

THE AMERICAN MINERALOGIST

JOURNAL OF THE MINERALOGICAL SOCIETY OF AMERICA

Vol. 19

DECEMBER, 1934

No. 12

THE STRUCTURES OF VERMICULITES AND THEIR COLLAPSE BY DEHYDRATION

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INTRODUCTION

The question whether vermiculites are distinct minerals has puzzled mineralogists for many years. A number of attempts have been made to find definite type formulas for them. Often they have been considered as "hydrated micas." It will be shown in the following pages that this idea comes very close to the truth, and that a vermiculite is a definite mineral species with a definite crystal structure. If, however, a so-called vermiculite contains alkalis to an appreciable extent a type of mineral results which is neither a vermiculite nor a mica but an "interstratification" of unit layers of these two. The x -ray diagrams for this type are different from either of the other two.

Preliminary and necessary for the investigation of the vermiculites was the knowledge of the structures of the micas as described by Pauling,¹ and Jackson and West,² of the chlorites by Pauling³ and McMurchy;⁴ and of the kaolin group by the writer.⁵ The structures of talc and pyrophyllite, suggested by Pauling⁶ and lately worked out by the writer,⁷ were also of great importance in the correct interpretation of the vermiculites.

In obtaining material for x -ray analysis the writer is especially indebted to Dr. C. S. Ross of the U. S. Geological Survey, and Dr. W. F. Foshag of the U. S. National Museum who supplied most of the specimens listed below.

¹ Pauling, Linus, *Proc. Nat. Acad. Sci.*, vol. **16**, pp. 123-129, 1930.

² Jackson, W. W., and West, J., *Zeit. f. Krist.*, vol. **76**, pp. 211-227, and vol. **85**, pp. 160-164, 1933.

³ Pauling, Linus, *Proc. Nat. Acad. Sci.*, vol. **16**, pp. 518-582, 1930.

⁴ McMurchy, R. C., *Zeit. f. Krist.*, 1934, vol. **88**, pp. 420-432, 1934.

⁵ Gruner, J. W., *Zeit. f. Krist.*, vol. **83**, pp. 75-88, 1932; vol. **83**, pp. 393-404, 1932; vol. **85**, pp. 345-354, 1933.

⁶ *Proc. Nat. Acad. Sci.*, vol. **16**, p. 126, 1930.

⁷ *Zeit. f. Krist.*, 1934, vol. **88**, pp. 412-419, 1934.

CHEMICAL DATA

The following twelve specimens were examined. Their chemical analyses are given in Table I.

- Specimen No. 1. Vermiculite from Bare Hills near Baltimore, Md. E. V. Shannon: *Am. Jour. Sci.*, vol. 15, p. 21, 1928. Pale yellow-green scales resembling talc. Catalogue No. 95647 of U. S. Nat. Museum.
- No. 2. "Protovermiculite" from Magnet Cove, Ark. F. W. Clarke and E. A. Schneider: *Am. Jour. Sci.*, vol. 42, p. 242, 1891. Large golden yellow books or scales. Only very little exfoliation. Sp. grav. = 2.05-2.10.
- No. 3. "Lucasite" from Corundum Hill, North Carolina. Th. M. Chatard: *U. S. Geol. Surv., Bull.* 42, p. 51, 1887. Yellowish brown, scaly. Catalogue No. 88507 of U. S. Nat. Museum.
- No. 4. Vermiculite from Wiant's Quarry near Pilot, Md. C. S. Ross, E. V. Shannon and F. A. Gonyer: *Econ. Geol.*, vol. 23, p. 542, 1928. Yellowish brown, compact, scaly aggregate. Talcose feel. Sp. grav. = 2.31.
- No. 5. Vermiculite from Webster, North Carolina. *Idem*, p. 536, Table 3, Analysis 4. Greenish yellow scales.
- No. 6. Vermiculite from Webster, North Carolina. *Idem*, Table 3, Analysis 1. Fine, greenish yellow scales.
- No. 7. Nickeliferous vermiculite from Webster, North Carolina. C. S. Ross and E. V. Shannon: *Am. Mineralogist*, vol. 11, p. 92, 1926. Apple green, small scales. Catalogue No. 95487 of U. S. Nat. Museum.
- No. 8. "Jefferisite" from Brinton Quarry, West Chester, Pennsylvania. F. W. Clarke and E. A. Schneider: *Am. Jour. Sci.*, vol. 40, p. 452, 1890. Brownish black large plates. Sp. grav. = 2.35. Exfoliates easily.
- No. 9. So called "vermiculite" from Libby, Montana. Commercial analysis by U. S. Bureau of Standards, Washington, supplied by C. S. Ross. Very dark greenish brown scales. Sp. grav. = 2.64. Exfoliates readily. Note the discrepancy in the analyses of the alkalies.
- No. 10. So called "vermiculite" from unknown locality. Brownish black large plates. Sp. grav. = 2.49. Exfoliates easily.
- No. 11. "Chloritic vermiculite" from Old Wolf Quarry, Chestnut Hill, Easton, Pa. Described by G. P. Merrill in *U. S. Geol. Surv., Bull.* 90, p. 19, 1892. Light yellowish green, scaly, talc-like. Does not exfoliate appreciably. Catalogue No. 70118 of U. S. Nat. Museum.
- No. 12. "Vermiculite" from Corundum Hill Mine near Franklin, N. C. Unanalyzed. Collected by C. S. Ross. Brownish to greenish black large scales. Harder than other vermiculites.

Additional information including optical data for these minerals may be found under their respective references.

As in the micas the chemical analyses differ considerably. Based on *x*-ray diagrams specimens 1 to 7 belong to the same species which is here designated as *vermiculite*. Specimens 9 and 10 belong to a species for which the name *hydrobiotite* is proposed. This name

TABLE I. ANALYSES OF SPECIMENS USUALLY CLASSIFIED AS VERMICULITES

	1	2	3	4	5	6	7	8	9	10	11
SiO ₂	36.12	34.03	32.97	35.92	36.54	34.92	34.76	34.20	41.0		43.71
TiO ₂	0.24					0.60					
Al ₂ O ₃	13.90	14.49	17.88	10.68	16.96	13.06	14.86	16.58	18.0		3.59
Fe ₂ O ₃	4.24	7.71	4.76	10.94	2.78	2.74	2.74	7.41	} 7.0		0.90
FeO	0.68	0.14	0.57	0.82	0.95	0.54	0.41	1.13			
NiO	0.28			none	2.32	3.24	11.25				
MnO	trace	0.09	trace								
MgO	24.84	20.89	22.36	22.00	19.78	23.92	18.18	20.41	21.0		38.58
CaO	0.18	1.88	none	0.44	0.06	0.24	0.40				
K ₂ O			} none						1.87*		
Na ₂ O			21.47	19.84	20.40	20.30	17.80	21.14	} 0.14*		
Total H ₂ O	18.94	21.19							11.0		11.25
H ₂ O-110°	99.42	100.42	100.01	100.64	99.79	99.56	100.40	100.87	100.0		100.38
H ₂ O 110°-400°	(-130°) 8.20	7.28	11.42	10.50	9.24	9.00	(-120°) 5.20				0.46
H ₂ O at red heat		(750°) 7.96	10.16*	4.34	3.80	5.00			} 15.44*		(-300°) 0.09
		3.92	10.05	5.00	7.36	6.30	12.60				10.70

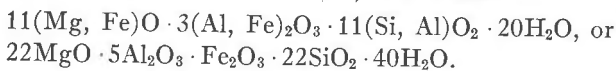
* Analyses by R. B. Ellestad of powders actually x-rayed.

was used long ago by Schrauf⁸ and others to designate biotite-like material high in water. Specimen No. 8 is a mixture of vermiculite and hydrobiotite since it gives both x-ray patterns. It will be observed that it contains 2% alkalis and less H₂O than typical vermiculite. No. 11 from Easton, Pa. cannot be classified at present, it has no characteristic vermiculite lines and may be a mixture of talc, chlorite and serpentine. No. 12 is a distinct mixture of biotite and vermiculite as it gives both diagrams.

TABLE II

	Average of analyses 1 to 7		Theoretical compositions
SiO ₂	35.04	35.04	36.71 = 22 SiO ₂
Al ₂ O ₃	14.55	14.55	14.15 = 5 Al ₂ O ₃
Fe ₂ O ₃	5.13	5.13	4.43 = Fe ₂ O ₃
FeO	0.59	25.20	24.62 = 22 MgO
NiO	2.44		
MgO	21.71		
CaO	0.46	19.99	20.09 = 40 H ₂ O
H ₂ O	19.99	19.99	
Total	99.91	99.91	100.00

To arrive at a working formula for vermiculite analyses 1 to 7 were averaged as shown in Table II. This formula has to be accommodated in the structure which as shown later consists of mica units, minus K₂O plus H₂O. Without the H₂O the structural formula would be (OH)₂Mg₃(Si₃Al)O₁₀ disregarding valencies. Remembering that Fe may replace Al or Mg, or both, and that more than 25% of Si may be replaced by Al the structural formula including H₂O may be expanded to (OH)₂(Mg,Fe)₃(Si,Al,Fe)₄O₁₀ · 4H₂O; or written in a different form, it becomes:



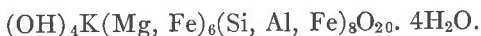
The amount of H₂O in this formula is based on the average H₂O content in Table II. The fact that the number of H₂O molecules in this analysis is an even whole number makes it fairly certain, from the structural point of view, that it is correct. This formula is similar to that proposed by Ross and Shannon⁹ which is 12MgO · 3Al₂O₃ · 12SiO₂ · 19½H₂O.

⁸ Schrauf, A., *Zeit. f. Krist.*, vol. 6, p. 381, 1882.

⁹ *Am. Mineralogist*, vol. 11, p. 92, 1926.

It is, of course, obvious that K^+ cannot be removed from a mica and H_2O substituted without having negative charges left over. These must be neutralized either by oxidation of Fe^{II} to Fe^{III} or by introduction of H^+ . Another possibility would be the substitution of F^- or OH^- for O^{--} . Which of these processes are operative is impossible to say at present. Usually there will not be enough Fe^{II} present whose oxidation could neutralize the loss of K . It is commonly thought that Fe^{III} occupies Al positions. This is not so likely in the vermiculites for the Al occupies chiefly Si positions in the $Si_3Al O_{10}$ layers. The Fe^{II} is in Mg positions to begin with. There is no reason why Fe on oxidation should move into Al positions. There would be no vacancies anyway.

The hydrobiotite analyses, 9 and 10, and 8 which is partly hydrobiotite, contain considerable amounts of alkalis. The x -ray diagrams show clearly that these minerals are made up of interstratified single or double layers of units of mica (M), and vermiculite (V). The interstratifications which exist in them can be at least two-fold both agreeing with x -ray data. They are: $M-V-M-V$ - and $V-V-V-M-M-V-V-V-M-M$ -. Other combinations of these layers are possible but become complicated. The formula for the first one would be:



X-RAY DATA

On account of the physical nature of the material the powder method was used exclusively. Grinding of the samples in agate mortars distorted the structural planes to such an extent that no satisfactory diagrams could be obtained. All the samples were filed, therefore, unless received in crushed form, and screened through bolting cloth. The powder was mounted on silk thread with collodion. The thicknesses of the samples did not exceed 0.7 mm. A goniometer head was used for centering the samples in the circular camera (radius = 57.3 mm.). Cu radiation was found to be unsatisfactory on account of its marked absorption by minerals containing iron. Fe radiation ($K_\alpha = 1.9321 \text{ \AA}$) was used instead. It gives very satisfactory results with sufficient time of exposure. Also, with the arrangement used for minimizing fogging by the zero beam it was possible to record the reflections of planes with spacings greater than $d = 14 \text{ \AA}$. This is essential since reflections of planes with large d are of greatest importance in interpreting the diagrams. A self-rectifying gas tube with an output of about 7 to 9 Ma at 35 Kv was used.

TABLE III. POWDER DIAGRAMS

No.	1.		2.		3.		4.	
	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>
1	13.4Å	8	13.6Å	9	13.7Å	9	13.6Å	10
2	7.03	1						
3	4.75	1	4.68	1				
4	4.45	1 <i>i</i>	4.41	0.5 <i>i</i>	4.43	1 <i>i</i>	4.43	2 <i>i</i>
5	3.91	1	3.88	1 <i>i</i>			3.91	1
6	3.537	4	3.537	3	3.548	3	3.541	4
7	3.126	1	3.129	0.5	3.104	1	3.137	1
8	2.838	3	2.838	3	2.852	3	2.840	5
9	2.6	1 <i>i</i>	2.630	1	2.630	1	2.620	2
10	2.521	2 <i>b</i>	2.535	1 <i>b</i>	2.526	1 <i>b</i>	2.530	2 <i>b</i>
11	2.366	4	2.375	3	2.375	3	2.372	4
12							2.256	0.5
13	2.192	1	2.182	0.5	2.193	1	2.192	1
14	2.129	0.5						
15	2.069	0.5	2.052	1	2.068	1	2.068	1
16	2.035	1			2.038	1	2.033	1
17	2.002	0.5	2.002	1 <i>b</i>	2.000	1	2.005	1
18	1.833	1	1.816	0.5	1.836	1	1.836	1
19	1.774	1						
20	1.732	0.5	1.732	0.5	1.733	0.5	1.730	1
21	1.664	2	1.657	1 <i>b</i>	1.668	3	1.670	3
22	1.584	0.5			1.585	0.5	1.588	0.5
23	1.570	0.5			1.571	1	1.573	1
24	1.526	4	1.530	4 <i>b</i>	1.527	3 <i>b</i>	1.526	6 <i>b</i>
25	1.496	1					1.500	0.5
26	1.462	0.5					1.465	0.5
27	1.441	2	1.432	1 <i>b</i>	1.441	2	1.445	2
28	1.429	1			1.428	1	1.433	1
29	1.352	1	1.348	0.5	1.354	0.5	1.353	1
30	1.321	3			1.328	3	1.330	3
31	1.312	1	1.314	2 <i>v.b.</i>	1.314	1		
32	1.289	1	1.290	0.5	1.291	1		
33	1.270	1			1.271	0.5		
Spacing of $d_{001} = 28.42$			28.38		28.50		28.46	

i = indistinct edge of line.*b* = broad line.*v.b.* = very broad line.*β* = a line produced by K β radiation of iron.

OF VERMICULITES. Fe RADIATION

5.		6.		7.		Indices
<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	
13.7Å	10	13.6Å	10	13.6Å	10	002
		7.04	0.5	7.12	5	004
		4.71	1			006
4.48	1 <i>i</i>	4.39	1 <i>i</i>	4.45	2 <i>b</i>	
3.90	1	3.92	1	3.94	1 <i>b</i>	008β
3.540	3	3.548	4	3.562	5	008
3.126	1	3.145	1	3.162	0.5 <i>i</i>	0010β
2.833	4	2.847	5	2.847	1 <i>i</i>	0010
2.609	2			2.6	1	130, 20 $\bar{2}$, 13 $\bar{2}$, 200 and
					<i>i v. b.</i>	13 $\bar{6}$ β, 204β
2.524	3 <i>b</i>	2.537	1 <i>v. b.</i>	2.48	3	132, 204, 134, 202
2.367	4	2.379	3 <i>b</i>	2.380	1 <i>b</i>	13 $\bar{6}$, 204
2.253	0.5					136, 208
2.185	1	2.188	1 <i>b</i>	2.133	0.5 <i>i</i>	206, 13 $\bar{8}$
2.059	1	2.069	1			20 $\bar{10}$, 138
		2.035	1			0014
1.998	1 <i>b</i>	2.002	1			13 $\bar{10}$, 208
1.828	1	1.833	1			13 $\bar{12}$, 2010
						0016
1.726	1	1.735	1	1.739	0.5 <i>i</i>	
1.661	3 <i>b</i>	1.668	2 <i>b</i>	1.676	2 <i>i</i>	13 $\bar{14}$, 2012
						1316β, 2018β
1.569	0.5	1.568	0.5 <i>b</i>			0018, 1314, 20 $\bar{16}$
1.524	5 <i>b</i>	1.530	3 <i>b</i>	1.526	6 <i>b</i>	060, 33 $\bar{2}$, 330, 334,
						13 $\bar{16}$, 2014
1.498	0.5	1.500	0.5	1.494	2 <i>b</i>	332, 33 $\bar{6}$
1.439	2	1.442	1	1.441	0.5 <i>i</i>	1316, 20 $\bar{18}$
1.425	1	1.429	1			0020
1.349	0.5	1.354	0.5			338, 33 $\bar{12}$
1.324	2	1.329	3		1	1318, 20 $\bar{20}$
1.312	2	1.316	1		<i>i v. b.</i>	
1.288	1	1.292	1	1.300		0022
1.268	1	1.276	0.5 <i>i</i>			
28.38		28.46		28.56		

Table III contains the powder diagrams of the seven vermiculites. Lack of space does not permit the giving of distances measured in mm. in the films and their corresponding Θ angles. Intensities I are estimated visually. No correction except for thicknesses of samples were applied. On account of a slight eccentricity of the camera, and other factors, readings above 3.0\AA are not as accurate as below that figure, especially is this true if they approach the zero beam. For the calculations of the unit cells only planes with d smaller than 3\AA were used. These are quite accurate as found by comparison with standard substances. Some of the vermiculites give much sharper x-ray patterns than others. The least satisfactory lines were found in nickeliferous vermiculite No. 7. Some of its lines could not be recorded with certainty.

TABLE IV. POWDER DIAGRAMS OF MINERALS FORMERLY DESIGNATED AS VERMICULITES

No.	8.		12.		9.		10.		11.		Indices
	d	I	d	I	d	I	d	I	d	I	
1	13.6	8	14.1	8							002 <i>V</i>
2	11.6	2			11.4	5 <i>b</i>	11.6	6 <i>b</i>			002 or 005 <i>h</i>
3			10.02	1							002 <i>m</i>
4			6.98	0.5					6.93	8	004 <i>c</i> and <i>V</i>
5			4.70	1							
6	4.47	1	4.50	1 <i>i</i>	4.48	1 <i>i</i>	4.48	1 <i>i</i>	4.47	2 <i>i</i>	
7			3.92	1 β					3.95	2 β	008 βc
8	3.53	3	3.56	3					3.55	7	008 <i>V</i> and <i>c</i>
9	3.43	3			3.39	4 <i>b</i>	3.42	3 <i>b</i>			007 or 0018 <i>h</i>
10			3.334	2					3.29	2	006 <i>m</i>
11			3.143	0.5 β							0010 β <i>V</i>
12					3.071	0.5			3.066	1	006 <i>t</i>
13									2.919	0.5	
14	2.833	2	2.854	4	2.873	1 β	2.859	1 β			0010 <i>V</i>
15									2.755	1	
16	2.609	4	2.636	3	2.596	5	2.601	4	2.619	2	
17			2.551	2 <i>b</i>							<i>m</i>
18	2.521	1 <i>b</i>	2.535	0.5							
19									2.434	4	<i>t</i> and <i>c</i>
20			2.334	3 <i>b</i>	2.394	3 <i>b</i>	2.395	2	2.391	2	

TABLE IV (Continued)

No.	8.		12.		9.		10.		11.		Indices
	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	
21	2.366	3 <i>b</i>					2.367	1 <i>b</i>			
22	2.241	0.5	2.256	0.5	2.220	1 <i>b</i>	2.252	0.5			
23	2.162	1	2.173	1 <i>b</i>	2.166	2 <i>b</i>	2.166	1 <i>b</i>			
24	2.058	0.5	2.075	1					2.125	3 <i>b</i>	
25			2.005	2 <i>b</i>	2.016	2	2.006	1	1.996	3	
26	1.918	1	1.918	0.5							
27	1.826	0.5	1.836	0.5β	1.842	0.5β	1.833	0.5β	1.847	0.5β	
23									1.809	2	
29									1.785	2	
30	1.723	1	1.734	1	1.734	0.5	1.725	0.5			
31	1.658	2 <i>b</i>	1.670	3 <i>b</i>	1.668	3 <i>b</i>	1.662	2 <i>b</i>	1.657	2 <i>b</i>	
32			1.566	0.5							
33	1.524	5	1.533	5	1.533	7	1.524	4	1.529	3	060 and others
34					1.517	0.5			1.492	3	
35			1.443	1	1.437	0.5			1.445	1	
36	1.426	0.5	1.429	1			1.425	0.5			
37	1.392	0.5			1.401	0.5	1.394	0.5	1.407	1	
38			1.357	1	1.346	0.5	1.339	1	1.357	2	
39			1.328	2	1.322	3					
40	1.312	1 <i>v. b.</i>	1.315	1			1.317	1			
41	1.288	1	1.292	1	1.298	1	1.289	1	1.301	2	
Spac- ing of <i>d</i> ₀₀₁	28.38 and 24.0		28.50 and 20.02		23.7 to 24.2		24.0		?		

V = reflection of vermiculite.
h = reflection of hydrobiotite.
m = reflection of mica.
t = reflection of talc.
c = reflection of chlorite.

Since these minerals are certainly composed of layer structures similar to the micas and chlorites, the possible reflections from the basal planes should be rather prominent and easily identified. This is the case as may be seen in the tables III, IV, and VII. These reflections are especially sharp and conspicuous when the samples are mounted on thread because the cleavage particles align themselves parallel to the thread and give observed intensities 3 to 4

times as great as calculated. This was explained by the writer in a paper on dickite.¹⁰

It is a curious fact that the *x*-ray diagrams of powders heated to 110° C. for 24 hours do not show any changes, though very considerable amounts of water are driven off at 110° C. as shown in Table I. Specimens 1, 2 and 10 were *x*-rayed after this treatment. Heating for 5 to 24 hours at 750° C. produces new diagrams which are the result of the collapse of the structures in a direction normal to the basal cleavage.

INTERPRETATION OF X-RAY DATA OF VERMICULITE

The first step in the interpretation of the diagrams was to compare them with those of micas, chlorites, the kaolin minerals and talc. Certain striking similarities are noticed if the basal plane reflections are disregarded. No detailed account can be given of them in this place. Suffice it to state that the width b_0 of the unit cell of any of these structures is always given approximately by a strong line, examples, No. 24, Table III and No. 33, Table IV.¹¹ The dimension a_0 of the unit cell in the direction of the *a* axis can be computed from this reflection since the layer lattices are made up of hexagons.¹² Recalculations for greater accuracy of these dimensions are carried out after the indices for most reflections have been determined.

The most important clue to the structure was found when it was realized that vermiculite on dehydration at 750° C. gave a diagram almost identical with that of talc as shown in Table V, which contains the talc diagram and its indices as far as it concerns the present discussion, the only differences are that the basal reflections and most of the others are more diffused and broader than in talc proper.¹³ This great similarity is also noticed in other properties of the dehydrated material. The scaly particles have a talcose feel and even look like talc in iron poor varieties. At this stage of the investigation the structures of talc and pyrophyllite were determined.¹⁴

¹⁰ *Zeit. f. Krist.*, vol. 83, p. 395, 1932.

¹¹ The distance d must be multiplied by 6 since the reflection 060 is the 6th order of the plane 010; d of 010 = b_0 .

¹² See papers on mica and kaolinite.

¹³ An explanation for this diffusion is to be found in the smaller grain size of individual particles after heating. They become too small for optimum reflective power.

¹⁴ *Op. cit.*

Talc consists of units like mica with the alkali layers absent as pointed out previously.¹⁵ If vermiculite dehydrates to a talc-like structure no other layers but those made up of volatile material can occupy the positions that are filled by the alkalis in mica. Obviously this must be mostly or entirely water. With this information it is possible to determine the entire structure. How these calculations are made has been described in previous papers.¹⁶ Agreement between theoretical and observed intensities is reached in vermiculite when the shift of one layer over the adjacent is approximately $1/3$ of the length of a_0 (expressed in degrees = 120°) parallel to the a axis but in the opposite direction from the shift in the micas, chlorites and talc, as shown diagrammatically in Fig. 1. The resulting β angle is $97^\circ 09' \pm 10'$. The atomic coordinates are given in degrees in Table VI.¹⁷

TABLE VI. ATOMIC COORDINATES OF C_{2h}^6 FOR VERMICULITE. FOUR EQUIVALENT ATOMS FOR EACH POSITION

Atom	X	Y	Z	Atom	X	Y	Z
Mg ₁	0°	0°	0°	O ₆	-58	30	138.5
Mg ₂	0	120	0	O ₇	122	30	138.5
Mg ₃	0	-120	0	O ₈	32	120	138.5
O ₁	-51	180	14	O ₉	51	180	166
O ₂	-51	60	14	O ₁₀	51	60	166
OH ₁	-51	-60	14	OH ₂	51	-60	166
O ₃	58	30	41.5	Si ₁	143	0	34
O ₄	-122	30	41.5	Si ₂	-37	60	34
O ₅	-32	120	41.5	Si ₃	-143	0	146
				Si ₄	37	60	146

Table VII contains the calculated theoretical intensities of important planes as compared with the average of the observed intensities of the first six diagrams of Table III. The dimensions for calculating the distances of Table VII were taken from the chlorite structure and are: $\beta = 97^\circ 8' 40''$, $a_0 = 5.31\text{\AA}$, $b_0 = 9.20\text{\AA}$, $c_0 = 28.46\text{\AA}$. The space group is C_{2h}^6 . The average dimensions of

¹⁵ Gruner, J. W., *Am. Mineral.*, vol. 16, p. 451 and Fig. 22, 1931.

¹⁶ *Zeit. f. Krist.*, vol. 83, p. 79 and p. 395, 1932.

¹⁷ The space group relationship of mica and vermiculite, both in C_{2h}^6 is this: The principal or para-glide planes (Paragleitspiegelebene, component = $c/2$) of vermiculite are the clino-glide planes (component = $c/2 + a/2$) of mica. The direction of gliding in vermiculite differs only by about $2\frac{1}{2}^\circ$ from that in mica in the same plane.

vermiculites are slightly larger. For example, $c_0 = 28.66\text{\AA}$ on an average. Allowance must be made for these slight differences in comparing Table VII with III.

Most interesting is the fact that the H_2O occupies a very definite thickness in the unit cell. This is shown by the figures at the

TABLE VII. THEORETICAL AND OBSERVED INTENSITIES FOR TWO MOLECULES OF VERMICULITE. NO ALLOWANCE IS MADE FOR THE GLANCING ANGLE

Indices	d	Theoretical Intensity	Observed Intensity	Indices	d	Theoretical Intensity	Observed Intensity	
002	14.12	451	10	20 $\bar{1}\bar{4}$	1.707	0		
004	7.06	21	0.3	13 $\bar{1}\bar{4}$	1.656	302	} 2.5	
006	4.71	13	0.5	2012	1.656	151		
020	4.60	55	1	0018	1.569	34		
008	3.530	137	3.5	1314	1.559	69	} 0.5	
0010	2.824	106	4	20 $\bar{1}\bar{6}$	1.558	34		
130	2.650	25		060	1.533	205		
20 $\bar{2}$	2.650	13		33 $\bar{2}$	1.533	412		
13 $\bar{2}$	2.635	39		330	1.524	250	} 4	
200	2.634	18	} 1	33 $\bar{4}$	1.524	164		
132	2.576	102		13 $\bar{1}\bar{6}$	1.513	214		
20 $\bar{4}$	2.575	53		2014	1.513	103		
13 $\bar{4}$	2.534	302	} 1.5	33 $\bar{2}$	1.498	35	} 0.5	
202	2.533	151		33 $\bar{6}$	1.498	36		
134	2.432	28		1316	1.428	405	} 1.5	
20 $\bar{6}$	2.431	13		20 $\bar{1}\bar{8}$	1.423	203		
13 $\bar{6}$	2.374	454	} 3.5	0020	1.412	62	} 1	
204	2.373	219		13 $\bar{1}\bar{8}$	1.389	0		
0012	2.353	13		2016	1.389	0		
136	2.250	27		338	1.347	67	} 0.5	
208	2.249	14		33 $\bar{1}\bar{2}$	1.347	61		
138	2.186	214	} 1	1318	1.314	405	} 2.5	
206	2.186	103		20 $\bar{2}\bar{0}$	1.314	204		
138	2.058	92	} 1	0022	1.284	53	} 1	
20 $\bar{1}\bar{0}$	2.058	48						
0014	2.017	104	1					
13 $\bar{1}\bar{0}$	1.996	57	1					
208	1.995	29	} 1					
1310	1.875	19						
20 $\bar{1}\bar{2}$	1.875	11	} 1					
13 $\bar{1}\bar{2}$	1.817	103						
2010	1.817	54						
0016	1.765	6						
1312	1.707	0						

bottom of Table III which give the heights of the unit cells measured normal to the base. If a single layer of talc ($=9.26\text{\AA}$, the unit cell is double this height) is subtracted from a single layer of vermiculite ($=14.23\text{\AA}$) the thickness of a water layer is found to be 4.97\AA . Almost the same figure may be obtained by subtracting

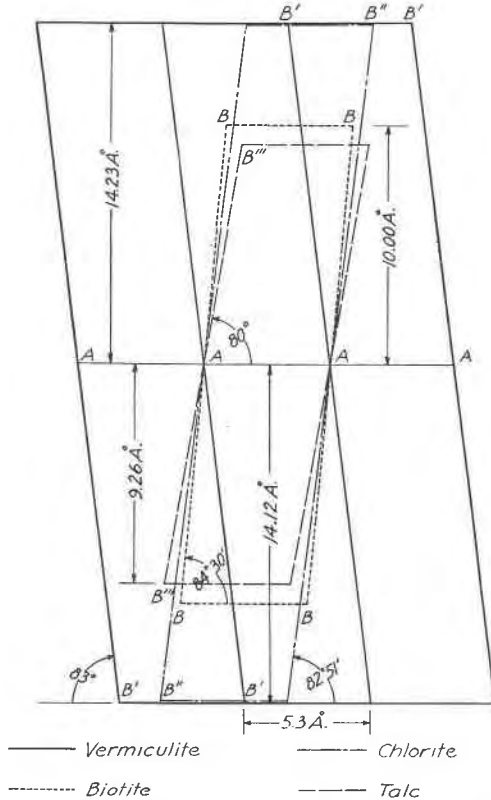


FIG. 1. Outlines of monoclinic unit cells of biotite, talc and chlorite superimposed on that of three unit cells of vermiculite. Plane of paper parallel to axial plane $a-c$.

the mica unit in chlorite from the chlorite unit ($14.12\text{\AA} - 9.28\text{\AA} = 4.84\text{\AA}$). Therefore, the H_2O layer requires a slightly larger space than the so-called brucite unit $6\text{Mg}(\text{OH})_2$ in chlorite. Expressed in another form, V of $6\text{Mg}(\text{OH})_2 = V$ of $8\text{H}_2\text{O}$ in layer structures. It is not possible at present to assign definite geometrical positions to H_2O in these layers. Nor can an explanation be given for the

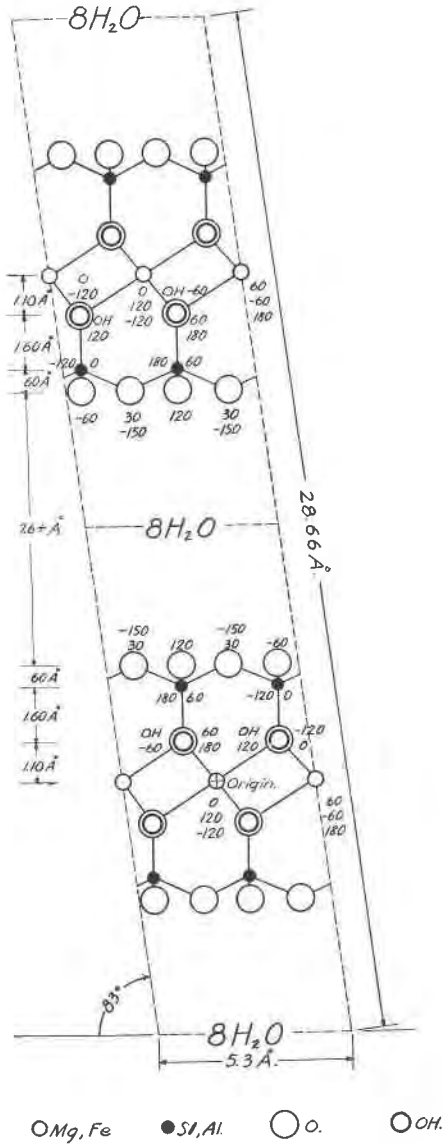


FIG. 2. Unit cell of vermiculite. The plane of the paper is the principal glide plane containing the origin of space group C_{2h}^6 . The y coordinates parallel the b axis are given in degrees. The origin is also a center of symmetry.

gradual dehydration as the temperature is raised. About 4 per cent of the H_2O held as OH in the mica units should, however, be stable even at low red heat.

Figure 1 illustrates the relative movement which a given point in a certain structure undergoes in order to reach a corresponding position in a new structure. For example in the change from biotite to vermiculite: The points *A-A-A-A* are identical points in a given layer. This layer remains stationary during all changes. The points *B-B* of biotite represent identical points to each other (not to *A*) in a plane parallel to the plane of the paper. When the structure expands to vermiculite the points *B* move in this plane to their nearest new positions *B'*. *B'* positions are identical to *B* positions as far as single layers of the structures are concerned. On dehydration the *B'* positions move in the same plane to the nearest corresponding *B'''* positions of the talc structure. *B''* positions are chlorite positions corresponding to *B* positions in mica.

INTERPRETATION OF X-RAY DATA OF HYDROBIOTITE

The diagrams of specimens 8, 9 and 10 in Table IV and their dehydrated products (Table VIII), presented puzzling features at first. The lines originating from basal reflections are broader and less agreement exists among them than in other similar structures. A number of different combinations of layers of vermiculites, micas, chlorites, brucite, and kaolinites were tried for unit cells and their basal reflections calculated. The same calculations were made for their dehydrated products. The only combinations that show any agreement with observed reflections are those listed under "Chemical data."

A stacking of alternate units of mica and vermiculite results in a unit cell 24\AA or a multiple of 24\AA high. Only two of its basal reflections, which are also the strongest theoretically, can be identified with certainty in the diagrams as lines 2 and 9. They have indices 002 and 007, respectively (Table IV). On dehydration such a unit cell shrinks to a height of 19.2\AA or a multiple of it (the sum of a unit of mica and talc). Its two theoretically strongest basal reflections appear in Table VIII as lines 1 and 5 with indices 002 and 006 or its multiples, respectively.

The observed lines for hydrobiotite and its dehydrated material also fit a unit cell with a height of 62\AA and 47.5\AA respectively, which has a stacking of 3 vermiculite to 2 mica units in the manner

given under chemical data, or in another combination, M-V-M-V-V-M-V-M-V-V-

It is not proposed that mica altering to hydrated material could do so only in ratios 1M:1V or 2M:3V, before it altered to vermiculites

TABLE VIII. POWDER DIAGRAMS OF MINERALS FORMERLY DESIGNATED AS VERMICULITES AFTER HEATING 24 HOURS AT 750° C.

No.	8.		12.		9.		10.		Indices
	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	
1	9.40	3	9.67m	3	9.56	3	9.56	3	002 or 005
2	4.46	1 <i>i</i>			4.53	1 <i>i</i>	4.50	1 <i>i</i>	
3			3.64m	0.5β					006 or 0015
4					3.57	1β			
5	3.174	1 <i>i</i>	3.238m	3	3.239	3	3.160	1 <i>b</i>	
6	3.003	1 <i>i</i>							
7	2.861	1β	2.861	0.5β	2.880	1β	2.873	1β	
8	2.596	2	2.596	2 <i>b</i>	2.613	4	2.601	3	
9	2.424	2	2.413	1 <i>b</i>	2.431	3 <i>b</i>	2.423	2 <i>b</i>	
10			2.256	0.5					
11	2.155	1	2.154	1 <i>b</i>	2.171	2 <i>b</i>	2.161	1 <i>b</i>	
12	2.061	0.5							
13			1.983	1	1.971	0.5	1.977	0.5 <i>i</i>	
						<i>i.b.</i>			
14	1.881	0.5	1.892	0.5	1.903	0.5	1.882	1	
15			1.829	0.5β	1.837	0.5β			
16	1.674	1 <i>b</i>	1.655	1 <i>b</i>	1.668	2 <i>b</i>	1.679	1	
17	1.628	1 <i>i.b.</i>					1.648	1	
18	1.522	3	1.522	3	1.532	5	1.524	3	
19	1.507	1			1.514	1	1.506	1	
20			1.453	0.5	1.461	0.5β	1.452	0.5β	
21	1.351	1 <i>b</i>	1.350	1	1.363	1 <i>b</i>	1.353	2	
22	1.313	0.5	1.317	0.5	1.323	2	1.315	1	
23	1.293	0.5			1.296	1	1.290	1	

m = definite mica reflection.

ulite entirely. Probably all types of irregularities may and do exist. When distinct diagrams, however, are recognized as in 8, 9 and 10, such distinct compounds must make up a large part of the specimen. A specimen of commercial "vermiculite" from near Salida, Colo., was x-rayed. No distinctive *basal* reflections could be recognized. This may mean that the ratio of any definite constituent to the sum of the others is so small that it is insufficient

for recording in the film, or that no definite unit cells, as far as the stacking of the layers is concerned, exist. No name has been suggested for such an heterogeneous arrangement of layers in one direction. The word *metacrystalline* is proposed to signify a state of partial change from one definite crystal structure to another without, however, attaining a homogeneous space group arrangement in one of the directions.

CONCLUSIONS

An *x*-ray study of analyzed vermiculite minerals reveals the following facts:

Vermiculite exists as a distinct mineral. Its structural formula is $(\text{OH})_2(\text{Mg}, \text{Fe})_3(\text{Si}, \text{Al}, \text{Fe})_4\text{O}_{10} \cdot 4\text{H}_2\text{O}$. Its formula based on the average of seven true vermiculites is



Fe^{II} which is oxidized in the change from mica to vermiculite probably continues to occupy its Mg positions in the structure. The loss of K^+ ions in this change is probably partly neutralized by the change of Fe^{II} to Fe^{III} .

The unit cell of vermiculite is monoclinic holohedral with the probable space group C_{2h}^6 , $a_0 = 5.3 + \text{\AA}$, $b_0 = 9.2 + \text{\AA}$. c_0 varies between 28.57 and 28.77 \AA in seven samples. $\beta = 97^\circ 09' \pm 10'$. The cell contains 4 molecules of the structural formula above. Its theoretical density is 2.13+.

The structure consists of $(\text{OH})_4\text{Mg}_6(\text{Si}, \text{Al})_8\text{O}_{20}$ sheets, like mica and talc, between which are interstratified layers of $8\text{H}_2\text{O}$ which occupy a space of definite thickness close to 4.9 \AA . Compared with the structure of the chlorites these $8\text{H}_2\text{O}$ occupy almost exactly as much space as the brucite layer $6\text{Mg}(\text{OH})_2$ in chlorite. Though almost half of the H_2O may be driven off at 110°C . no essential changes occur in the powder diagrams of specimens treated in this manner.

On heating vermiculite to 750°C . a collapse to the talc structure occurs. The well known exfoliation on heating seems to be a simple mechanical disintegration of larger particles due to the formation of steam.

The old term hydrobiotite is used again to designate interstratification of "molecular" layers of biotite with vermiculite resulting in a new *x*-ray pattern. The word meta-crystalline is proposed for such an arrangement and signifies a perfectly normal

space group arrangement in all but one direction. In the latter the sequence of layers or of units is heterogeneous to a certain extent. It may, however, as in specimens 9 and 10 approach a definite ratio of 1:1=biotite units:vermiculite units.

X-ray diagrams are necessary to distinguish vermiculite from hydrobiotite.

SUSSEXITE FROM IRON COUNTY, MICHIGAN

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In 1930 seamanite, a new manganese phosphoborate was reported from the Chicagon Mine in Iron County, Michigan.¹ Associated with the seamanite, but occurring in thin veinlets from 1mm. to 3mm. wide, was a white to yellowish-buff colored mineral which upon subsequent examination was shown to be sussexite. The sussexite occurs in the veinlets as irregular matted masses of fibers with the fibers lying parallel to the plane of the vein. These veins run through both the red "soft ore" hematite and the highly altered and porous cherty gangue. The gangue separates easily from the veins leaving thin sheets of the felted fibers of sussexite. Small cavities or vugs within the veins are lined with yellow, transparent crystals of seamanite and in many instances they are implanted directly upon the sussexite. All the specimens in our possession were collected for the seamanite although the sussexite is by far the more prevalent mineral.

Sussexite has a hardness of 3+ and a specific gravity of 3.0 to 3.1. It is slowly soluble in cold concentrated mineral acids and in hot dilute acids. The elongation is negative, extinction parallel, and the indices of refraction for sodium light are: $\alpha=1.642$, $\beta=1.713$, and $\gamma=1.721$ (all ± 0.003). The fibers are flattened so that most of them yield α and β . Those resting on an edge give γ and exhibit a pronounced color dispersion which is greater than that of the methylene iodide mixtures used for the index determinations.

The analysis given in Table 1 was made upon selected material which was crushed and washed with cold dilute hydrochloric acid to remove small acicular crystals of seamanite and microscopic cube-like rhombohedrons of calcite. Boron was determined by titration in the presence of mannitol, and the other oxides by ordinary gravimetric methods. H_2O+110° was determined by the direct method recommended by Penfield using separate samples of approximately one gram each. It is interesting to point out that