

THE STRUCTURE OF VERMICULITE AND SOME INTERSTRATIFICATIONS

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ABSTRACT

The inference of Gruner that unsatisfactory powder photographs of vermiculite resulted from distortion of the structural planes by grinding has not been substantiated. The unit cell parameters of a true vermiculite were found to be $a_0 = 5.24 \pm 0.02 \text{ \AA}$, $b_0 = 9.17 \pm 0.02 \text{ \AA}$, $c_0 = 28.60 \pm 0.05 \text{ \AA}$, $\beta = 94^\circ 36' \pm 24'$, while the structural formula worked out as $(\text{Mg}_{2.37}, \text{Fe}^{3+}_{0.37} \text{X}_{0.26}) (\text{Al}_{1.28}, \text{Si}_{2.72}) \text{O}_9 (\text{OH})_3 \cdot 4\text{H}_2\text{O}$, where X represents the remaining octahedral cations. The determined density of the thin flakes was 2.28 g/cm^3 and taking this value along with the volume of the unit cell (1370 \AA^3) and the "molecular weight" calculated from the above formula, the number of formula units per unit cell worked out as $Z = 4.03$. Some 'vermiculite' samples contain small groups of mica layers, but the non-basal mica reflections are not observable. The structures of these interstratifications and also of interstratifications containing chlorite are considered. Electron micrographs of vermiculite and the interstratified minerals are presented.

INTRODUCTION

In view of the similarity of the structure of vermiculite (monoclinic holohedral) to that of chlorite, Gruner (1934) assigned to vermiculite a probable space group $C2/c-C^6_{2h}$ and obtained from powder photographs the lattice dimensions $a_0 = 5.3 \text{ \AA}$, $b_0 = 9.2 \text{ \AA}$, $c_0 = 28.57\text{--}28.77 \text{ \AA}$, $\beta = 97^\circ 9' \pm 10'$ with four units of the formula $(\text{Mg}, \text{Fe})_3 (\text{Si}, \text{Al}, \text{Fe})_4 \text{O}_{10} (\text{OH})_2 \cdot 4\text{H}_2\text{O}$ per unit cell. From a single crystal study Hendricks and Jefferson (1938) obtained the parameters $a_0 = 5.33 \pm 0.05 \text{ \AA}$, $b_0 = 9.18 \pm 0.05 \text{ \AA}$, $c_0 = 28.85 \pm 0.1 \text{ \AA}$, $\beta = 93^\circ 15'$, and assigned to the mineral a pseudo space group $Cc-C_2^4$. The position and character of the water layers in the proposed structure were revealed by the one-dimensional and two-dimensional Fourier syntheses of Walker and collaborators (Walker and Milne, 1951; Mathieson and Walker, 1952).

Gruner (1934) observed that interlayering of equal numbers of mica and vermiculite layers in the interstratified mineral hydrobiotite of formula $\text{K}(\text{Mg}, \text{Fe})_6 (\text{Si}, \text{Al}, \text{Fe})_8 \text{O}_{20} (\text{OH})_4 \cdot 4\text{H}_2\text{O}$ gives a basal reflection at about 11.5 \AA . More complex combinations and interstratifications of mica and vermiculite layers in typical hydrobiotites give basal reflections in the range $11.4\text{--}12.1 \text{ \AA}$ and in general the 14 \AA basal reflection of vermiculite is absent (Walker, 1951). Comparable to the interstratification of layers with two different degrees of hydration to form hydrobiotite is the formation of an interstratified vermiculite-chlorite structure by the interlayering of

some brucite layers with mica-type and water layers: when the number of chlorite layers is small, the distinguishing characteristics are few (Hendricks and Jefferson, 1938). Recently, Midgley and Midgley (1960) have reported that commercial 'vermiculite' samples comprised not only pure vermiculites but also hydrobiotite, vermiculite-hydrobiotite, montmorillonite-mica and vermiculite-chlorite.

Hendricks and Teller (1942) treated mathematically the diffraction effects arising from the random distribution of layers in interstratifications—a treatment which has led to the calculation by Brown and MacEwan (1951) of the types of diffraction pattern likely to be given by different random interstratifications in different proportions.

X-RAY STUDY

Gruner (1934) observed that satisfactory powder photographs of vermiculite could not be obtained with samples powdered by grinding. He attributed this to distortion of the structural planes and preferred powdered samples obtained by filing and screening. He mounted the powder with collodion on silk thread. As against this, Mackenzie and Milne (1953) have shown that vermiculite is reasonably stable to several hours' grinding. In the present investigation powder photographs of vermiculite taken on the Nonius Guinier camera (using Fe $K\alpha$ and Cu $K\alpha$ radiations) were found to be almost identical irrespective of whether the powders were prepared by grinding or by filing and screening. For the Guinier camera the powdered sample was spread without adhesive as a thin layer (about 0.1 mm thick) in between polythene sheets on the sample holder, but when photographs were taken on the Philips large powder cameras (with a special adapter for the slit system) it was packed into Lindemann glass capillary tubes of < 0.3 mm diameter. Basal reflections were also recorded from oriented thin flakes on the Unicam single crystal camera.

The lattice parameters calculated from a number of reflections on the powder photograph as well as from zero-layer Weissenberg photographs about the a and b axes of a true vermiculite (sample 8247) are $a_0 = 5.24 \pm 0.02 \text{ \AA}$, $b_0 = 9.17 \pm 0.02 \text{ \AA}$, $c_0 = 28.60 \pm 0.05 \text{ \AA}$, $\beta = 94^\circ 36' \pm 24'$ —this angle being about one degree larger than the angle obtained by Hendricks and Jefferson (1938). The observed spacings on the powder pattern are in excellent agreement with the values calculated for a vermiculite with these crystallographic constants (Table 1). The difference between the interplanar spacings calculated by Gruner* (1934) on the basis of $\beta = 97^\circ 9'$ (the value for the chlorite structure) and the spacings of the first 25 reflections observed for this sample will be clearly observable on comparing the values in Table 1 with those in Table 7 of Gruner (1934). Relative values of the intensities of some reflections, measured by the Moll recording microphotometer, are also listed in Table 1 for com-

*Some of the reflections in the powder photographs of Gruner (1934, Table 3) were not indexed by him.

TABLE 1—X-ray powder diffraction data for a true vermiculite (Indian Museum No. 8247, Ajmer-Marwar).

Indices	$d_{calc.}(\text{\AA})$	$d_{obs.}(\text{\AA})$	$I_{obs.}$	$F_{calc.}^*$	Theoretical intensity†
002	14.26	14.15	10	256	451
004	7.13	7.14	1.5	10	21
006	4.75	4.76	1	68	13
020	4.58	4.57	6	ms	55
112	4.414	4.41	1	—	—
022	4.363	4.35 } b_{\ddagger}	1	ms	—
112	4.240	4.24 }	—	—	—
008	3.564	3.56	2.5	145	137
0010	2.851	2.85	3	304	106
132	2.613	2.615	5	—	39
200	2.611			48	18
202	2.605			112	13
132	2.575	2.570	5	—	102
202	2.533	2.525	4.5	96	151
204	2.519			240	53
134	2.441			—	28
204	2.391	2.430	0.5	32	219
0012	2.375	2.380 } b	3.5	97	13
206	2.370			296	13
136	2.346			—	454
220	2.270	2.265	0.5	—	—
136	2.268			—	27
222	2.266			—	—
206	2.215	2.200 } b	0.5	120	103
208	2.192			128	14
138	2.162			—	214
138	2.080	2.080 b	0.5	—	92
0014	2.036	2.04 } b	1	105	104
208	2.031			144	29
2010	2.007			80	48
1310	1.976	1.975	0.5	—	57
2012	1.832	1.82 } b	0.5	120	11
1312	1.802			—	103
0016	1.782			92	6
1312	1.731	1.725 } b	1	—	0
312	1.714			—	—
310	1.710			—	—
314	1.693	1.695	0.5	—	—
2012	1.691			16	151
2014	1.672			—	—
1314	1.644	1.665	1.5	216	0
2014	1.547	1.543	1	—	302
2016	1.530	1.528	7	144	108
060	1.528			184	34
332	1.516			280	205
330	1.513	1.514	2.5	—	412
1316	1.505	1.502	1.5	—	250
334	1.501			—	214
				—	164

* According to Hendricks and Jefferson (1938); contribution of interlayer water molecules neglected.

† According to Gruner (1934).

‡ b —Broad

parison with the structure factors calculated by Hendricks and Jefferson (1938) and the theoretical intensities for two formula units of vermiculite calculated by Gruner (1934).

The same portion of the true vermiculite sample (8247) was used both for X-ray study and for chemical analysis. The trace constituents, K, Ni, Ti and Mn (Table 2) were not considered in deriving

TABLE 2—Chemical analysis and molecular composition of the true vermiculite sample 8247.

Chemical analysis		Ionic composition	
SiO ₂	34.92	Si ⁴⁺	2.72
Al ₂ O ₃	13.97	Al ³⁺	1.28
Fe ₂ O ₃	6.25	Fe ³⁺	0.37
FeO	0.52	Fe ²⁺	0.03
MgO	20.37	Mg ²⁺	2.37
CaO	2.15	Ca ²⁺	0.18
Na ₂ O	0.32	Na ⁺	0.05
K ₂ O	0.08		
H ₂ O	21.00		
*Rem.	0.42	O : H	4.01 : 7.95 (leaving aside (OH) ₈ and O ₉)
Total	100.00	$\Sigma C(1, 2, 3, 4)^+ =$	+21.04
		$\Sigma A(1, 2)^- =$	-21.00

* Remainder includes Ni, Ti, Mn, etc.

Analyst Dr. S. Banerjee.

the ionic formula. According to Hendricks and Jefferson (1938), Mg²⁺, Fe³⁺, Fe²⁺, Ca²⁺ and Na⁺ are all in octahedral co-ordination, although the ionic radii of Ca²⁺ and Na⁺ are in fact too large for normal isomorphous replacement of Mg²⁺ and Fe³⁺. On this basis the structural formula of the true vermiculite is (Mg_{2.37}Fe³⁺_{0.37}Fe²⁺_{0.03}Ca_{0.18}Na_{0.05})(Al_{1.28}Si_{2.72})O₆(OH)₃·4H₂O, whereas Hendricks and Jefferson (1938) obtained the value 3.5H₂O for the composition of the true vermiculite of Gruner (1934). The density values determined for thin flakes and fine grains by the suspension method in bromoform diluted with acetone all fell in the range 2.25-2.30 g/cm³, giving a mean density $\eta = 2.28$ g/cm³. Using this value together with the volume calculated from the unit cell parameters and the formula weight calculated from the structural formula ($M = 466$), the number of formula units per unit cell works out as $Z = 4.03$. Taking $Z = 4$ the theoretical density is 2.26 g/cm³, which is very close to the determined value, although the precise density of vermiculite in its natural state is not available (Grim, 1953).

In samples 7947 and R951 (Table 3) the relative intensities of the basal reflections of vermiculite, hydrobiotite and mica indicate that large groups of vermiculite layers and small groups of mica layers occur as distinct units along with hydrobiotite units. The non-basal reflections of mica are not, however, observable. The 'p' values (proportion of payers) determined from the graphs of Brown and

TABLE 3—X-ray powder diffraction data for interstratifications containing vermiculite.

Indices	Indian Museum No. 7947 (Chatru, Hazaribagh)		Indian Museum No. R951 (Mogok, Burma)	
	$d(\text{\AA})$	I	$d(\text{\AA})$	I
002 v	14.0	7	14.1	8
00 l_x h	11.7	7	12.1	3
002 m	10.0	2.5	9.99	4
004 m	5.0 } b, d	1.5	5.0 d	0.5
020 v	4.9 } d	6	4.56	7
hkl v	4.56 } d	0.5	—	—
	4.42 } d			
	4.25 } d			
008 v	3.56	1.5	3.56	1.5
00 l_y h	3.44	3.5	3.45	2
006 m	3.35	2	3.34	1.5
0010 v	2.86	1	2.86	1
hkl v }	2.615	10	2.62 } b	8
200 v }			2.60 } b	
hkl v }	2.575	3	2.573	2
hkl v }	2.525	2.5	2.528	1.5
hkl v }	2.375	5	2.380	4
0012 v }				
hkl v }	2.265 b	1.5	2.270	0.5
hkl v }	2.180 d	1	2.175	1.5
hkl v }	1.720 } b	1.5	1.710	1
	1.690 } b			
hkl v }	1.670	2	1.670	1.5
hkl v }	1.540	0.5	1.543	2.5
hkl v }	1.527	9	1.528	10
060 v }				
hkl v }	1.512	1.5	1.513	2

KEY: v —Vermiculite reflection; m —mica reflection; h —hydrobiotite reflection; b —broad; d —diffuse.

MacEwan (1951) indicate that in sample 7947 layers of vermiculite and mica are randomly interstratified in the proportion 1:1 whereas in sample R951 they are in the proportion 3:2; in both instances these interstratifications make up a large part of the sample. That the 00 l_y reflection of hydrobiotite is relatively stronger than the 008 reflection of vermiculite and the 006 reflection of mica, which are of almost equal intensity, is attributed to the fact that the reflections from successive layers of the larger units in this interstratification are more or less in phase.

In sample 7684 (Table 4) vermiculite and chlorite layers are interstratified almost regularly as is evidenced by the enhanced intensities of the 00 l reflections. The reflection at 10.3Å may be due to this interstratification rather than to mica units since the most characteristic reflection of mica (the 006 reflection) was not recorded. For sample 7683 (Table 4) the reflections at 15.0Å, 14.0Å, 12.6Å, 10.6Å and 10.0Å indicate more complex interstratifications since enhanced intensities due to vermiculite-chlorite were not observed.

TABLE 4—X-ray powder diffraction data for interstratifications containing vermiculite.

Indices	Indian Museum No. 7684 (Bilichi, Coimbatore)		Indian Museum No. 7683 (Ariyakarundaupalli, Salem)	
	$d(\text{\AA})$	I	$d(\text{\AA})$	I
—	—	—	15.0	3
002 v }	14.1	10	14.0	5
001 c }			12.6	2
—	10.3	1.5	10.6 b	4
002 m			10.0 d	1.5
004 v }	7.14	2.5	—	—
002 c }			5.0 d	0.5
004 m	—	—	—	—
006 v }	4.76	3	4.57	8
003 c }			4.41	0.5
020 v	4.57	7	4.24	
hkl v }	4.41	1	—	—
	4.25 b			
008 v }	3.56	4	3.56	1.5
004 c }			3.35	2.5
006 m	—	—	2.85	0.5
0010 v }	2.85	3.5	2.615	10
005 c }			2.570	0.5
hkl v }	2.615	6	2.520	1
200 v }			2.385	7
hkl v }	2.570	5.5	2.27 b	2
hkl c }			2.25 b	
hkl v }	2.525	6	2.170 b	3
hkl c }			2.020 b	0.5
0012 v }	2.380	7	1.720	1
006 c }			1.670	2
hkl v, c }	2.265	1.5	1.540	1
hkl v }			1.527	8
hkl c }	2.165	0.5	1.513	2
0014 v }			1.502	1.5
007 c }	2.015 b	1	—	—
hkl v, c }			—	—
hkl v }	1.720	1.5	—	—
hkl c }			—	—
hkl v, c }	1.670	1	—	—
hkl v, c }			—	—
060 v }	1.540	3	—	—
060 c }			—	—
hkl v, c }	1.527	8	—	—
hkl v }			—	—
hkl v, c }	1.515	0.5	—	—
hkl v, c }	1.502	1.5	—	—

KEY: v —Vermiculite reflection; c —chlorite reflection; m —mica reflection;
 b —broad; d —diffuse.

However, since this sample is rich in potassium (Table 5) it may contain appreciable amounts of K-saturated vermiculite layers. The sample after glycerol treatment gives reflections at 17.6\AA (2.5^*), 14.0\AA (4), 10.6\AA (5) and 10.0\AA (2), and after heat treatment at 520°C for one hour at 14.0\AA (1) and 10.0\AA (10); the changes in the higher angle reflections were not significant. This sample may be considered as a complex interstratification of K-saturated vermiculite-mica with montmorillonite.

Three samples of vermiculite (Nos. 8247, 7947 and 7683) were examined spectrographically using a Hilger Large Quartz Spectrograph. Samples of 5 mg mixed with 5 mg spectrographically pure carbon powder were excited in carbon electrodes using the cathode-layer arc technique at 7.9A and 220 V D.C. The results indicated that, although the absolute amounts of the elements differed from sample to sample, Al, Fe, Mg and Si were major components, Ca, K, Mn, Na, Ni and Ti were minor components, and that Cr, Cu, Ga, Li, Pb, Sn, V and Zn were present in trace amounts.

TABLE 5—Amounts of alkalis in some samples of vermiculite.

Alkali*	Sample No. 8247	Sample No. 7947	Sample No. 7683
K ₂ O	0.08	3.35	6.15
Na ₂ O	0.32	0.22	0.19

* Determined by photometer.

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ELECTRONOPTICAL STUDY

Little information regarding the appearance of vermiculite and its interstratifications under the electron microscope is available (Davies *et al.*, 1950), but Grim (1953) has suggested from structural considerations that the particle shape of vermiculite should be similar to that of illite.

For electron microscope examination about 0.1 mg of finely powdered vermiculite was dispersed in 10 ml distilled water by vigorous shaking. After standing, a fine drop of the supernatant liquid was deposited from a capillary pipette on to a collodion-covered copper grid, excess liquid removed by means of filter paper, and the specimen dried in air. A Siemens Elmiskop 1 was used at 60 kV, the magnification being kept down to $8000\times$ and the illumination to a minimum in order to avoid undue temperature rise in the specimen.

The electron micrographs for true vermiculite (No. 8247), for interstratified mica-vermiculite-hydrobiotite (No. 7947) and for the complex interstratification of K-saturated vermiculite-mica-montmorillonite (No. 7683), show differences in shape of the particles

*Values in brackets indicate intensities.

(Fig. 1). The micrograph for the true vermiculite (Fig. 1a) shows some imperfect rhomb-shaped particles, one of which is almost a parallelogram: the dimensions were in the range $0.2\text{--}0.4\mu$, but units as small as 0.01μ were visible. Larger units with complicated outlines are probably due to lack of proper dispersion. The particles of the mica-vermiculite-hydrobiotite (Fig. 1b) have a rounded irregular

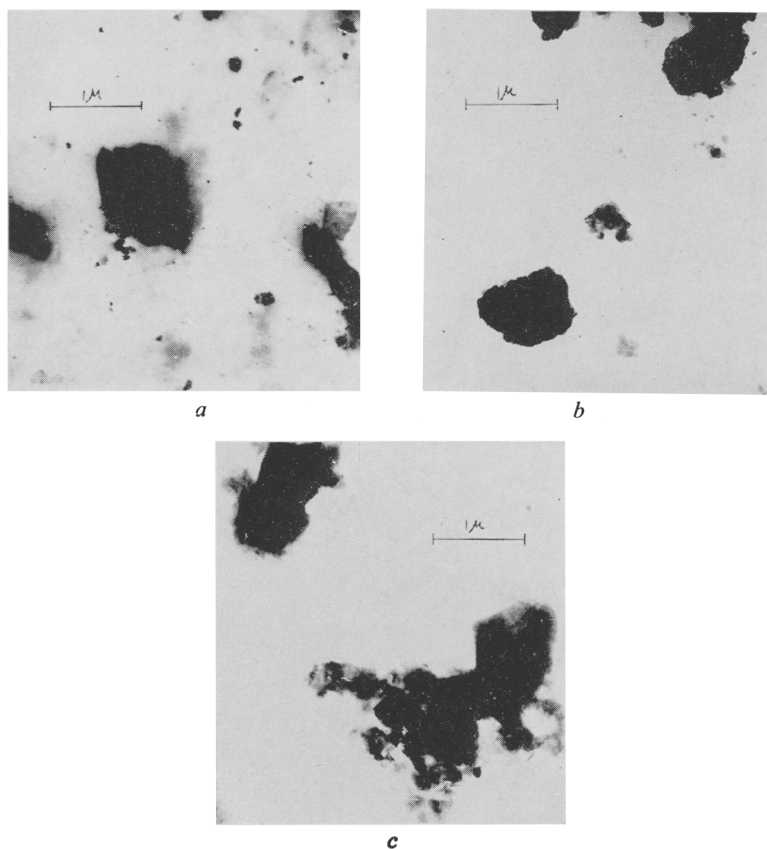


FIG. 1—Electronmicrographs of: (a) true vermiculite (8247); (b) mica-vermiculite-hydrobiotite (7947); (c) K-saturated vermiculite-mica with montmorillonite (7683).

appearance with some straight edges; the edges are sharply defined and the particles are $0.1\text{--}1\mu$ across. The shape and size of some of these particles are reminiscent of those of Fithian illite (Grim, 1953). The outlines of the larger units of the K-saturated vermiculite-mica-montmorillonite (Fig. 1c) are mostly irregular and rounded; occasionally, however, the edges are sharp and straight.

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