

INTERPRETATION OF THE COMPOSITION OF VERMICULITES AND HYDROBIOTITES¹

by

MARGARET D. FOSTER

U.S. Geological Survey, Washington, D.C.

ABSTRACT

Formulas calculated from modern analyses of vermiculites and hydrobiotites show that these minerals resemble phlogopites and magnesian biotites in tetrahedral and octahedral layer composition, but usually have a higher proportion of trivalent octahedral cations. None of the formulas studied resembles those of ferroan biotites in composition.

In a few formulas the negative layer unit charge and the neutralizing positive interlayer charge are as high as those found in phlogopite; about 1.00 in the half-cell formula, but in most vermiculite formulas the charge on the layer unit and the interlayer charge are considerably lower than in phlogopite. Such a decrease in the amount of these charges may be due to oxidation of Fe^{2+} to Fe^{3+} , which would increase the positive octahedral charge, and, consequently, decrease the layer unit charge. Oxidation of Fe^{2+} to Fe^{3+} also explains the higher proportion of trivalent octahedral cations in vermiculites and hydrobiotites.

Few papers furnish both cation exchange data and analyses of the samples studied; consequently it is difficult to correlate interlayer charge and cation exchange capacity, but empirically the interlayer charge multiplied by 200 yields a value that approximates the cation exchange capacity, provided the Mg has been allotted correctly between octahedral and interlayer positions.

On the basis of composition and charge relations, vermiculites may be interpreted as formed from phlogopites or magnesian biotites by replacement of K by Mg.

INTRODUCTION

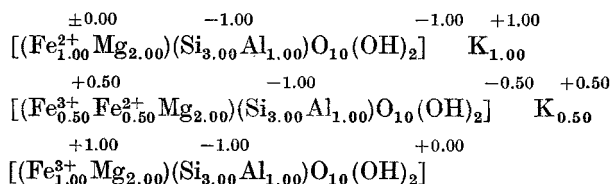
The mineralogical status of vermiculite puzzled mineralogists until Gruner (1934) showed that it is a distinct mineral with a definite crystal structure similar to that of mica and talc, but with H_2O molecules instead of K between the layers. Because of these H_2O molecules, Gruner and some other investigators, among them Kazantzev (1934), Walker (1950), and Roy and Romo (1957), have favored hydration, with H_2O molecules replacing K cations, as the main factor in the alteration of a trioctahedral mica to vermiculite. Gruner (1934, p. 561) suggested that the positive charges lost by removal of K are made up by oxidation of Fe^{2+} to Fe^{3+} , or by introduction of H^+ . As another possibility he suggested substitution of F^- or $(\text{OH})^-$ for O^{2-} . He considered that oxidation of Fe^{2+} probably partly compensated for the loss of

¹ Publication authorized by the Director, U.S. Geological Survey.

K, but that usually there would not be enough Fe^{2+} present whose oxidation could furnish the positive charges necessary for complete neutralization. Roy and Romo (1957, p. 607) state, however, that "all analyzed samples [of vermiculite] are high in iron" and that "there appears to be no well-authenticated case of a true phlogopite weathering to a vermiculite". These authors believe that the rarity of vermiculites with low iron contents supports the postulate that the leaching of K is coupled with oxidation of Fe^{2+} to balance the charge.

A quite different vermiculitization process, which is independent of the iron content of the parent mica, was advanced by Barshad (1948). In this process the main factor in the alteration of a trioctahedral mica to a vermiculite is replacement of K by Mg, with H_2O molecules accompanying the Mg cations as water of hydration. In this replacement of one cation by another, charge balance is maintained throughout, and assumption of a concurrent but independent reaction to supply positive charges is not necessary. Nor is the composition of the structural layers affected; the alteration affects only the interlayer cations. However, this does not exclude the possibility that oxidation may occur before, during or after replacement of K, but if it does, it is an independent reaction, not a part of the vermiculitization process.

These two different processes that have been proposed to explain the alteration of trioctahedral micas to vermiculites require quite different compositions in the parent minerals and would produce final materials having certain definite compositional characteristics. In one the parent mineral must contain enough Fe^{2+} that its oxidation to Fe^{3+} would furnish the positive charges necessary to compensate for the charges that are lost with the K. As the K in a trioctahedral mica occupies one position in the half-cell formula, the initial mica must also contain at least enough Fe^{2+} to occupy one position, or about 15 percent of FeO. Consequently, according to this postulate a trioctahedral mica having much less than this amount of FeO would not be a likely parent mineral for vermiculite. During the course of vermiculitization, oxidation of Fe^{2+} to Fe^{3+} would progressively increase the positive octahedral charge. As the negative tetrahedral charge would not change, this would result in a progressive decrease in the negative charge on the layer unit, and in the positive interlayer charge necessary to neutralize it, as in the hypothetical formulas given below:



In vermiculite, the end product, the positive charge on the octahedral layer would balance the negative tetrahedral charge, the layer unit would be neutral, and there would be no interlayer cations, exchangeable or non-exchangeable, but only H_2O molecules in the interlayer.

TABLE IA.—ANALYSES OF VERMICULITES (IN ORDER OF DECREASING Mg CONTENT)

Analysis number	Percent											Total	
	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	FeO	MgO	MnO	CaO	Na ₂ O	K ₂ O	H ₂ O+		H ₂ O—
1	37.41	10.39	0.50	6.22	0.95	28.10	—	0.02	0.29	0.29	11.63	4.69	100.57 ¹
2	46.55	10.50	1.06	1.51	1.39	27.55	0.04	2.55	0.59	0.17	4.30	3.50	99.85 ²
3	35.36	13.61	0.26	0.24	2.60	27.48	0.22	0.37	0.05	0.10	10.36	10.74	99.32 ³
4	34.86	14.46	0.61	6.17	2.60	27.25	0.22	0.27	0.19	0.02	12.11	1.49	100.25
5	38.4	9.8	0.28	2.6	0.29	27.2	0.02	0.00	0.04	0.04	20.9	—	99.7 ⁴
6	36.61	8.40	0.89	4.50	0.09	26.91	0.02	0.00	0.00	0.05	22.10	—	100.61 ⁵
7	35.93	9.05	0.93	5.11	0.16	26.15	0.02	0.50	0.16	0.00	11.32	10.36	100.89 ⁶
8	37.94	11.44	0.50	4.05	0.09	25.84	0.07	0.01	0.01	0.05	9.67	10.34	100.15 ⁷
9	35.54	11.42	0.50	7.20	0.15	24.79	0.01	0.08	—	—	9.46	11.65	100.80
10	36.12	13.90	0.24	4.24	0.68	24.84	trace	0.18	—	—	10.74	8.20	99.42 ⁸
11	36.6	12.6	0.7	0.5	1.7	24.4	0.01	0.6	0.1	0.1	7.2	14.3	99.58 ⁹
12	34.88	13.15	0.42	8.26	0.44	24.24	0.18	0.10	—	—	8.58	9.91	100.16
13	36.72	13.15	0.41	4.69	0.59	23.59	—	0.15	—	0.42	20.05	—	99.95 ¹⁰
14	34.60	13.63	—	4.15	1.80	22.88	—	0.04	0.39	0.05	11.68	9.80	99.07 ¹¹
15	35.92	10.68	—	10.94	0.82	22.00	—	0.44	—	—	19.84	—	100.64
16	31.55	15.90	0.61	1.42	5.68	21.68	0.03	0.28	0.25	0.20	11.25	11.36	100.21
17	35.66	12.48	1.80	7.47	0.48	21.51	0.01	—	1.24	0.42	9.49	9.15	99.99 ¹²
18	39.82	15.42	0.11	4.77	1.48	19.86	0.12	1.74	0.35	0.71	7.54	7.20	99.90 ²
19	33.92	16.20	1.01	7.12	1.50	19.12	0.06	0.03	<0.02	0.04	10.04	11.08	100.12
20	29.3	10.0	1.3	4.5	0.22	19.0	0.10	4.2	0.18	0.10	17.7	—	99.22 ¹³
21	35.78	18.12	0.62	9.18	0.23	17.79	—	2.72	—	—	7.42	—	100.00 ¹⁴
22	33.92	13.63	0.74	8.71	2.44	17.03	1.13	none	2.92	0.30	6.30	12.85	100.34 ¹⁵
23	37.40	16.86	0.19	12.15	4.70	15.38	0.27	2.10	0.42	1.01	4.64	3.00	99.30 ¹⁵
24	36.06	20.48	0.64	15.91	3.12	12.95	—	3.54	trace	0.12	7.82	—	100.64
25	32.37	12.38	2.80	15.07	1.52	9.77	0.40	2.88	—	—	6.54	16.32	100.05

- 1 Includes 0.08 percent NiO.
- 2 Includes 0.14 percent P_2O_5 .
- 3 Includes 0.51 percent F, and 0.44 percent CO_2 . Total adjusted for O = F is 98.88.
- 4 Includes 0.03 percent P_2O_5 , and 0.1 percent CO_2 .
- 5 Includes 0.49 percent Cr_2O_3 (\approx 0.03 formula position), and 0.55 percent F. Total adjusted for O = F is 100.38.
- 6 Includes 0.48 percent Cr_2O_3 (\approx 0.03 formula position), 0.05 percent P_2O_5 , and 0.67 percent F. Total adjusted for O = F is 100.61.
- 7 Includes 0.10 percent NiO (\approx 0.01 formula position), 0.02 percent CO_2 , and 0.02 percent P_2O_5 .
- 8 Includes 0.28 percent NiO (\approx 0.02 formula position).
- 9 Includes 0.53 percent Cr_2O_3 (\approx 0.03 formula position), 0.04 percent P_2O_5 , and 0.2 percent F. Total adjusted for O = F is 99.50.
- 10 Includes 0.18 percent P_2O_5 .
- 11 Includes 0.05 percent F.
- 12 Includes 0.28 percent P_2O_5 .
- 13 Includes 0.12 percent P_2O_5 , 2.3 percent CO_2 , and 10.0 percent $BaSO_4$.
- 14 Includes 8.14 percent loss on ignition.
- 15 Includes 0.01 percent P_2O_5 , 0.30 percent Cl, and 0.06 percent F.
- 16 Includes 0.06 percent NiO, and 1.12 percent P_2O_5 .

TABLE 1B.—DATA FOR WRITING FORMULAS CALCULATED FOR ANALYSES IN TABLE 1A

Analysis	Octahedral positions occupied by						Octahedral charge	Tetrahedral Al + Fe ³⁺ (=) charge	Layer unit charge	Interlayer cations	
	Al	Fe ³⁺	Fe ²⁺	Mn	Mg	Total				Charge	Positions
1	0.00	0.17	0.06	—	2.77	3.00	+0.17	1.13	-0.94	+0.97	0.52
2	0.08	0.08	0.08	—	2.76	3.00	+0.16	0.78	-0.62	+0.64	0.37
3	0.15	0.01	—	—	2.83	2.99	+0.14	1.14	-1.00	+0.97	0.49
4	0.00	0.28	0.16	0.01	2.55	3.00	+0.28	1.36	-1.08	+1.08	0.54
5	0.00	0.14	0.02	—	2.84	3.00	+0.14	0.94	-0.80	+0.80	0.40
6	0.00	0.10	<0.01	—	2.87	3.00 ¹	+0.13	0.99	-0.86	+0.86	0.43
7	0.00	0.15	0.01	—	2.81	3.00 ²	+0.18	1.05	-0.87	+0.87	0.44
8	0.06	0.24	<0.01	—	2.69	3.00 ³	+0.30	1.02	-0.72	+0.70	0.35
9	0.00	0.39	0.01	—	2.60	3.00	+0.39	1.14	-0.75	+0.74	0.37
10	0.14	0.25	0.04	—	2.55	3.00 ⁴	+0.39	1.15	-0.76	+0.76	0.38
11	0.19	0.03	0.12	—	2.63	3.00 ⁵	+0.25	1.02	-0.77	+0.76	0.39
12	0.00	0.48	0.03	0.01	2.48	3.00	+0.48	1.24	-0.76	+0.76	0.38
13	0.16	0.28	0.04	—	2.45	2.93	+0.30	1.07	-0.77	+0.74	0.39
14	0.17	0.26	0.12	—	2.45	3.00	+0.43	1.15	-0.72	+0.72	0.36
15	0.00	0.55	0.06	—	2.39	3.00	+0.55	1.12	-0.57	+0.56	0.28
16	0.25	0.09	0.40	—	2.26	3.00	+0.34	1.34	-1.00	+0.98	0.49
17	0.08	0.46	0.03	—	2.43	3.00	+0.54	1.11	-0.57	+0.57	0.40
18	0.41	0.22	0.09	0.01	2.25	2.98	+0.59	0.97	-0.38	+0.40	0.26
19	0.35	0.44	0.10	—	2.11	3.00	+0.80	1.22	-0.42	+0.44	0.22
20	0.05	0.33	0.02	0.01	1.92	3.00	+0.38	1.14	-0.76	+0.73	0.39
21	0.00	0.53	0.01	—	1.92	2.86	+0.65	1.24	-0.59	+0.56	0.28
22	0.13	0.54	0.17	0.08	2.10	3.02	+0.71	1.20	-0.49	+0.50	0.50
23	0.24	0.68	0.29	0.02	1.69	2.92	+0.76	1.23	-0.47	+0.49	0.32
24	0.36	0.87	0.19	—	1.40	2.82	+0.87	1.39	-0.52	+0.54	0.27
25	0.20	1.01	0.11	0.03	1.30	2.65	+0.51	1.10	-0.59	+0.56	0.28

¹ Includes 0.49 percent Cr₂O₃ (≅ 0.03 formula position), and 0.55 percent F. Total adjusted for O = F is 100.38.
² Includes 0.48 percent Cr₂O₃ (≅ 0.03 formula position), 0.05 percent P₂O₅, and 0.67 percent F. Total adjusted for O = F is 100.61.
³ Includes 0.10 percent NiO (≅ 0.01 formula position), 0.02 percent CO₂, and 0.02 percent P₂O₅.
⁴ Includes 0.28 percent NiO (≅ 0.02 formula position).
⁵ Includes 0.53 percent Cr₂O₃ (≅ 0.03 formula position), 0.04 percent P₂O₅, and 0.2 percent F. Total adjusted for O = F is 99.50.

LOCALITY AND REFERENCE FOR ANALYSES IN TABLE 1

1. Zöblitz, Saxony, Germany. Matthes, Siegfried (1950) Vorkommen von Vermiculit in Mitteldeutschen Serpentininen: *Neues Jahrb. Mineralogie*, Monatshefte no. 2, p. 34.
2. Jebel Bou Ifoloussene, Haut Atlas de Midelt, Morocco. Agard, J., Destombes, J., and Jeanette, A. (1953) Les gisements de vermiculite du Haut Atlas de Midelt: Morocco Service des Mines et de la Carte géologique, Notes et Mem. No. 117, *Notes du Service géologique*, v. 7, p. 281.
3. Near Llano, Texas. Barnes, V. E., and Clabaugh, S. E. (1961) Vermiculite deposits near Llano, Texas: 10th National Clay Conference Field Excursion, Univ. Texas Guidebook no. 30, p. 51.
4. Maaninka, Posio, Nordfinnland. Volborth, A. (1953) Vermiculite aus Maaninka, Posio, Nordfinnland: *Comm. Geol. Finnlande*, Bull. 159, v. 27 (*C.R. Soc. Geol. Finlande*, v. 26), p. 5.
5. Franklin, North Carolina. Schnepfe, M. M. (1960) Cation exchange with vermiculite: in *Short Papers in the Geologic Sciences*, U.S. Geol. Survey Prof. Paper 400B, Art. 71, p. B162, no. 7, U.S. Nat. Museum no. 101,933.
6. Loolekop, Palabora, Northeast Transvaal, South Africa: Gevers, T. W. (1949) Vermiculite at Loolekop, Palabora, Northeast Transvaal: *Geol. Soc. South Africa Trans.*, v. 51, p. 154.
7. Loolekop, Palabora, Northeast Transvaal, South Africa: Gevers, W. T. (1949) Vermiculite at Loolekop, Palabora, Northeast Transvaal: *Geol. Soc. South Africa Trans.*, v. 51, p. 154.
8. Burnsville, 3 miles north of, Yancey County, North Carolina, Kulp, J. L., and Brobst, D. A. (1954) Notes on the dunite and the geochemistry of vermiculite at the Day Book dunite deposit, Yancey County, North Carolina: *Econ. Geol.*, v. 49, p. 216.
9. Uzumine, Fukushima Prefecture, Japan. Omori, K. (1958) Mode of occurrence and chemical composition of Mg-vermiculite from Odaka and Uzumine, Fukushima Prefecture: *J. Mineral. Soc. Japan*, v. 3, pp. 478-485.
10. Bare Hills, near Baltimore, Maryland, Shannon, E. V. (1928) Vermiculite from the Bare Hills, near Baltimore, Md.: *Amer. J. Sci.*, v. 15, p. 22.
11. Amba, eastern Sierra Leone, Africa. Dumham, K. C., Phillips, R., Chalmers, R. A., and Jones, D. A. (1958) The chromiferous ultrabasic rocks of eastern Sierra Leone: *Overseas Geolog. and Mineralog. Resources Bull.*, Suppl. no. 3, p. 27.
12. Odaka, Fukusima Prefecture, Japan. Omori, K. (1958) Mode of occurrence and chemical composition of Mg-vermiculite from Odaka and Uzumine, Fukusima Prefecture: *J. Mineral. Soc. Japan*, v. 3, pp. 478-485.
13. Transvaal, South Africa. Keay, J., and Wild, A. (1961) Hydration properties of vermiculite: *Clay Minerals Bull.*, v. 4, no. 25, p. 222.
14. Röhrenhof, Fichtelberg, Bavaria, Germany. Matthes, Siegfried (1950) Vorkommen von Vermiculite in mitteldeutschen Serpentininen: *Neues Jahrb. Mineralogie*, Monatshefte no. 2, p. 34.
15. Wiant's Quarry, near Pilot, Md. Ross, C. S., Shannon, E. V., and Gonyer, F. A. (1928) The origin of nickel silicates at Webster, North Carolina: *Econ. Geol.*, v. 23, p. 542.
16. Kaslinskaia, Dacha, Urals, U.S.S.R. Sokolov, G. A. (1931) The corundum plagioclases of Kaslinskaia Dacha in the Urals: *Geol. Prosp. Service U.S.S.R. Trans.*, no. 56, p. 21.
17. South Kitui, Kenya. Varley, E. R. (1948) Vermiculite deposits in Kenya: *Imper. Inst. Bull.*, v. 46, p. 350.
18. Encampment, Wyo. Hagner, A. F. (1944) Wyoming vermiculite deposits: *Geol. Survey Wyoming Bull.*, v. 34, p. 9, no. 1.
19. Chester County, Pa. Grudeno, A. (1954) An X-ray examination of the structure of vermiculite: *Svenska Forskningsinst. Cement Betong vid Kgl. tek. Högskol. Stockholm*, Handl. no. 22, p. 8, C.
20. Hillside, Colo., U.S. Nat'l Museum no. 107,474. Schnepfe, M. M. (1960) Cation exchange with vermiculite: in *Short Papers in the Geologic Sciences*, U.S. Geol. Survey Prof. Paper 400 B, Art. 71, p. B162.

21. Burguillos del Cerro, Badajoz, Spain. Gonzalez, F., Chaves, Fca. Tristan de, and Chaves, M. (1954) Characterization and properties of a vermiculite from Badajoz: *Anales edafol. y fisiol. vegetal (Madrid)*, v. 13, p. 76.

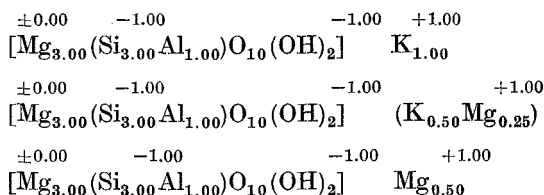
22. Young River, Eucla Division, Western Australia. Ellis, H. A., and Grace, J. N. A. (1944) The Young River vermiculite deposits, Young River, Eucla Division, Western Australia: Dept. Mines Western Australia, Rept. 1944, p. 82.

23. Glenrock, Wyo. Hagner, A. F. (1944) Wyoming vermiculite deposits: *Geol. Survey Wyoming Bull.*, v. 34, p. 9, no. 3.

24. Malavanghatta, Mysore, India. Radhakrishna, B. P. (1952) Vermiculite, its occurrence, properties, and uses: *Mysore Geol. Dept. Rec.*, v. 47, p. 27-55.

25. District de Tete (Matema), Mozambique. Behier, J. (1957) Minerais de provincia de Moçambique: *Moçambique Serv. Geol. Bull.*, no. 22, p. 15.

In the vermiculitization process advanced by Barshad, the composition of the parent mica is not so prescribed. A phlogopite containing little or no Fe^{2+} would serve as well as a highly ferrous biotite, as illustrated below:



In this vermiculitization process the structural layers are not involved, and the layer and interlayer charge relations remain the same, unless altered by coincident reactions unrelated to the vermiculitization process itself, such as oxidation of Fe^{2+} . Oxidation of Fe^{2+} would result in a decrease in negative layer unit charge and in the amount of positive interlayer charge necessary for neutralization. If oxidation occurs before or during replacement of K, the amount of K, and the amount of Mg necessary for replacement, would be less than before oxidation. If oxidation occurs after replacement, some of the replacing Mg would be released. Whenever oxidation took place the net result would be a lower negative layer unit charge and a lower positive interlayer charge and, consequently, a lower cation exchange value unless some Fe^{3+} has been removed from the structure.

In the present study, the compositional characteristics, charge relations, and cation exchange capacities of hydrobiotite and vermiculite are examined for the information they can give as to the process by which a trioctahedral mica is converted to a vermiculite.

SELECTION OF ANALYSES

Analyses of vermiculites and hydromicas were selected from the literature for this study. The analyses in Table 1A are restricted to those in which 1.00 percent or less K_2O is reported, with the exception of no. 25, which reports 1.01 per cent K_2O . Table 2A contains analyses in which more than 1 percent K_2O is reported. Many analyses of so-called vermiculite report several percent

TABLE 2A.—ANALYSES OF HYDROBIOTITES (IN ORDER OF DECREASING Mg CONTENT)

Analysis number	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	FeO	MgO	MnO	CaO	Na ₂ O	K ₂ O	H ₂ O+	H ₂ O—	Total
1	38.03	9.53	0.27	5.12	0.30	26.94	—	0.13	—	4.57	14.90	—	99.97 ¹
2	38.4	9.4	0.72	4.6	0.50	26.2	0.02	0.61	0.06	4.2	12.7	—	98.33 ²
3	38.53	8.35	1.12	6.31	0.64	25.74	0.03	0.00	0.00	4.73	—	14.58	101.08 ³
4	35.95	16.80	7.95	1.30	1.32	23.85	0.02	0.00	1.92	6.95	2.52	1.75	100.33
5	39.37	12.08	1.25	5.45	1.17	23.37	0.30	1.46	0.80	2.46	5.18	6.02	99.97 ⁴
6	44.32	6.63	1.32	7.65	2.05	21.92	1.01	3.22	0.74	2.30	3.37	3.28	100.35 ⁵
7	36.7	12.2	1.0	8.0	0.76	20.0	0.10	1.6	0.14	2.5	16.4	—	99.56 ⁶
8	36.4	12.2	1.0	7.3	0.50	19.7	0.10	2.1	0.14	2.0	17.4	—	99.09 ⁷
9	35.07	14.37	0.74	7.99	9.24	19.10	0.11	—	—	6.29	6.63	0.81	100.35
10	38.88	22.33	0.97	9.85	0.97	15.25	—	—	0.36	3.03	8.45	—	100.09
11	37.45	14.92	1.35	13.69	1.26	14.09	0.06	0.69	0.24	4.44	5.90	5.95	100.04
12	34.84	12.00	2.44	18.27	1.00	13.00	0.78	2.22	0.52	4.70	7.62	2.63	100.07 ⁸
13	32.8	17.7	2.2	14.7	1.9	10.6	0.19	1.4	0.10	2.4	15.8	—	100.00 ⁹

¹ Includes 0.18 percent P₂O₅.
² Includes 0.02 percent P₂O₅ and 0.9 CO₂.
³ Includes 0.12 percent Cr₂O₃ (≅ 0.01 octahedral position), 0.01 P₂O₅, and 0.92 F. Total adjusted for O = F is 100.68.
⁴ Includes 0.60 percent CO₂, 0.03 Li₂O, 0.03 ZrO₂, 0.03 BaO, 0.15 P₂O₅, 0.02 Cl, 0.02 SO₃, 0.18 S.
⁵ Includes 0.81 percent P₂O₅, 1.17 CO₂, 0.03 BaO, 0.02 Cl, 0.08 SO₃, and 0.43 S.
⁶ Includes 0.05 percent P₂O₅ and 0.1 CO₂.
⁷ Includes 0.05 percent P₂O₅ and 0.2 CO₂.
⁸ Includes 0.05 percent P₂O₅.
⁹ Includes 0.11 percent P₂O₅, and 0.1 CO₂.

TABLE 2B.—DATA FOR WRITING FORMULAS CALCULATED FOR ANALYSES IN TABLE 2A

Analysis	Octahedral positions occupied by						Octahedral charge	Tetrahedral Al+Fe ³⁺ (-) charge	Layer unit charge	Interlayer cations	
	Al	Fe ³⁺	Fe ²⁺	Mn	Mg	Total				Charge	Positions
1	0.00	0.11	0.02	—	2.82	2.95	+0.01	1.05	-1.04	+1.03	0.74
2	0.00	0.16	0.03	—	2.74	2.93	+0.02	0.99	-0.97	+0.97	0.70
3	0.00	0.14	0.04	—	2.81	3.00	+0.15	0.99	-0.84	+0.83	0.65
4	0.20	0.07	0.08	—	2.64	2.99	+0.25	1.29	-1.04	+1.01	0.98
5	0.06	0.31	0.07	0.02	2.54	3.00	+0.37	1.06	-0.69	+0.66	0.51
6	0.00	0.30	0.13	0.06	2.42	2.91	+0.12	0.76	-0.64	+0.61	0.47
7	0.07	0.48	0.05	0.01	2.19	2.80	+0.15	1.08	-0.93	+0.93	0.60
8	0.12	0.44	0.03	0.01	2.18	2.78	+0.12	1.05	-0.93	+0.92	0.57
9	0.00	0.41	0.59	0.01	2.00	3.01	+0.43	1.34	-0.91	+0.93	0.77
10	0.65	0.53	0.06	—	1.62	2.86	+0.90	1.22	-0.32	+0.32	0.32
11	0.24	0.79	0.08	—	1.62	2.73	+0.49	1.11	-0.62	+0.60	0.54
12	0.00	1.02	0.06	0.05	1.54	2.67	+0.36	1.23	-0.87	+0.92	0.74
13	0.40	0.91	0.13	0.01	1.15	2.60	+0.51	1.31	-0.80	+0.76	0.51

LOCALITY AND REFERENCE FOR ANALYSES IN TABLE 2

1. Transvaal, South Africa. Keay, J., and Wild, A. (1961) Hydration properties of vermiculite: *Clay Minerals Bull.*, v. 4, no. 25, p. 222.
2. Loolekop, Palaboro, Northeast Transvaal, South Africa. Schnepfe, M. M. (1960) Cation exchange with vermiculite, in *Short Papers in the Geologic Sciences*, U.S. Geol. Survey Prof. Paper 400B, Art. 71, p. B162, no. 8. U.S. Nat. Mus. No. 106779.
3. Loolekop, Northeast Transvaal, South Africa. Gevers, T. W. (1949) Vermiculite at Loolekop, Northeast Transvaal: *Geol. Soc. South Africa Trans.*, v. 51, p. 154.
4. Bou Ifouloussène (Anemzi), Haut Atlas de Midelt, Morocco. Agard, J., Destombes, J., and Jeanette, A. (1953) Morocco Service des Mines et de la Carte géologique: *Notes et Mem.* no. 117, *Notes du Service géologique*, v. 7, p. 285, no. 5.
5. Loolekop, Palaboro, Northeast Transvaal, South Africa. Schwellnus, C. M. (1938) Vermiculite deposits in the Palaboro area, N.E. Transvaal: South Africa Dept. Mines, Geol. Ser. Bull. no. 11, p. 27, no. 7.
6. Loolekop, Palaboro, Northeast Transvaal, South Africa. Schwellnus, C. M. (1938) Vermiculite deposits in the Palaboro area, N.E. Transvaal: South Africa Dept. Mines, Geol. Ser. Bull. no. 11, p. 27, no. 2.
7. Libby, Montana. Schnepfe, M. M. (1960) Cation exchange with vermiculite: in *Short Papers in the Geologic Sciences*, U.S. Geol. Survey Prof. Paper 400B, Art. 71, p. B162, no. 6. U.S. Nat. Mus. no. 97,385.
8. Libby, Montana. Schnepfe, M. M. (1960) Cation exchange with vermiculite: in *Short Papers in the Geologic Sciences*, U.S. Geol. Survey Prof. Paper 400B, Art. 71, p. B162, no. 1. U.S. Nat. Mus. no. 92,626.
9. Buldymisky deposits, Upper Ufaleisk region, Urals, U.S.S.R. Amelandov, A. S., and Ozerov, K. N. (1934) The Buldymisky deposit of vermiculite: *Mineral. Syr'e*, v. 9, no. 2, p. 23.
10. L'O. de Jazinde, Haute-Loire, France. Forestier, F. H., and Rouger, C. (1956) Nouveau gisements de vermiculite (Haute-Loire); Étude de quelques minéraux, Colloque sur la géologie et la mineralogie du Massif Central Français: Clermont-Ferrand Université Fac. Sci., pub. 2, p. 154, RX10.
11. Kwekivu, Tanganyiki Territory, Africa. Williams, G. J., and Skerl, A. F. (1940) Mica in Tanganyika Territory: Dept. of Lands and Mines, Bull. 14, p. 31.
12. O,Tarbalout, n,Hammou, Haut Atlas de Midelt, Morocco. Agard, A., Destombes, J., and Jeanette, A. (1953) Les gisements de vermiculite du Haut Atlas de Midelt: Morocco Service des Mines et de la Carte géologique, *Notes et Mem.* no. 117, *Notes du Service géologique*, v. 7, p. 281.
13. Spruce Pine, North Carolina. Schnepfe, M. M. (1960) Cation exchange with vermiculite: in *Short Papers in the Geologic Sciences*, U.S. Geol. Survey Prof. Paper 400B, Art. No. 71, p. B162, no. 2. U.S. Nat. Mus. no. 98,359.

of K_2O . By either process of vermiculitization such analyses represent specimens in which replacement of K is only partial, and in which the vermiculitization process is not complete. Gruner (1934, p. 561) found that the X-ray patterns of the samples he studied that contained several percent of alkalies showed clearly an interstratification of single and double layers of units of mica and vermiculite which resulted in a new X-ray pattern. The old term hydrobiotite, formerly used to designate biotite-like material high in water, was used by Gruner to designate such interstratifications.

In selecting analyses for study, all analyses published before 1900 were excluded. This restriction inevitably excludes some good analyses, but it also eliminates a large number that are unreliable or unsatisfactory because of failure to purify the analyzed sample properly, inaccurate methods of analysis,

as, for example, determination of ferrous iron, or incompleteness of analysis. As the contents of bivalent iron and trivalent iron is of particular importance in this study, analyses that do not report both FeO and Fe₂O₃ were also excluded. Also eliminated were analyses that do not report CaO and alkalis, unless the summation clearly indicated the essential absence of these constituents.

STRUCTURAL FORMULAS

This study of the composition, charge relations, and cation exchange capacity of vermiculites and hydrobiotites is based on structural formulas calculated from the analyses given in Tables 1A and 2A. Data for writing the formulas are given in Tables 1B and 2B. Because vermiculites and hydrobiotites have a layer structure like that of trioctahedral and other micas, the same method was used in calculating structural formulas for them as was used in calculating the formulas for trioctahedral micas (Foster, 1960, p. 13). If cation exchange data were not available, the cations were distributed as follows: (a) all the silicon was allotted to the tetrahedral group, together with enough Al to bring the total to 4.00. If there was not enough Al to complete the tetrahedral group, sufficient Fe³⁺ was then allotted to the tetrahedral group to complete it. (b) Any remaining Al and Fe³⁺, with the Fe²⁺, Ti, Cr, Ni, Mn, plus all the Mg or enough Mg to fill three positions were assigned to the octahedral group. (c) Any remaining Mg, plus the Ca, Na, and K, were assigned to interlayer positions. This manner of distributing Mg cations between octahedral and interlayer positions results in a minimum of interlayer Mg; some of the Mg assigned to octahedral positions may actually be interlayer Mg. Among the trioctahedral micas all three octahedral positions are not usually occupied unless the number of octahedral trivalent cations is less than 0.25. In formulas of trioctahedral micas in which trivalent cations occupy more than 0.25 octahedral positions, the total number of octahedral positions occupied tends to decrease with increase in the number of trivalent octahedral cations (Foster, 1960, p. 19). It is probable that the octahedral layers of vermiculites are similarly deficient in occupancy, and that the assignment of enough Mg to the octahedral group to complete it is erroneous. The best means of ascertaining how the Mg should be distributed is to determine the amount of interlayer Mg displaced by cation exchange. In some formulas assignment of all the Mg to octahedral positions still results in a deficiency of octahedral cations. Even in the vermiculites represented by such formulas, however, some of the Mg may belong in interlayer positions and be exchangeable.

Where the cation exchange capacity was known, Mg was first allotted to interlayer positions in sufficient quantity to satisfy, with the Ca and Na present, the exchange data requirements, and the rest was assigned to the octahedral group. In the few formulas in which distribution of Mg could be made on the basis of cation exchange data, octahedral occupancy was usually less than 3.00 positions. This supports the conjecture above that the octahedral group of some vermiculites, assumed here to have 3.00 positions occupied, may actually have fewer than this number of positions occupied.

Before calculating formulas for analyses in which CO_2 is reported, CaO equivalent to the CO_2 is deducted from the total CaO reported, and only the CaO remaining is included in the calculation of the vermiculite formula. If there is not enough CaO present to satisfy the amount of CO_2 reported, MgO sufficient to satisfy the remainder of the CO_2 is also deducted. In sample no. 20 cation exchange data indicated, however, that part of the CaO is exchangeable. Consequently only the nonexchangeable CaO was deducted as CaCO_3 , and the remainder of the CO_2 was satisfied by deducting the proper amount of MgO.

COMPOSITIONAL RELATION BETWEEN VERMICULITES, HYDROBIOTITES, AND TRIOCTAHEDRAL MICAS

The relation between magnesium, other bivalent cations such as Fe^{2+} and Mn^{2+} , and the octahedral trivalent cations, Al and Fe^{3+} , in the octahedral layers of formulas calculated from 135 published analyses of trioctahedral

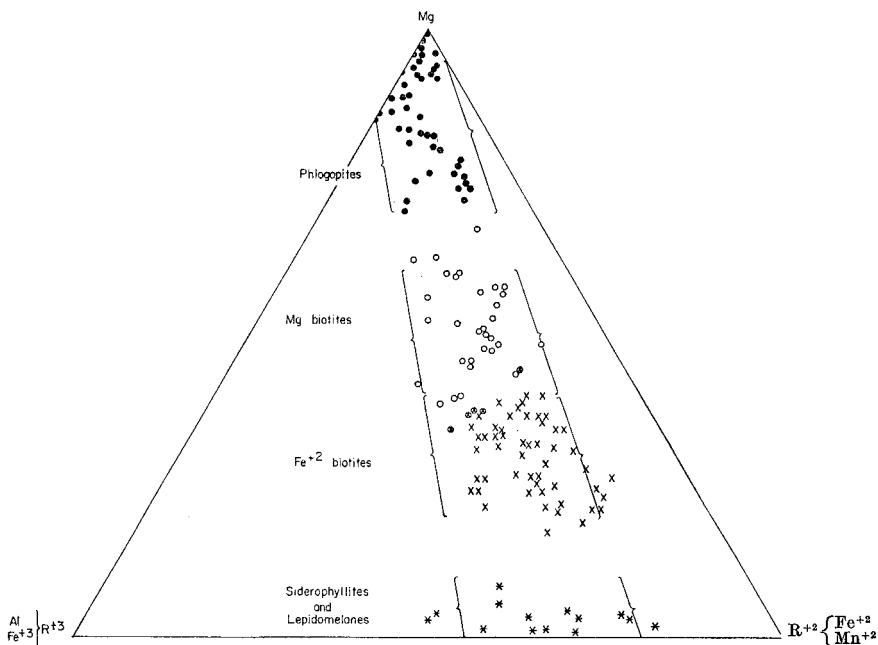


FIGURE 1.—Relation between Mg, Fe^{2+} (+ Mn^{2+}), and octahedral R^{3+} (Al, Fe^{3+}) in trioctahedral micas.

micas is shown in Fig. 1. The group of points at the top of the triangular diagram represent the composition of octahedral layers in trioctahedral micas in which magnesium occupies more than 70 percent of the octahedral positions; that is, phlogopites. The points in the upper half of the middle

group represent the composition of the octahedral layers of biotites in which magnesium is dominant over bivalent iron, and the points in the lower half of the middle group represent the composition of the octahedral layers of biotites in which bivalent iron is dominant over magnesium. The points at the base of the triangle represent the composition of the octahedral layers of siderophyllites and lepidomelanes, which are high in bivalent iron but contain little or no magnesium. The relation of vermiculites and hydrobiotite to trioctahedral micas in octahedral composition is shown in Fig. 2, in which

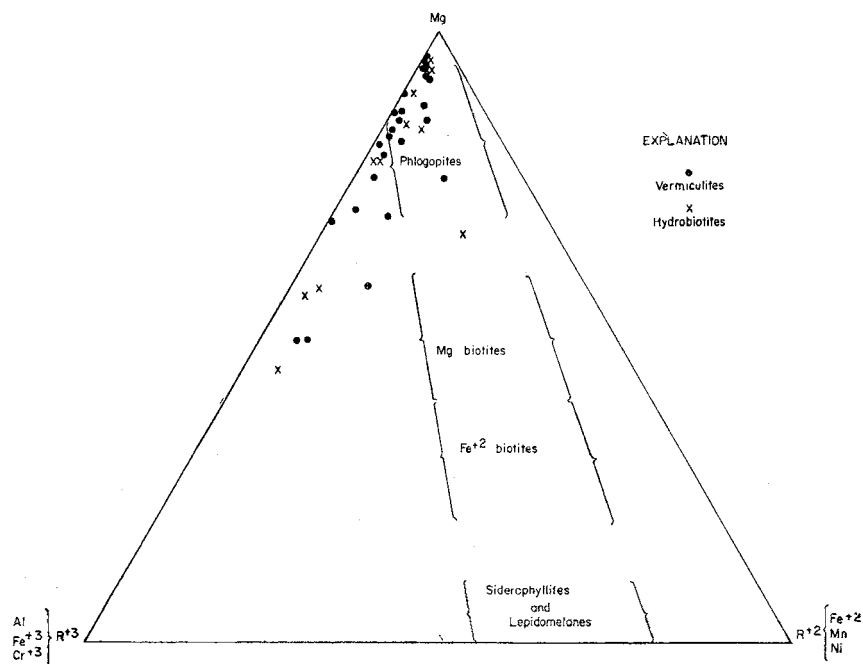


FIGURE 2.—Relation between Mg, R^{2+} (Fe^{2+} , Mn, Ni), and octahedral R^{3+} (Al, Fe^{3+} , Cr^{3+}) in vermiculites and hydrobiotites.

the magnesium, bivalent cation, and octahedral trivalent cation relation in calculated formulas of vermiculites and several hydrobiotites are plotted, with the areas occupied by phlogopites, biotites, and siderophyllites-lepidomelanes in Fig. 1 indicated by brackets. Most of these points representing the Mg, R^{2+} and octahedral R^{3+} relation in vermiculites fall in or to the left of the phlogopite area with a few falling to the left of the magnesium biotite area, but none fall below the magnesium biotite area into or to the left of the ferrous iron biotite area. Thus the octahedral composition of most of these vermiculites is similar to that of phlogopite, except for a higher proportion of R^{3+} with respect to R^{2+} in some that causes the points representing them to fall to the left of the phlogopite or magnesium biotite area. More than half of

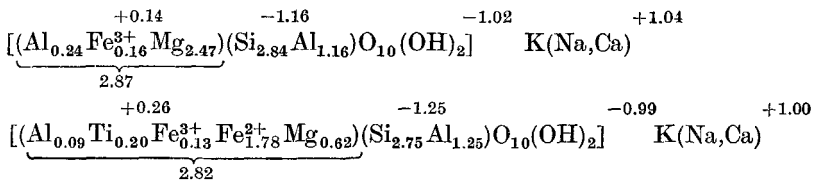
the points representing the Mg, R²⁺, and octahedral R³⁺ relation in hydrobiotites also fall in or just to the left of the phlogopite area, one falls between the phlogopite and the magnesium biotite area, and the rest fall considerably to the left of the magnesium biotite area. Like the points representing vermiculites, none of the points representing hydrobiotites fall below the magnesium biotite area.

The tetrahedral groups of the half-cell formulas for the vermiculites and hydrobiotites studied are similar to those of trioctahedral micas in that Si generally occupies fewer than 3.00 positions, and trivalent cations more than 1.00 position. Like some phlogopites and biotites, some vermiculites and hydrobiotites do not contain enough Al to complete the tetrahedral group, and require the allotment of some Fe³⁺ to that group for its completion.

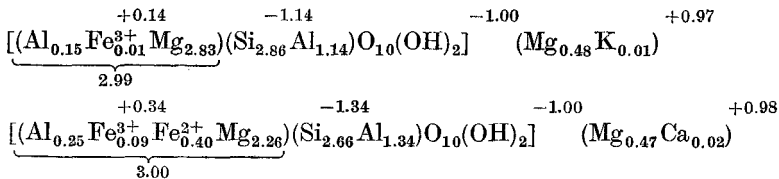
Most of the vermiculites and hydrobiotites were low to moderate in Fe₂O₃ content, less than one-fourth of the analyses contained more than 10 percent, and in only one formula did Fe³⁺ occupy as much as one octahedral position (1.01). In phlogopites and magnesian biotites, FeO is generally higher than Fe₂O₃, whereas in vermiculites and hydrobiotites Fe₂O₃ is generally higher than FeO. In only two vermiculites and one hydrobiotite is FeO higher than Fe₂O₃. This greater proportion of Fe₂O₃ to FeO in many phlogopites and hydrobiotites probably accounts for the fact that most of the points representing the Mg:R²⁺:R³⁺ relation in them fall to the left side of the phlogopite area or to the left but outside the phlogopite and magnesian biotite areas.

LAYER CHARGE RELATIONS

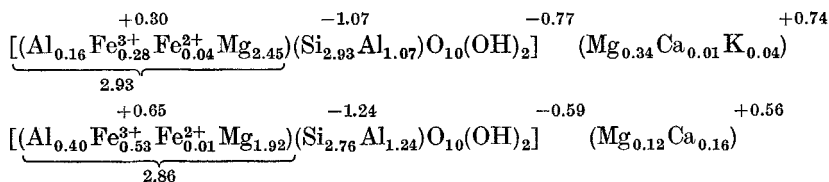
In half-cell formulas of trioctahedral micas, the octahedral layer has a positive charge about equal to the amount that the negative tetrahedral charge exceeds 1.00, so that the residual layer unit charge is about -1.00, as illustrated in the following formulas:



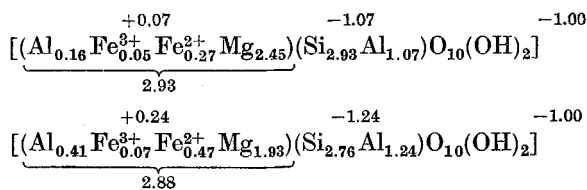
In a few of the vermiculite formulas there is a similar relation between the positive octahedral charge and the negative tetrahedral charge, so that the residual unit charge is also close to -1.00, as in the formulas for nos. 3 and 16, Table 1A, below:



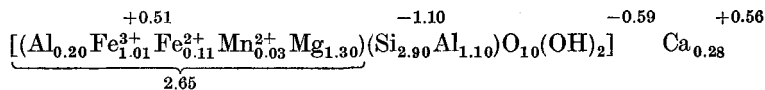
However, in most vermiculite formulas, the positive octahedral charge is greater than the excess of the tetrahedral charge over -1.00 , so that the residual negative layer unit charge and the corresponding positive interlayer charge are consequently less than 1.00 , as in these formulas for nos. 13 and 21, Table 1A:



The low layer unit and interlayer charges in these and many of the other vermiculite and hydrobiotite formulas may be due to oxidation of Fe^{2+} to Fe^{3+} . Such oxidation would increase the positive octahedral charge by an amount equivalent to the amount of bivalent iron oxidized and result in an equivalent decrease in the negative layer unit and positive interlayer charges. In the formulas above, the amount of Fe^{3+} is a little greater than the decrease in the layer unit and interlayer charges, assuming these charges to have been 1.00 or close to 1.00 in the parent mineral. Reduction of most of the trivalent iron to bivalent iron in the above formulas, as below,

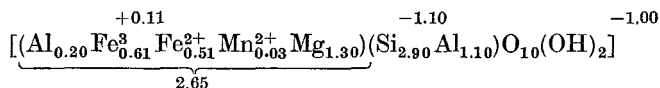


produces layer units with a negative charge of 1.00 . Similarly most of the other formulas contain enough octahedral trivalent iron to account for the low layer unit and interlayer charges. It should be borne in mind that all Fe^{3+} is not necessarily the result of oxidation during or after alteration to vermiculite. Almost all phlogopites and biotites contain some Fe^{3+} , and some contain considerable Fe^{3+} . Only one analysis, no. 25, Table 1A, yielded a formula,

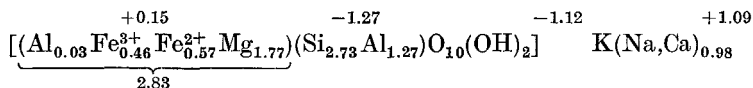


with enough Fe^{3+} to have furnished the positive charges necessary to compensate for those lost with K, as postulated by Roy and Romo (1957, p. 607). However, if the oxidation of iron had taken place concurrently with the leaching of the K, the octahedral layer charge should have been about $+1.00$, the layer unit should have been neutral, and there should have been no interlayer cations. The fact that the octahedral charge is only $+0.51$ indicates that this vermiculite was formed from parent material that already

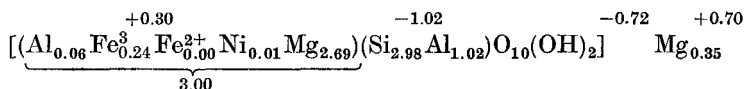
contained considerable trivalent iron, as well as considerable bivalent iron, as in the following formula for the layer unit,



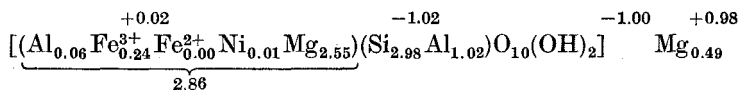
which is comparable in Fe^{3+} and Fe^{2+} content with the formula for analysis no. 35a (Foster, 1960, Table 11, p. 41).



The low layer unit charges and correspondingly low interlayer charges in some of the vermiculite formulas may also be due to the allocation of too much Mg to the octahedral layer. The method used in allocating Mg between the octahedral group and interlayer positions in the absence of cation exchange data results in a maximum of octahedral cations and a maximum octahedral charge, with, consequently, minimum layer unit and interlayer charges. If, for example, in the following formula for analysis no. 8, Table 1A,



Mg is apportioned differently, with less to the octahedral group and more to interlayer positions, layer unit and interlayer charges of about -1.00 and $+1.00$ can be obtained:



Whether the low layer and interlayer charges in the formulas for some of these vermiculites are due predominantly to oxidation of bivalent iron or to erroneous distribution of Mg between octahedral and interlayer positions can be decided only by determination of the exchangeable cations. In the formulas for nos. 13 and 21, Table 1A, used to illustrate the effect of Fe^{3+} on the layer unit and interlayer charges, cation exchange data were available upon which to base allotment of the Mg cations. The low layer unit and interlayer charges in these formulas therefore must be due to oxidation of bivalent iron. For most of the other formulas, cation exchange data are not available, and consequently the reason for the low charge values is unresolved.

CATION EXCHANGE CAPACITY

A comparison of positive interlayer charges with determined cation exchange capacities shows that a simple empirical relation exists between them. This is illustrated in Table 3, which shows that if the positive charges carried by the interlayer cations, as reported by Barshad (1948, p. 674) on some of Gruner's samples, is multiplied by 200, the resultant figure is close

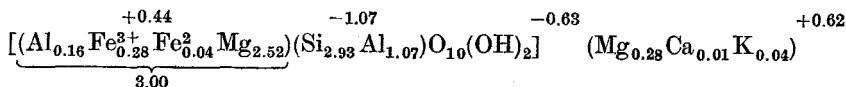
TABLE 3.—RELATION BETWEEN INTERLAYER CATIONIC CHARGE AND CATION EXCHANGE CAPACITY

Sample number (Gruner, 1934)	Interlayered cations			Interlayer charge	Factor	Interlayered meq/100 g air-dry basis	
	Mg	Ca	Σ			Calc.	Detnd.
	Formula positions						
2	0.153	0.171	0.324	+0.648	200	129.6	133.1
3	0.360	—	0.360	+0.720	200	144.0	148.8
4	0.276	0.036	0.312	+0.624	200	124.8	130.5
5	0.218	0.005	0.223	+0.446	200	89.2	93.4
8	0.271	—	0.271	+0.542	200	108.4	112.0

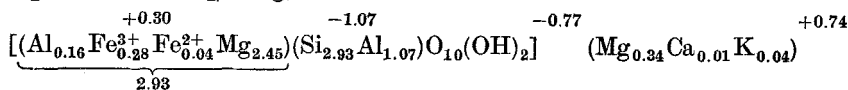
to Barshad's values for the cation exchange capacities for the same samples. This fortuitous relation permits the estimation of cation exchange capacity from the amount of interlayer charge carried by the exchangeable cations.

Applying this calculation to the formulas calculated from the analyses in Table 1, the estimated cation exchange capacities of these vermiculites vary from about 80 to a little more than 200 meq/100 g, as they vary in interlayer charge from 0.40 to slightly more than 1.00. As has already been pointed out, however, the layer unit and interlayer charges in some of the formulas may be erroneous because the manner of distributing Mg between octahedral and interlayer positions tends to produce minimum layer unit and interlayer charges. Consequently cation exchange capacity values estimated from such charges would also represent minimum values. Only in formulas in which the interlayer charge is close to the maximum is it probable that the distribution of Mg is approximately correct. For example, if in calculating the formula for the white Llano vermiculite, no. 3, Table 1A, the Mg is distributed in the manner herein described, the interlayer charge, +0.97, multiplied by 200, gives a figure, 194, which is very close to the reported cation exchange capacity, 195–200 (personal communication, R. Rowland).

The error that may be introduced by assignment of all the Mg to the octahedral group, or enough of it to make a total of 3.00 positions occupied, is illustrated by formulas calculated for analysis no. 13, Table 1A, for which cation exchange data are available. Distribution of Mg in the usual manner yields the following formula:



whereas if the Mg is allotted on the basis of the cation exchange capacity reported, 145 meq/100 g, the formula is revised as below:



Considering the interlayer K as non-exchangeable, the sum of the charges on the interlayer Mg and Ca is +0.72, which, multiplied by 200, yields 144 as the estimated cation exchange capacity.

Unfortunately, papers that report analyses of vermiculite do not usually report cation exchange data, and papers that report cation exchange data do not usually publish analyses of the material studied. In making use of or referring to any analyses, some authors use or refer to analyses made, in some instances, as much as 75 years ago of material from the same locality, although it is well known that samples from the same locality may differ greatly in composition. As a result, data by which exchangeable cation charge and cation exchange capacity may be correlated are scarce. The empirical relation herein mentioned, although subject to error because of incorrect allotment of Mg, does permit at least an estimation of minimum exchange capacity if only an analysis is available.

SUMMARY AND CONCLUSIONS

Most of the formulas calculated from analyses of vermiculites and hydrobiotites resembled those of phlogopites in composition except for a slightly higher proportion of trivalent octahedral cations. The rest of the formulas were similar to those of magnesian biotites, but also showed a considerably higher proportion of octahedral trivalent cations.

The higher proportion of octahedral trivalent cations in phlogopites and hydrobiotites may be attributed to the greater proportion of trivalent iron, whereas in phlogopites and vermiculites the greater proportion of iron is generally bivalent. The fact that the $\text{FeO}:\text{Fe}_2\text{O}_3$ relation in hydrobiotites is much the same as in vermiculites suggests that oxidation took place prior to or during the early part of the vermiculitization process.

Only a few vermiculites and hydrobiotites had layer unit charges and interlayer charges comparable to those of phlogopites and magnesian biotites. The lower layer unit and interlayer charges found in most vermiculites and hydrobiotites may be attributed to the fact that most of the iron is trivalent. The additional positive charges resulting from oxidation of iron increase the octahedral charge and hence decrease the layer unit and interlayer charges. In most of the formulas the number of additional positive charges that can be attributed to oxidation of iron is sufficient to make up for the deficiency in the layer unit and interlayer charges. On the other hand, they are not sufficient to have compensated for the loss of K charges, except in one vermiculite formula. However, the charge relations in this formula indicate that only about half of the octahedral Fe^{3+} contributed to the octahedral charge, indicating that the rest must have been present as Fe^{3+} in the parent mineral.

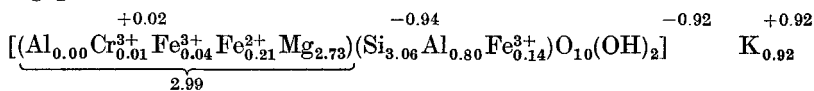
In some of the formulas the low layer unit and interlayer charges may also be at least partly due to the manner in which Mg was distributed between octahedral positions. First filling the octahedral positions before allotting

any Mg to the interlayer positions results in a maximum of octahedral positions and hence of octahedral positive charge and a minimum of layer unit and interlayer charges. In many vermiculites and hydrobiotites, as in the trioctahedral micas, it is probable that octahedral occupancy is deficient, so that such an allotment of Mg is erroneous and more Mg should have been allotted to the interlayer, resulting in higher layer unit and interlayer charges.

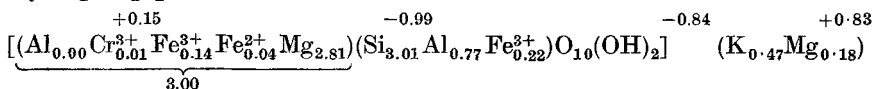
A vermiculite formed from a phlogopite by simple replacement of K by Mg, and in which there has been no oxidation of iron, should have layer unit and interlayer charges comparable with those of phlogopite, which is close to 1.00 in a half-cell formula. Such a vermiculite would have a cation exchange of about 200 meq/100 g. The considerably lower interlayer charges in the formulas calculated for vermiculites, due to oxidation of iron or erroneous allotment of Mg, or both, indicate considerably lower cation exchange capacities, one estimated as low as 80 meq/100 g. In some of the hydromicas the cation exchange capacity is even lower, particularly in those containing much K.

All the vermiculites had layer unit and interlayer charges, and hence cation exchange capacity, which they would not have had if they had been formed from trioctahedral mica by replacement of K ions by H₂O molecules, with accompanying oxidation of Fe²⁺ to Fe³⁺. All but one of them are too low in Fe³⁺ to have furnished enough positive charges to have compensated for those lost with K. The composition, charge relations and cation exchange capacity of these vermiculites can be best interpreted as derived from phlogopite or magnesian biotite by replacement of K by Mg, with, in some, oxidation of some of the bivalent iron, which has decreased the layer unit and interlayer charges, and hence the cation exchange capacity. Such a vermiculitization process is nicely illustrated by the following structural formulas calculated from analyses of contiguous samples of phlogopite, hydrophlogopite, and vermiculite, from Loole Kop, Palabora, South Africa (Gevers, 1949, p. 154):

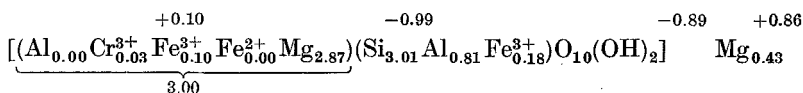
Phlogopite:



Hydrophlogopite:



Vermiculite:



REFERENCES

- Barshad, Isaac (1948) Vermiculite and its relation to biotite as revealed by base exchange reactions, X-ray analyses, differential thermal curves, and water content: *Amer. Min.*, v. 33, pp. 655-678.
- Foster, M. D. (1960) Interpretation of the composition of trioctahedral micas: U.S. Geol. Survey Prof. Paper 354-B, pp. 11-49.
- Gevers, T. W. (1949) Vermiculite at Loolekop, Northeast Transvaal: *Geol. Soc. South Africa Trans.*, v. 51, pp. 133-173.
- Gruner, J. W. (1934) The structures of vermiculites and their collapse by dehydration: *Amer. Min.*, v. 19, pp. 557-575.
- Kanzantzev, V. P. (1934) On the structure and properties of vermiculite: *Mem. Soc. Russe Min.*, ser. 2, v. 63, pp. 464-480.
- Roy, Rustom, and Romo, L. A. (1957) Weathering studies. 1. New data on vermiculite: *J. Geol.*, v. 65, pp. 603-610.
- Walker, G. F. (1950) Trioctahedral minerals in the soil-clays of north-east Scotland: *Min. Mag.*, v. 29, pp. 72-84.