samples were saturated with different cations by treating them with neutral solutions of corresponding cations. The materials thus obtained were subjected to *x*-ray analysis, differential thermal study, and water content determination at various temperatures.

RESULTS OF *X*-RAY STUDY

An explanation of ion fixation appeared when the *x*-ray patterns of the variously saturated vermiculites were studied (Table 7). Those adsorbed cations which produce contracted lattices are more or less fixed against replacement by a cation which itself produces a contracted lattice, but ions which produce an expanded lattice can replace an ion adsorbed with-

in a contracted lattice apparently by being able to expand the lattice gradually as it enters the lattice from the edges.

As shown in Table 7, vermiculite exhibits remarkable differences when saturated with different cations. These differences are clearly revealed by the x-ray diffraction patterns and also by the differential thermal curves. In the light of this evidence, the moisture content of the

TABLE 7. BASAL REFLECTIONS (d002) FOR VERMICULITES AND BIOTITE SATURATED WITH VARIOUS CATIONS AND DRIED AT VARIOUS TEMPERATURES

Saturating Cation		Mg^{++}	Ca^{++}	Ba^{++}	Li$^+$	Na$^+$	K$^+$	NH$_4^+$	Rb$^+$	Cs$^+$	K$^+$ 75% Ca & Mg 25%
Vermiculite No. 2	Air Dry	14.33	15.07	12.56	12.56	12.56	10.42	11.24	11.24	11.97	
Heated to	750° C.	9.40	9.55	10.27	9.55	9.55	10.27	9.25	10.46	11.22	
Heated to	255° C.		{12.25, 10.20}				{12.38, 10.20}					
Vermiculite No. 1	Air Dry	14.33	15.07			12.56	10.42	11.14			
Heated to	750° C.	9.50	9.50			9.60	10.27	9.25			
Heated to	450° C.	{13.91, 12.48, 9.95}				{12.28, 10.49}	10.27				
Vermiculite No. 3	Air Dry	14.92									
Heated to	750° C.	9.60									
Vermiculite No. 4	Air Dry	14.33	15.07			12.48	10.34				11.77
Biotite	Air Dry	14.47					10.29				

TABLE 8. BASAL REFLECTIONS (d002) FOR VERMICULITE SAMPLES WHICH HAVE UNDERGONE THE FOLLOWING BASE EXCHANGE REACTIONS: NATURAL X→KX→NaX→MgX

Sample Air Dry	Natural (MgX)	KX	NaX	MgX
Vermiculite No. 1	14.33	10.42	12.56	14.33
Vermiculite No. 2	14.33	10.42	12.56	14.33

variously saturated vermiculite assumes special significance. Accordingly, samples were x-rayed after having been heated to various temperatures. The results show that the lattice contracts as water is expelled. Measurements of the basal (d002) spacings show the following:

(1) The Mg saturated (natural) material—and Ca saturated materials have the widest spacing—the latter having a slightly wider spacing than the former.

(2) The NH$_4$, K, Rb, and Cs saturated materials have the narrowest spacing. The spacing of the K saturated material, however, is

identically the same as that of biotite. Not only the 00*l* spacing but also the rest of the spacings are the same as that of biotite.

(3) The Ba, Li, and Na saturated material gave a spacing which is narrower than that of the Mg and Ca saturated material, but wider than that of the NH_4, K, Rb, and Cs saturated material. The difference is approximately the width of one water molecule—2.60 Å.

It is interesting to note that the intensity of the reflections of the *d*002 spacing varied considerably with the exchangeable ion. Following is approximately the order of intensity for the different cations $Ca = Mg > Ba = Li = Na = K > Rb > Cs$, the last two giving weak, broad, and quite diffused lines.

(4) Upon complete dehydration, at 750° C., the spacings of the Mg, Ca, Na, Li, and NH_4 saturated materials approximate the spacing of talc. The spacing of the Ba and Rb saturated material altered to that of biotite and a small but significant change also took place in the Cs saturated material. On the other hand, heating to 750° C. produced but little change in the spacing of the K saturated material.

DIFFERENTIAL THERMAL CURVES, AND WATER CONTENT AT VARIOUS TEMPERATURES

The nature of hydration of the natural vermiculites as well as of vermiculites saturated with the various cations is most clearly revealed by the differential thermal curves shown in Figures 1, 2, 3, and 4. It is seen that three groups of curves were obtained which parallel the three groups of the *x*-ray diffraction patterns—namely, (1) the natural and Ca saturated vermiculites, (2) the Ba, Li and Na saturated vermiculites, and (3) the K, NH_4, Rb, and Cs saturated vermiculites. The significant portion of the curves is found in the endothermic trough, representing water losses, at the lower temperatures. These curves show the following:

(1) The curves for natural and Ca saturated materials have two troughs, the lowest point of the first being at about 150° C. and of the second at about 240° C. for Ca and at about 260° C. for natural vermiculites, the latter being largely saturated with Mg^{++}.

(2) The Ba, Li, and Na saturated vermiculites have only one trough the lowest points of which range from 140° C.–160° C.

(3) The NH_4, K, Rb, and Cs vermiculites have no trough at low temperatures and behave as if they are anhydrous.

Since these troughs represent water losses their significance appears when this water loss is determined for each trough separately.
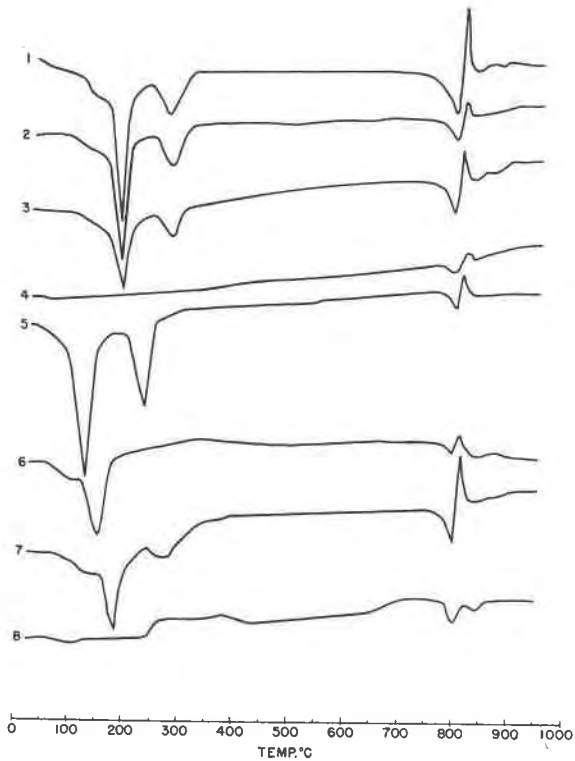
FIG. 1. Differential thermal curves of vermiculite no. 1.
1. natural
2. natural and H_2O_2 treated
3. natural and heated to 550°C. and then rehydrated
4. natural and heated to 800°C. and then rehydrated
5. Ca saturated
6. Na saturated
7. Mg saturated after being Na saturated
8. NH_4 saturated

The results of such determination are given in Tables 9 and 10. They show that the moisture loss corresponding to the first trough was about 12.85 per cent for Mg and Ca saturated material; for the second trough, it was 2.6 per cent, and between 250° C. and 500° C., 1.3 per cent. The moisture loss corresponding to the endothermic break in the curves for Ba, Li, and Na saturated materials was about 8.5 per cent and an additional 2.7 per cent moisture was lost between 150° to 500° C. The K, Rb, and Cs materials showed a loss of about 3 per cent between air temperature and 500° C.
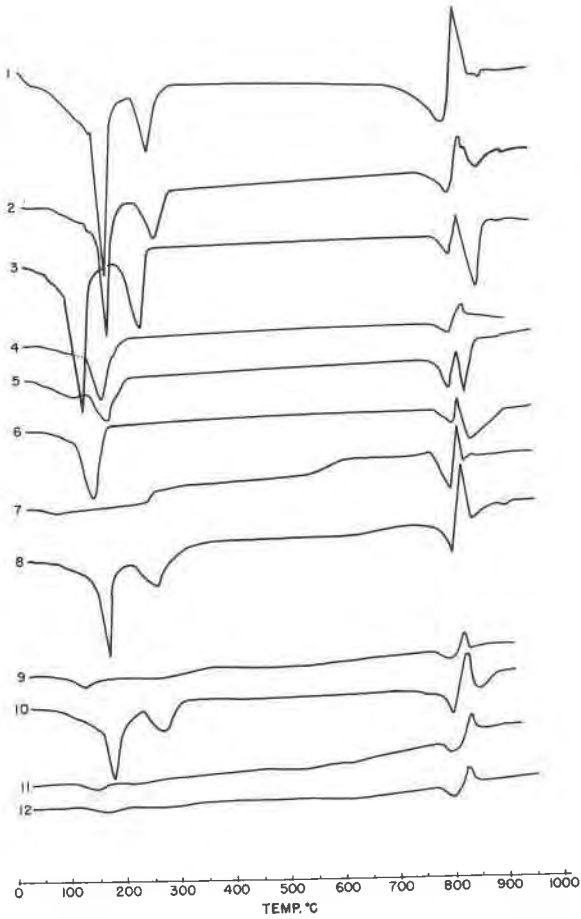
Fig. 2. Differential thermal curves of vermiculite no. 2.

1. natural
2. natural and H_2O_2 treated
3. Ca saturated
4. Ba saturated
5. Li saturated
6. Na saturated
7. NH_4 saturated
8. Mg saturated after being NH_4 saturated
9. K saturated
10. Mg saturated after being K saturated
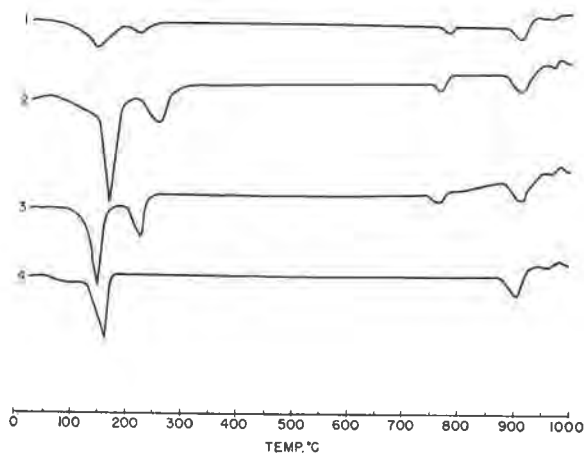11. Rb saturated
12. Cs saturated

FIG. 3. Differential thermal curves of vermiculite no. 4.
1. natural
2. Mg saturated
3. Ca saturated
4. Na saturated

The moisture content assumes special significance when it is calculated as mols per exchangeable ion (Tables 9 and 10). It will be noted that Mg and Ca saturated vermiculite lost 10 mols H_2O per adsorbed cation when heated to 150° C., 2 mols between 150 and 250° C., and 1 mol between 250 and 500° C. When Ba saturated, 6 mols H_2O per Ba ion were driven off by heating to 150° C., and 2 additional mols upon heating from 150 to 600° C. When Li and Na saturated, 3 mols H_2O per adsorbed ion were driven off by heating to 150° C., and one additional mol upon heating from 150° to 500° C. On the other hand, the total water loss below 600° C. for K, Rb, and Cs saturated vermiculite was about one mol per adsorbed cation.

When the water content of the materials is compared with the expansion of the lattice, the results indicate that Mg and Ca saturated vermiculite expanded a distance equivalent to about two layers of water molecules and the expansion of the Ba, Li and Na vermiculite was approximately equal to one layer of water molecules.

The vermiculites rehydrate very rapidly after having been dehydrated by heating, even when heated to 550° C. Only when heated to 700° C. or higher, does vermiculite lose the property of rehydration. This is well illustrated by curves 1 and 3 of Figure 1, which have almost identical shapes for unheated (no. 1) and for a sample preheated to 550° C. and then exposed to the atmosphere (Curve 3). The rehydration is very rapid with material only slightly ground. This may account for the apparent
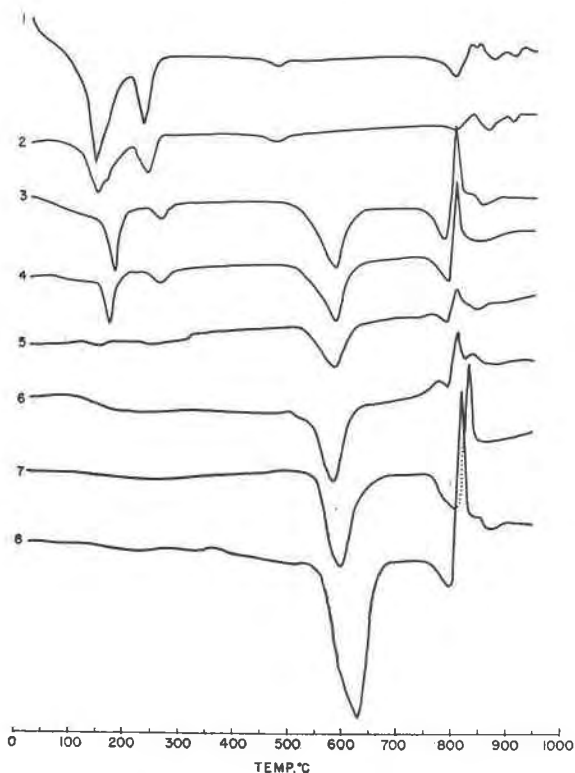
FIG. 4. Differential thermal curves of vermiculites no. 3 and no. 5, prochlorite, chlorite, and ripidolite.
1. natural vermiculite no. 3
2. vermiculite no. 3 H_2O_2 treated
3. natural vermiculite no. 5
4. natural and H_2O_2 treated vermiculite no. 5
5. K saturated vermiculite no. 5
6. prochlorite from Chester, Vermont
7. chlorite from Chester, Vermont
8. ripidolite from West Chester, Pa.

lack of contraction, as reported by Gruner, upon heating vermiculite to 300° or 400° C. It will be noted that samples heated to 255 and 400° C. and then x-rayed (Table 7), showed two or more 002 lines. This was probably due to rehydration of a part of the sample during the brief time required to pack the samples in tubes.

As is well known, one of the characteristic properties of vermiculite is that of exfoliation upon sudden heating to a high temperature. It was found, however, that vermiculite loses this property, if the water is driven off slowly by gradually heating to 250° C. The water is lost just

TABLE 9. LOSS IN WATER AT VARIOUS TEMPERATURES FROM VERMICULITE NO. 2
SATURATED WITH VARIOUS CATIONS

Temper-atures	20–150° C.		150–250° C.		250–550° C.		150–550° C.		550–600° C.	550–800° C.	Total
Exchange-able Ion	%	Mols H₂O Per Adsorbed Cation	%	Mols H₂O Per Adsorbed Cation	%	Mols H₂O Per Adsorbed Cation	%	Mols H₂O Per Adsorbed Cation		%	%
Mg^{++}	12.85	10	2.65	2	1.32	1				4.59	21.31
Ca^{++}	12.90	10	2.68	2	1.32	1				4.85	21.75
Ba^{++}	8.50	6					2.73	2		3.31	14.54
Li^+	8.30	3					2.83	1		4.79	15.92
Na^+	8.50	3					2.92	1		4.92	16.34
K^+	1.21	0.3					2.46	0.8		2.73	6.40
Rb^+	1.50	0.5					1.60	0.5		2.62	5.72
Cs^+	1.71	0.5					2.29	0.7		2.26	6.26
							H₂O %	NH₃ %	H₂O % NH₃ %		
NH_4^+	1.67						0.40	0.38	2.57 2.43	4.22	8.86

as readily by unground as by ground material. After being slowly dehy-
drated, unground vermiculite was then suddenly heated to high temper-
ature, but it did not exhibit exfoliation. This suggests that the exfoliation
depends on rapid formation of water vapor between lattice layers.

This property of exfoliation by vermiculite is also lost by saturation
with K^+, Rb^+ and Cs^+. The loss of this property in these cases is ap-
parently for the same reasons as with the slowly heated natural vermicu-
lites, that is, the absence of water between lattice layers.

TABLE 10. LOSS IN WATER AT VARIOUS TEMPERATURES FROM NATURAL VERMICULITES
AND FROM VERMICULITES AND BIOTITE SATURATED WITH VARIOUS CATIONS

Temperatures		20–150° C.		150–250° C.		250–400° C.		400–600° C.	600–900° C.	Total
Vermiculite No.	Exch. ion	%	Mols H₂O per Adsorbed Cation	%	Mols H₂O per Adsorbed Cation	%	Mols H₂O per Adsorbed Cation	%	%	%
1 Natural	Ca, Mg	13.07	10	2.62	2	1.31	1		4.85	21.75
3 Natural	Ca, Mg	11.95	10	2.39	2	1.20	1	0.52	4.28	20.34
5 Natural	Mg	5.79	10	1.32	2	0.65	1	4.09	4.70	16.55
4 Natural	Mg, Ca, K	3.30	10	0.65	2	0.34	1		1.60	5.89
4	Mg	12.30	10	2.48	2	1.21	1		4.10	20.09
4	Ca	12.47	10	2.48	2	1.23	1		4.35	20.53
4	Na	7.46	3	2.35	1				4.50	14.31
4	K	1.20		0.25					1.60	3.05
Biotite 1μ	K	0.34							1.24	1.59
	Mg	12.77		2.70		1.45				

THE NATURE OF THE HYDRATION AND THE EXPANSION OF
THE NH₄, K, Rb AND Cs VERMICULITES

The loss in weight of NH_4 saturated vermiculite is of special interest, because it represents the loss of both water and NH_3. To determine how much of the weight loss was due to NH_3 and how much to H_2O, the loss in NH_3 was determined by difference, that is, the amount of NH_4^+ left after each heating was determined and subtracted from the original amount present. The results show that (a) the loss in weight up to a temperature of 255° C. is of water alone, (b) the loss between 255° C.—550° C. is relatively small and consists of equal amounts of NH_3 and H_2O in terms of equivalents, (c) the loss between 550° C.–600° C. is considerable and also consists of equivalent amounts of NH_3 and H_2O, and (d) between 600° C.–800° C. the loss consists of water alone and is equal to the crystal lattice water i.e. OH^- of the octahedral layer. The total amounts of NH_3 lost per 100 grams of air dry NH_4 saturated material amounts to 2.81% or 165 m.e., which is the base exchange capacity of this sample. It is interesting to note that the loss in NH_3 is accompanied by the loss of an equivalent amount of water. This indicates that each NH_4^+ is closely associated with one water molecule and that the energy of binding between them must be large. The combined loss of NH_3 and water causes the unground NH_4 vermiculite to exfoliate upon rapid heating to a high temperature.

The strong association between NH_4^+ and water molecules may explain the slightly wider spacing of NH_4 vermiculite as compared with the heated K vermiculite, as shown in Table 7. Each K ion probably occupies the cavity formed by the hexagonal rings of oxygens in opposite lattice layers and the number of such cavities is about equal to the number of K^+ when fully K saturated. Each of these cavities in the NH_4 saturated material, however, must accommodate not only an NH_4^+ but also a water molecule. Since NH_4^+ is larger than the single cavity, it brings about a slight expansion (0.97Å) of the lattice. A similar situation possibly exists in the Rb, Cs, and K saturated samples, but differences in ion size must be taken into consideration in explaining the different degrees of expansion of the lattice of these materials.

Upon dehydration, the water molecules, which may possibly occupy the cavities formed by the hexagonal rings of oxygens opposite the exchangeable ions, are lost, and as a result, the exchangeable ions can extend into these cavities. If the radius of the exchangeable ion is larger than the radius of a sphere that can just fit into two opposite cavities when lattice layers are just touch, the lattice will remain expanded. Calculations show that the radius of such a sphere is 1.67Å and that of the radii of K^+, Rb^+ and Cs^+ in a coordination number of twelve (7)

are 1.56Å, 1.67 Å, and 1.84 Å, respectively. It is seen that only the radius of Cs^+ is larger than the radius of the sphere just described and as a result the lattice in which Cs^+ is present remains expanded even after dehydration (Table 7).

CHANGES AT IGNITION IN THE CRYSTAL LATTICE OF VERMICULITE SATURATED WITH VARIOUS CATIONS

An examination of the portion of the differential thermal curve in the neighborhood of ignition temperature reveals a small endothermic effect in the Ba, K, and Rb vermiculites followed by a small exothermic effect, whereas Mg, Ca, Li, and Na vermiculites showed a large endothermic effect followed by a still larger exothermic effect.

Moisture determinations showed that the endothermic effect is caused by loss in water, the magnitude of the effect being proportional to the amount of the water lost (Table 9).

The diffraction patterns of the moderately heated Mg, Ca and Na vermiculites reveal a contracted lattice with basal spacings of 9.95 Å, 10.20 Å and 10.20 Å respectively, which closely approximate the $d002$ spacings of biotite. However, these spacings contracted to 9.40 Å, 9.55 Å, 9.55 Å, respectively upon ignition. This contraction is believed to be responsible for the exothermic effect shown by the differential thermal curves. Since the contraction of the K vermiculite is small—about 0.15 Å—the exothermic effect is likewise small.

Calculations show that the thickness of a single lattice layer is about 10.20 Å. It seems, therefore, that the contraction at ignition represents a change within the lattice layer itself. The loss of the OH ions from the octahedral layer at high temperature is in harmony with this view. The still narrower basal spacing of the heated NH_4 vermiculite (after NH_3 was completely removed) is believed to be brought about by a further contraction. This contraction, however, may be explained by the manner of the superimposition of the hexagonal oxygen rings of the linked tetrahedra of opposite lattice layers. If the layers with a thickness of 9.47 Å are superimposed in a tetrahedral fashion, calculations show that the $d002$ spacing would be 9.15 Å, and this is about the basal spacing observed in the heated NH_4 vermiculite.

THE CONVERSION OF HYDROBIOTITE AND BIOTITE TO VERMICULITE

Since the x-ray diffraction patterns and hydration properties indicate that K saturated vermiculite closely resembles true biotite, experiments were made to convert by base exchange, biotite and the "hydrobiotite" as described by Gruner (2), into vermiculite.

The materials used in these experiments were vermiculite no. 4, one of the hydrobiotites described by Gruner, and a true biotite.

The experimental procedure employed was similar to that used in reconverting the artificially prepared potassium vermiculite into true vermiculite (Mg saturated) as described previously. Vermiculite no. 4, the so-called hydrobiotite, was converted into Mg, Ca, and Na saturated forms, as well as completely saturated with K^+. The true biotite was converted only to the Mg saturated form.

The conversion of the vermiculite samples took place quite readily both when ground lightly by hand and with unground material exfoliated with H_2O_2. The conversion, however, of biotite was found to proceed very slowly with material only lightly ground. From the path the exchangeable ions take in entering or leaving the lattice of vermiculite, as was shown previously, it was anticipated that the conversion will be most rapid with small particles. This was verified by determining the amount of potassium exchanged in a given time for different particle size fractions as obtained by sedimentation (Table 13). Only material of particle size $< 1\mu$ was completely converted by leaching for a period of three months. Since only small amounts of biotite were used, only x-ray patterns and the water content were determined. The results are shown in Tables 7 and 10. These, however, amply demonstrate the conversion. Sufficient amounts of the converted hydrobiotite were obtained to determine the x-ray diffraction patterns (Table 7), differential thermal curves (Fig. 3), and moisture content (Table 10), and to make additional base exchange studies (Tables 11 and 12).

TABLE 11. BASES EXCHANGED FOR NH_4^+ BY LIGHTLY GROUND OR H_2O_2 TREATED
UNGROUND VERMICULITE NO. 4 WHEN LEACHED WITH N
NEUTRAL NH_4Ac FOR A PROLONGED PERIOD
Milliequivalents per 100 grams air dry material

Exchangeable Bases				NH_4^+ Adsorbed
Ca^{++}	Mg^{++}	K^+	Σ	
21.4	15.8	0.8	37.0	36.5

The x-ray diffraction patterns, the differential thermal curves, the water content, as well as its relation to the exchangeable ion, and the NH_4 exchange capacity of the converted hydrobiotites clearly show that this hydrobiotite was converted into vermiculite by simple base exchange.

The base exchange studies show that (1) the exchangeable bases of this natural hydrobiotite consist of about 75% K^+, 15% Ca^{++}, and 10% Mg^{++}, (2) that the water content of the natural material is due to the presence of the exchangeable Ca^{++} and Mg^{++}, and (3) that the K^+ exchanges for NH_4^+ to a very limited extent but quite readily for Mg^{++}, Ca^{++}, or Na^+.

TABLE 12. BASES REPLACED FROM NATURAL VERMICULITE NO. 4 WHEN LEACHED WITH N NEUTRAL $MgCl_2$ SOLUTION, AND NH_4^+ ADSORBED BY THE Mg SATURATED SAMPLE

Milliequivalent per 100 grams air dry material

Exchangeable Bases				NH_4^+ Adsorbed	
Replaced by Mg	Replaced by NH_4^+		Σ	On basis of natural material	On basis of Mg saturated material
K^+	Ca^{++}	Mg^{++}			
121.5	21.4	15.8	158.7	160.0	138.2

The x-ray diffraction patterns and the water content of biotite converted to the Mg saturated form, are also identical to that of Mg saturated vermiculites, as may be seen in Tables 7 and 10. It is interesting to point out that the amount of water that was gained by biotite upon leaching with a salt solution is proportional to the K^+ replaced and depends on the kind of ion which replaced it. For example, one sample of

TABLE 13. THE REPLACEMENT OF INTERLAYERED POTASSIUM FROM VARIOUS SIZED PARTICLES OF BIOTITE* BY LEACHING WITH SOLUTIONS OF $MgCl_2$, $CaCl_2$, AND NaCl

Milliequivalents per 100 gram air dry material

	$MgCl_2$	$CaCl_2$	NaCl
Fraction			
1–5μ	81.3		17.7
5–50μ	13.9	8.1	4.4
>50		3.3	

* These biotite fractions were leached for two months with the respective salt solutions prior to the additional three weeks of leaching during which the potassium replaced was determined.

biotite, when leached with a $MgCl_2$ solution, lost 82.8 m.e. K per 100 grams, and gained 9.34% water (at 250° C.), or about 12.5 water molecules per exchangeable ion; another biotite sample when leached with a $MgCl_2$ solution lost 57.5 m.e. K per 100 grams and gained 5.78% water (at 140° C.) or about 11 water molecules per exchangeable ion.

THE STRUCTURAL FORMULA OF VERMICULITE

The structural formula of vermiculite as given by Gruner and later by Hendricks and Jefferson is: $(OH)_2(Mg,Fe)_3(Si,Al,Fe)_4O_{10} \cdot 4H_2O$.

Although this formula indicates isomorphous substitution of Al and Fe^{+++} for Si ions in the tetrahedral layer, the charge resulting from this substitution apparently was assumed to be balanced by the presence of Fe^{+++} in the octahedral layer, and not by cations between lattice layers. Essentially this structure is that of a neutral lattice similar to talc with water molecules between the layers. The first indication that this formula is not entirely satisfactory was Gruner's preparation of NH_4-micas from vermiculites (3). On the basis of his formula Gruner could not find a satisfactory explanation for the conversion of supposedly neutral talc-like layers of the vermiculite to charged layers of the mica type. The existence of charged water molecules was postulated but no further work was done to substantiate it.

The results reported in this paper show clearly that vermiculite is essentially a mica with Mg^{++} or Mg^{++} and Ca^{++} instead of K^+ occupying interlayer positions, and that these cations can readily be exchanged for other cations some of which produce the true mica structure. It has also been shown that biotite and Gruner's hydrobiotite can be converted into vermiculite.

These results indicate that the structural formula of vermiculite as proposed by Gruner needs modification. Some provision must be made for the interlayer exchangeable cations. Essentially the only structural difference between vermiculite and mica is that layers of water are present in the natural vermiculites or vermiculite artificially prepared from biotite, whereas such water is absent from ordinary mica.

Accordingly chemical formulas were calculated from the analyses of vermiculites listed by Gruner (2), using Harvey's (4) method. The amount of each cation found by analysis is calculated per 22 negative charges which corresponds to the summation of negative charges of a lattice half unit of mica. The cations were distributed as follows: (*a*) All the silica was placed in tetrahedral coordination, and enough Al^{+++} and Fe^{+++} to make a total of four. (*b*) the remaining Al^{+++} and Fe^{+++} together with Fe^{++}, Ti, Mn, Ni, Cr, and enough Mg ions to fill the three positions, were assigned to octahedral coordination. (*c*) The remaining Mg^{++} and all the Ca^{++} were assigned to interlayer positions. This manner of distributing the Mg ions between the octahedral and interlayer position results in a minimum of interlayer cations. The actual distribution, however, of the Mg ion may not necessarily be as indicated. There is no valid reason for filling all the three octahedral spaces and consequently Mg ions may be shifted from octahedral to interlayered position. The only means at our disposal of ascertaining the actual distribution of the Mg ions is by determining the interlayered cations by means of base exchange. Calculations, nevertheless, will indicate the degree of iso-

TABLE 14. CALCULATED DISTRIBUTION OF CATIONS IN A LATTICE LAYER OF VERMICULITE

Sample No. (Gruner 2)	Tetrahedral Coordination			Octahedral Coordination							Interlayered			Interlayered m.e./100 grams air dry basis	H_2O Mols
	Si	Al	Fe^{+3}	Al	Fe^{+3}	Fe^{+2}	Ni	Mn	Mg	Σ	Mg	Ca	Σ	Σ	
2	2.760	1.240		.145	.471	.010		.006	2.368	3.000	.153	.171	.324	133.1	4.73
3	2.655	1.345		.352	.288	.038			2.322	3.000	.360		.360	148.8	4.76
4	2.863	1.045	.092		.579	.055	.148		2.366	3.000	.276	.036	.314	130.5	4.31
5	2.907	1.093		.498	.166	.063			2.125	3.000	.218	.005	.223	93.4	4.45
8	2.721	1.279		.295	.450	.076			2.179	3.000	.271		.271	112.0	4.69

morphous substitution of Al and Fe^{+++} for Si ions and whether or not the remaining cations exceeds the number required to fill the three octahedral positions.

The calculated lattices are given in Table 14. It may be seen that the extent of the isomorphous substitution of Al and Fe^{+++} for Si ions is within the range found in the micas. It is interesting to note that some of the values obtained for the interlayer cations lie in the range obtained experimentally for vermiculite no. 1, 2, and 3 reported herein. The values for the interlayer cations which are considerably less than those obtained experimentally may indicate that Mg ions should be shifted from the octahedral to interlayer positions.

Regardless of the difficulty of determining by calculation the right amount of interlayer Mg, the calculations support the experimental findings that Mg and Ca ions are present in interlayer positions in vermiculite.

Taking into consideration the experimental results as well as the calculated results for interlayer cations, the formula for vermiculite may be written as follows:

$$(H_2O)_x(Mg,Ca)_y(Al,Fe,Mg)_z(Si,Al,Fe)_4O_{10}(OH)_2$$

where x represents mols of H_2O, y, the interlayer ions, which may range from 0.22–0.36, and z, the octahedral ions, 3 or less. The exact quantities of x, y, and z can only be determined experimentally.

VERIFICATION OF THE EXISTENCE OF VERMICULITE-CHLORITE MIXTURES

As a result of calculating the distribution of cations in the lattice for certain vermiculites, Hendricks and Jefferson (5) found that there are too many magnesium ions to fill the three octahedral spaces available for cations. Such a surplus also appears in Table 14. Hendricks and Jefferson concluded "that the surplus of atoms with octahedral coordination is that they are partially present in brucite-like layers, $R_3^{++}(OH)_6$ between the talc layers thus forming a chlorite-like structure." This conclusion has been only partially verified, for only in certain vermiculites does the excess of octahedral ions indicate a chlorite like structure, whereas in others, as has already been shown, the surplus ions are present as exchangeable ions, and therefore they occupy interlayer positions.

The existence of a vermiculite-chlorite like structure as proposed by Hendricks and Jefferson was verified experimentally, however, by x-ray and thermal methods. Base exchange determination and dehydration data also yielded supporting evidence. The sample of vermiculite from Lenni-Delaware Co., Pa., (sample no. 5) is apparently a vermiculite-

chlorite. The base exchange capacity of this sample was 65 m.e. as measured by the NH_4^+ adsorbed, and the exchangeable base was found to be Mg^{++} (Table 1). This low NH_4 capacity, as compared with the other vermiculites, was not due to the presence of K^+, as in the vermiculite from Libby, Montanta, for K^+ was absent from this sample, and the amount of K^+ the material was able to adsorb by exchange was equal to the NH_4 capacity as seen in Table 3.

The water content of this vermiculite at low temperature, as seen in Table 10, was less than in the true vermiculite but its relation to the exchangeable base was identical to that of the true vermiculites as seen in Tables 9 and 10.

Both of these properties indicate a similarity to the true vermiculites. They only differ in magnitude, being about half those of the true vermiculites.

The differential thermal curve of this sample together with those of two chlorites and a prochlorite are given in Figure 4. It is clearly seen that the portion of the curve at the lower temperature is similar to that of true vermiculite, whereas the portion of the curve at high temperatures is similar to that of the chlorites.

TABLE 15. INTERPLANAR SPACINGS OF VERMICULITE, Mg-SATURATED BIOTITE, AND NATURAL AND K-SATURATED VERMICULITE NO. 5, AND RIPIDOLITE

Vermiculite No. 1 and No. 2	Mg-Saturated Biotite	Vermiculite No. 5 Natural	Vermiculite No. 5 K-Saturated[1]	Ripidolite Natural	Ripidolite K-Saturated[2]
14.33Å	14.47Å	14.47Å	14.47Å	14.47Å	14.47Å
			10.50	—	
		7.23	7.23	7.16	7.16
		4.77	4.77	4.76	4.76
4.55	4.55	4.55	4.55	4.55	4.55

[1] Intensity of the reflections were weak.

[2] No change in intensity of the reflections.

The x-ray diffraction patterns of the natural materials also re eals a very clear distinction between the true vermiculite and the true chlorites. The clearest distinction is shown by the wide spacings. The first and second spacings of vermiculites 1 and 2, and the vermiculites prepared from hydrobiotite and the biotite are found at about 14.33 Å and 4.55 Å, and no other spacings appear between these two (Table 15). The chlorites—ripidolite and prochlorite, however, have two additional spacings which lie between the 14.33 Å and the 4.55 Å spacings; namely at about 7.20 Å and at about 4.76 Å, with intensities about equal to

that of the 14.33 Å line. As was shown previously, when the true vermiculite is saturated with potassium, the x-ray pattern obtained is that of biotite. In contradistinction to vermiculite it was found that when ripidolite and prochlorite were leached with potassium salts no change took place in their x-ray diffraction pattern.

The x-ray diffraction pattern of the natural vermiculite-chlorite sample under discussion was similar to that of chlorite (Table 15) with the exception that the intensity of the 7.2 Å line was only about half that of the 14.47 Å line. The difference between the true chlorite and this vermiculite-chlorite was best brought out when the latter was saturated with K. The x-ray pattern of chlorite remained, but the intensities of the 14.47 Å, 7.23 Å and the 4.76 Å spacings were greatly weakened. A new spacing, that of biotite, appeared at about 10.4 Å the intensity of which was very weak.

The foregoing together with the results obtained by Gruner indicate that there are four general classes of vermiculite-like minerals found in the state of nature, namely, (1) true vermiculite in which Mg^{++} occupies interlayer positions corresponding to K^+ in biotite. This material contains water between lattice layers. (2) Vermiculite-biotite mixtures, (3) vermiculite-chlorite mixtures, and (4) biotite-chlorite mixtures. Gruner's sample 11 appears to belong in the last named class.

In a paper to follow, certain aspects of the present investigation will be considered from a point of view not adequately covered herein. The relations of vermiculites to the three layer clay minerals will also be discussed.

SUMMARY

1. It has been shown that vermiculite has pronounced base exchange property. Its base exchange capacity is approximately 50 per cent greater than of montmorillonite. The exchangeable cation in certain samples is exclusively Mg. Samples from other localities contain exchangeable Mg and Ca ions.

2. The exchange process is reversible as between Na, Ca, Mg, and K ions, but not completely as between K, NH_4, Rb, and Cs ions. The latter behavior of the exchange process has been known as "fixation."

3. Large flakes of vermiculite undergo base exchange upon leaching with salt solutions almost as readily as fine grained samples.

4. One of the most unique properties discovered is that the kind of exchangeable ion present between the lattice layers determines: (a) the degree of expansion of the lattice, and (b) the degree of hydration and the nature of the differential thermal curves of the material.

5. When K saturated, the properties of vermiculite closely approximate those of ordinary biotite.

6. Gruner's hydrobiotite may be looked upon as ordinary biotite interleaved with vermiculite containing replaceable Mg and Ca ions. It can be converted completely into vermiculite by leaching with $MgCl_2$ solution or into biotite by leaching with KCl solution.

7. It was shown that vermiculite may be interleaved with chlorite as Hendricks et al. suggested.

8. Ordinary biotite can be converted into vermiculite by prolonged leaching with $MgCl_2$ solution.

9. It follows therefore that vermiculite is simply Mg mica with Mg ions playing the same role as K ions play in micas.

10. A new formula is proposed for vermiculite.

REFERENCES

1. BARSHAD, I., A pedologic study of California Prairie soils: *Soil Sci.*, **61,** 423–442 (1936).
2. GRUNER, J. W., The structure of vermiculites and their collapse by dehydration: *Am. Mineral.*, **19,** 557–574 (1934).
3. GRUNER, J. W., Ammonium mica synthesized from vermiculite: *Am. Mineral.*, **24,** 428–433 (1939).
4. HARVEY, C. O., Some notes on the calculation of molecular formulas for glauconite: *Am. Mineral.*, **28,** 541–543 (1943).
5. HENDRICKS, S. B., AND JEFFERSON, M. E., Crystal structure of vermiculites and mixed vermiculite-chlorites: *Am. Mineral.*, **23,** 851–862 (1938).
6. MARTIN, J. C., OVERSTREET, R., AND HOAGLAND, D. R., Potassium fixation in soils in replaceable and nonreplaceable forms in relation to chemical reactions in the soil: *Soil Sci. Soc. Am. Proc.*, **10,** 94–101 (1945).
7. PAULING, L., The nature of the chemical bond: *Cornell Univ. Press* (**1940**).