

Chemical Composition of Soil Vermiculite Clays as Related to their Genesis

ISAAC BARSHAD and FAWZY M. KISHK

Department of Soils and Plant Nutrition, University of California
Berkeley, California, U.S.A.

Received August 2, 1969

Abstract. Chemical and mineralogical analyses of the clay fraction of eleven soils containing a large amount of vermiculite clay and representing a wide range of parent materials revealed that two types of vermiculite clays exist: (1) An aluminous type in which Al^{3+} substitutes for Si^{4+} in tetrahedral positions in the same order of magnitude as in the coarse grained vermiculites and micas, and with Al^{3+} as the dominant octahedral ion. (2) A silicious type in which only Si^{4+} occupies the tetrahedral positions, and with Fe^{3+} and Mg^{2+} as the dominant octahedral ions. The aluminous vermiculite clay was found to occur in soils derived from acid igneous rocks and is usually associated with mica, whereas the silicious type was found to occur in soils derived from basic igneous rocks which do not contain mica. Because of this close association of these two types to their parent material, it was concluded that the aluminous vermiculite is a product of alteration of mica whereas the silicious type is a product of synthesis from primary oxides of silica, alumina, iron, and magnesium. Both types of vermiculite clays tend to be dioctahedral in contrast to the trioctahedral nature of the coarse-grained vermiculite.

Introduction

Since the discovery of the relationship between the coarse-grained vermiculite and biotite or the other coarse-grained micas (BARSHAD, 1948; WALKER, 1949; FOSTER, 1963) and the relation between vermiculite and the montmorillonite group of clay minerals (BARSHAD, 1950; WALKER, 1957) many investigators have reported on the basis of X-ray analysis the occurrence in soils of a clay mineral similar to vermiculite.

An intensive investigation by BARSHAD (1966) which correlated the occurrence of vermiculite clay in soils with the factors of soil formation revealed that in any one soil the amount of vermiculite clay relative to the other clay minerals is strongly influenced by the mean annual precipitation under which the soil is developing regardless of its parent material and that under intermediate range of precipitation vermiculite may frequently be the dominant clay mineral. This study also indicated that vermiculite clay present in soils derived from acid igneous rocks is most likely a product of alteration of the mica minerals which occur in them, whereas vermiculite clay present in soils derived from basic igneous rocks is most likely a product of synthesis since mica minerals were essentially absent in their parent material.

The foregoing study of BARSHAD and those of other reporting the occurrence of vermiculite clays in soils was based primarily on X-ray analysis. A study of these reports discloses, however, that with the exception of X-ray data, very little else is known about these clays. It has been assumed generally that the

properties of vermiculite clays are similar to those of coarse-grained vermiculites. This lack of information on vermiculite clays per se is due primarily to the absence in nature of clay deposits of nearly pure vermiculites similar to those found for the montmorillonites and kaolinites. The discovery by BARSHAD of soils containing relatively large amounts of vermiculite clay of different origin offered an opportunity to rectify this situation by studying the following properties of these clays:

- 1) Total chemical composition and the related structural formulas.
- 2) The morphology of the particles as revealed by the electronmicroscope.
- 3) The cation exchange capacity.
- 4) K^+ and NH_4^+ fixation capacities.
- 5) The d(001) X-ray diffraction peak as affected by cation saturation and cation exchange capacity.
- 6) The effect of state of oxidation of crystal structure iron on 3, 4, and 5.

The ideal scheme for accomplishing such an investigation would have been to develop first a technique by which it would be possible to separate and purify the vermiculite clay from the other minerals associated with it in the soil, and then measure the properties of this purified clay. However, preliminary studies of three different techniques of separation, namely, electrophoresis, differential settling rates, and differential chemical dissolution, proved to be unsatisfactory for reasons such as an extremely low yield by the first method, an incomplete separation by the second method, and damaging effects on the clay by the third method. Consequently, measurements of various properties were made on the clay fraction as a whole and some of the properties of the vermiculite clay were then ascertained by calculations and deductions. To make such calculations it was necessary to determine the mineralogical composition of the samples by all the available techniques as devised by BARSHAD (1965) and by ALEXIADES and JACKSON (1966).

The chemical composition of the coarse-grained vermiculite species which occur naturally either as a hydrothermal product, as prepared in the laboratories by replacement of K^+ with Mg^{2+} by cation exchange procedures, or as altered coarse-grained particles in soils exhibit a range in composition very similar to that of the naturally occurring micas (BARSHAD, 1948; WALKER, 1951 and 1961; FOSTER, 1963; COOK and RICH, 1962; BOETTCHER, 1966). These vermiculites contain Al^{3+} in tetrahedral position in the same range of substitution for Si^{4+} as in micas, namely, from 1.0 to 1.4 in every 4 tetrahedra. The number of ions in octahedral position may range between 2 and 3. Among the pure hydrothermal products the number of ions in octahedral positions tends to be 3 and Mg^{2+} is dominant. When iron is present it tends, as a rule, to be in the Fe^{3+} state (BOETTCHER, 1966). The total number of cations in the interlayer position can vary from 0.6 to 1.0 per half unit cell. In the course of „vermiculitization“ of micas, the primary change of importance is a replacement of K^+ with Mg^{2+} or Ca^{2+} or both (BARSHAD, 1948). It has been suggested by BARSHAD (1955) and FOSTER (1963) that in mica species containing Fe^{2+} iron, vermiculitization may be accompanied by oxidation of Fe^{2+} to Fe^{3+} and, consequently, by a reduction in the number of interlayer cations and/or in the octahedral ions. The kind of changes which actually may take place can only be detected by chemical analysis.

Materials and Methods

Materials

Eleven soils high in vermiculite clay content and representing a wide range of parent materials were selected for this study. Five soils — Taiwan, Josephine, Melbourne, Shaver, and Masterson — were derived from sedimentary, acid igneous or metamorphic rocks which contained mica.

Four soils — Aiken, Sweeney, Auburn, and Boomer — were derived from basic igneous rocks or in their metamorphised state (greenstone) which did not contain mica.

Two soils — Neuns and Yorkville — are thought to represent an intermediate group between the above mentioned two groups of soils. They were derived from metamorphized basic igneous rocks which contained chlorite and mica.

The source and description of these soils are given in Table 1. All but the Taiwan, Aiken, Sweeney, and Auburn soils samples were obtained from the official soil survey collection of the University of California at Berkeley. The Taiwan, Aiken, Sweeney, and Auburn samples were obtained from BARSHAD'S collection.

Table 1. *Soils containing vermiculite clays*

Sam- ple No.	Soil series and Reference No.	Great soil group	Location	Parent material	Clay ($< 2 \mu$) content	pH of soil	Mode of formation of vermiculite clay
1	Taiwan 11A	lateritic red earth	Eastern Taiwan, China	fine grain schist	20%	5.7	alteration of mica
2	Josephine 62-12-24-4	gray brown podzolic	Humboldt Co., California	sandstone and shale	65%	5.4	alteration of mica
3	Melbourne 61-12-31-5	brown podzolic	Humboldt Co., California	sandstone and shale	42%	5.2	alteration of mica
4	Shaver 59-10-18-1	podzolic	Fresno Sierra, California	quartz diorite	24%	6.6	alteration of mica
5	Masterson 58-52-22-3	podzolic	Tehama Co., California	mica schist	20%	5.3	alteration of mica
6	Neuns 58-52-14-3	podzolic	Tehama Co., California	greenstone	18%	6.4	alteration and synthesis
7	Yorkville 54-12-1-3	prairie	Humboldt Co., California	chloritic greenstone	35%	6.0	alteration and synthesis
8	Aiken 13B	red podzolic	Lytonville, California	greenstone	30%	6.0	synthesis
9	Sweeney 18-24	prairie	San Mateo Co. California	basalt	40%	6.4	synthesis
10	Auburne 0-8	non calcic brown	Merced Co., California	greenstone	40%	6.0	synthesis
11	Boomer 58-52-26-7	brown forest	Tehama Co., California	basalt	30%	5.7	synthesis

Methods

Since the primary objective of the present study was to determine the chemical composition of the vermiculite clays occurring in soils without extracting a pure vermiculite clay fraction, it was necessary to determine quantitatively the mineralogical composition of the whole clay fraction. These methods are described by BARSHAD (1965) and by ALEXIADIS and JACKSON (1966).

The operational steps involved in these methods were as follows:

(1) Extraction of the $< 2 \mu$ clay fraction of the soil and preparing it in a sodium-saturated state, freed of organic matter, air dried at room temperature, ground to pass a 140 mesh screen and stored in air-tight vials. This material was the „stock“ for the following quantitative analyses: (a) total chemical analysis, (b) differential thermal analysis, (c) thermogravimetric analysis, (d) free oxides analysis, and (e) cation-exchange capacity measurements of the „stock“ samples before and after a treatment for removal of adsorbed „fixed“ complex aluminium ions.

(2) Mineral identification was carried out by X-ray diffraction by the method of Barshad (1960a).

To facilitate the determination of the quantitative mineralogical composition of the samples by BARSHAD'S method (1965) the analyses were converted from an air dry basis to an ignition weight basis and are reported in Tables 2, 3, and 4. On the basis of these analyses and with the quantitative analysis for kaolinite, halloysite, and gibbsite by the differential thermal method (BARSHAD, 1965) it was then possible to ascertain the mineralogical composition of the samples as reported in Table 5.

The „extra crystal structure water“ reported in Table 3 was equated to the increase in the cation exchange capacity upon the removal of the „fixed“ adsorbed aluminium ions. This „extra water“ is a product of the interchange

Table 2. Chemical analyses of sodium saturated $< 2 \mu$ fractions of soils. In percentages of weight of clay after ignition)

	1	2	3	4	5	6	7	8	9	10	11
SiO ₂	50.89	44.92	46.45	42.60	44.30	48.50	48.22	45.99	50.23	56.40	48.50
Al ₂ O ₃	32.19	36.28	33.95	40.50	32.10	20.73	18.82	18.75	11.10	20.40	21.40
Fe ₂ O ₃	10.01	14.36	13.39	8.83	13.16	13.28	11.93	20.30	15.73	14.49	17.75
TiO ₂	1.64	1.33	1.90	1.73	1.95	1.32	0.65	4.76	2.18	2.20	2.83
MnO	0.57	0.03	0.12	0.54	0.40	0.27	0.19	0.57	0.28	0.07	0.33
CaO	trace	trace	trace	0.95	0.36	3.16	0.49	1.83	3.88	0.09	1.83
MgO	1.58	1.26	1.90	2.25	4.36	9.59	15.40	5.14	12.15	3.40	4.74
K ₂ O	2.53	1.06	1.27	0.92	1.75	1.20	2.39	0.97 ^a	0.57	0.25	0.32
Na ₂ O ^b	—	—	—	—	0.47	0.73	0.32	0.27	1.18	0.50	—
Na ₂ O ^c	0.59	0.74	1.02	1.68	1.15	1.22	1.55	1.42	2.70	2.20	2.30
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

^a 0.51% assigned to K feldspar and 0.46% to mica.

^b Nonexchangeable.

^c Exchangeable Na₂O before treatment with a solution of 0.2 N NaOH + 0.5 NaCl.

Table 3. Free oxides, exchangeable Na_2O , and extra crystal structure H_2O of the sodium saturated $< 2 \mu$ fraction of the soils. (In percentage of weight of clay after ignition)

	1	2	3	4	5	6	7	8	9	10	11
Al_2O_3	2.34	3.65	6.60	8.36	4.20	3.52	2.07	2.12	1.52	—	4.13
SiO_2	7.30	4.26	3.40	—	3.40	3.53	2.29	4.09	—	0.60	4.20
Fe_2O_3	8.22	12.13	11.19	5.22	9.76	6.60	2.96	15.59	10.17	9.26	11.04
TiO_2	—	—	—	—	—	—	—	4.76	2.18	2.20	2.87
MgO	—	—	—	—	—	—	—	—	1.20	—	—
Na_2O^a	1.98	2.29	2.26	2.39	2.08	2.11	1.98	1.98	3.04	2.35	2.45
Na_2O^b	1.87	2.10	2.10	2.19	1.98	1.95	1.74	1.79	2.75	2.20	2.30
H_2O^c	0.38	0.37	0.31	0.28	0.26	0.28	0.19	0.15	0.10	0.04	0.04

^a Exchangeable Na_2O after treatment with a solution of 0.2 NaOH + 0.5 N NaCl for three hours at 70°C to remove "fixed" aluminium ions.

^b Exchangeable Na_2O contributed by the sum of vermiculite plus mica fraction or vermiculite plus montmorillonite fraction.

^c Extra crystal structure water.

Table 4. Thermogravimetric analyses of sodium saturated $< 2 \mu$ fraction of the soil. (In percentages of weight of clay after ignition)

Sample No.	25 to 200°C	200 to 350°C	350 to 960°C	Sample No.	25 to 200°C	200 to 350°C	350 to 960°C
1	6.51	3.00	6.68	7	5.56	0.96	7.02
2	6.85	5.43	6.77	8	6.06	1.86	5.95
3	8.40	4.28	5.87	9	8.21	1.25	4.79
4	5.67	4.23	7.25	10	10.32	1.14	7.36
5	5.81	2.15	6.99	11	6.50	1.67	6.97
6	5.33	1.15	6.87				

Table 5. Mineralogical composition (mode) of $< 2 \mu$ fraction of soils containing vermiculite clays. (In percentages of weight of clay after ignition)

	1	2	3	4	5	6	7	8	9	10	11
Vermiculite	30.4	36.1	36.9	36.3	36.9	30.7	30.0	34.2	30.0	31.0	33.0
Mica	25.3	10.6	12.7	9.2	17.5	12.0	23.9	5.0	—	2.5	—
Montmorillonite	—	—	—	—	—	—	—	—	23.3	15.0	4.2
Chlorite	—	—	—	—	—	12.0	29.2	—	—	—	—
Halloysite	—	25.6	18.3	28.0	—	—	—	21.4	—	30.0	29.6
Kaolinite	23.0	—	—	—	18.8	10.8	—	—	—	—	—
Gibbsite	—	4.4	5.4	5.0	—	—	—	—	—	—	—
Quartz	5.0	5.0	7.0	4.0	3.5	—	5.0	—	—	5.0	—
Feldspar ^a	—	—	—	4.7	5.8	21.8	5.2	14.1	32.6	4.3	10.9
Free oxides ^b	17.0	19.5	20.6	13.5	17.5	13.1	7.0	26.6	15.1	12.1	22.2
Total	101.6	101.7	101.5	100.8	99.9	101.0	100.6	101.3	101.0	99.9	99.9
^a An				4.7	1.8	15.6	2.5	9.1	19.2	—	—
Ab				—	4.0	6.2	2.7	2.3	10.0	4.3	9.0
Or				—	—	—	—	2.8	3.4	—	1.9

^b See Table 3.

reaction — the reaction which causes the soil to become unsaturated (BARSHAD, 1960b). Its amount should be known to enable an accurate calculation of the structural formulas. The reason for this will be discussed in the appendix.

By subtracting the sum of the chemical constituents belonging to kaolinite, halloysite, gibbsite, the feldspars, the amorphous constituents and oxides reported in Table 3 from the total chemical analyses of the samples, the remaining elements were then allocated to vermiculite and mica, or vermiculite, mica, and chlorite, or to vermiculite and montmorillonite. By adding to these constituents the appropriate amounts of exchangeable Na_2O and "the extra structure water" as reported in Table 3 and recalculating the quantities on a 100 per cent basis, we obtained the chemical analyses as reported in Tables 6, 7, and 8. A method similar

Table 6. *Chemical analyses of the sodium saturated vermiculite clays containing mica. (In percentages of weight of clay after ignition)*

	1	2	3	4	5
SiO_2	46.55	46.85	52.92	47.10	42.46
Al_2O_3	34.20	35.27	27.30	27.50	31.90
Fe_2O_3	3.33	4.77	4.44	7.92	6.08
TiO_2	3.05	2.85	3.83	3.83	3.49
MnO	1.06	—	0.24	1.25	0.72
MgO	2.94	2.70	3.83	4.94	7.80
K_2O	4.71	2.27	2.56	2.00	3.13
Na_2O	3.46	4.50	4.23	4.81	3.55
H_2O^a	0.70	0.79	0.65	0.63	0.86
Total	100.00	100.00	100.00	100.00	100.00
Vermiculite	52.9	77.3	74.4	80.0	68.7
Mica	47.1	22.7	25.6	20.0	31.3

^a Extra crystal structure water.

Table 7. *Chemical analyses of the sodium saturated vermiculite clays containing mica and/or chlorite. (In percentages of weight of clay after ignition)*

	6	7	7	7
SiO_2	57.60	60.74	53.85	45.75
Al_2O_3	4.74	17.12	13.72	18.50
Fe_2O_3	10.75	12.60	7.28	10.80
TiO_2	3.05	—	1.21	0.78
MnO	0.07	—	—	0.23
MgO	15.75	4.84	15.92	18.52
K_2O	2.80	—	4.44	2.88
Na_2O	4.57	4.70	3.23	2.31
H_2O^a	0.65	—	0.35	0.23
Total	100.00	100.00	100.00	100.00
Vermiculite	72.00	100.00	55.6	41.5
Mica	28.0	—	44.4	28.8
Chlorite	—	—	—	29.3

^a Extra crystal structure water.

Table 8. *Chemical analyses of the sodium saturated vermiculite clays containing montmorillonite. (In percentages of weight of clay after ignition)*

	8	9	10	11
SiO ₂	64.10	63.75	66.70	62.20
Al ₂ O ₃	5.30	—	12.04	—
Fe ₂ O ₃	10.12	9.95	9.04	18.20
MnO	1.67	0.57	0.15	0.83
MgO	13.60	20.35	7.38	12.70
Na ₂ O	5.21	5.38	4.69	6.07
Total	100.00	100.00	100.00	100.00
Vermiculite	100.0	56.4	67.4	89.0
Montmorillonite	—	43.6	32.6	11.0

to this one for ascertaining the chemical composition of a clay mineral in the presence of others was described in detail by JACKSON and MACKENZIE (1964) and used previously by SAWHNEY and JACKSON (1958) to determine the chemical composition of soil montmorillonites.

The structural formulas for the samples were then calculated on the basis of 10 oxygen and 2 hydroxyl ions, for the vermiculite together with the accessory mineral, and for each mineral separately by a method described in the appendix. The results are reported in Tables 9, 10, and 11.

Discussion

I. Chemical Composition and Structural Formulas

An examination of the data of the chemical composition of the clays as expressed by percentage composition or by the structural formulas (Table 2 and Tables 6 to 11) reveals that even without any reference to the mineralogical composition, two distinct clay mineral species appear to be represented by these analyses — those which are high in Al₂O₃ (samples 1 to 5) and those which are low in Al₂O₃ (samples 6, 8, 9, 10 and 11). When corrections were applied in accordance with the mineralogical composition of the samples this difference becomes even more exaggerated. Therefore, in spite of any inaccurate or wrong assumptions which might have been made in calculating the chemical composition and structural formulas of the clays which are dominantly vermiculite, it may be concluded that two distinct species of vermiculite exist. The differences between the two species are noted most distinctly by the structural formulas. They are as follows:

(1) Those in which there is at least one aluminium ion in four tetrahedral positions and those in which there is none, that is, only Si⁴⁺ is present. Thus, with respect to the tetrahedral composition there is no doubt that the former samples are similar in composition to the coarse-grained vermiculites previously reported by several authors (BARSHAD, 1948; FOSTER, 1963; WALKER, 1951) whereas the latter samples are entirely different from any previously reported vermiculites.

Table 9. Structural formulas (on a basis of 10 oxygens and 2 hydroxyls) for sodium saturation vermiculite clays associated with mica

No.	Mode vermi- cullite	Tetrahedral coordination					Octahedral coordination					Interlayered coordination					
		Si	Al	Σ	net ^a charge	Al	Fe ³⁺	Ti	Mg	Mn	H	Σ	net ^b charge	Na	K	Σ	meq ^c
1	53	2.90	1.10	4.0	-1.10	1.44	0.16	0.14	0.27	0.05	0.30	2.36	+0.30	0.43	0.37	0.80	212
	100	2.90	1.10	4.0	-1.10								+0.49	0.61	—	0.61	166
	—	2.90	1.10	4.0	-1.10								+0.10	0.20	0.80	1.00	262
2	77	2.87	1.13	4.0	-1.13	1.47	0.21	0.13	0.25	—	0.34	2.40	+0.40	0.55	0.18	0.73	194
	100	2.87	1.13	4.0	-1.13								+0.49	0.64	—	0.64	173
	—	2.87	1.13	4.0	-1.13								+0.13	0.20	0.80	1.00	263
3	75	3.24	0.76	4.0	-0.76	1.24	0.20	0.18	0.35	0.02	0.25	2.24	+0.03	0.52	0.21	0.73	181
	100	3.24	0.76	4.0	-0.76								+0.12	0.64	—	0.64	166
	—	3.24	0.76	4.0	-0.76								-0.24	0.20	0.80	0.80	262
4	80	2.89	1.11	4.0	-1.11	0.93	0.44	0.24	0.46	0.07	0.26	2.40	+0.39	0.57	0.15	0.72	198
	100	2.89	1.11	4.0	-1.11								+0.44	0.67	—	0.67	182
	—	2.89	1.11	4.0	-1.11								+0.11	0.20	0.80	1.00	264
5	69	2.69	1.31	4.0	-1.31	1.12	0.29	0.16	0.75	0.03	0.19	2.65	+0.62	0.44	0.25	0.69	181
	100	2.69	1.31	4.0	-1.31								+0.73	0.60	—	0.60	144
	—	2.69	1.31	4.0	-1.31								+0.33	0.20	0.80	1.00	262

^a Charge difference between 16 and the sum of the charges of the cations.

^b Charge difference between 6 and the sum of the charges of the cations.

^c Milliequivalents per 100 g ignited weight basis.

Table 10. *Structural formulas (on a basis of 10 oxygens and 2 hydroxyls) for sodium saturated vermiculite clays associated with mica and chlorite*

No.	Mode	Tetrahedral coordination					Octahedral coordination					Interlayered coordination				
		Si	Al	Σ	net ^a charge	Al	Fe ³⁺	Ti	Mg	H	Σ	net ^b charge	Na	K	Σ	meq ^c
6	vermiculite	3.82	0.18	4.0	-0.18	0.20	0.55	0.15	1.11	0.27	2.28	-0.66	0.60	0.24	0.84	207
	—	3.82	0.18	4.0	-0.18	—	—	—	—	—	—	-0.64	0.82	—	0.82	185
	100	3.82	0.18	4.0	-0.18	—	—	—	—	—	—	-0.82	0.20	0.80	1.00	263
7 ^d	—	3.15	0.85	4.0	-0.85	0.77	0.55	0.04	1.87	0.15	3.38	+0.24	0.29	0.32	0.61	136
	56	3.40	0.60	4.0	-0.60	0.43	0.36	0.05	1.52	0.21	2.57	-0.18	0.42	0.36	0.78	199
	100	3.40	0.60	4.0	-0.60	—	—	—	—	—	—	+0.02	0.58	—	0.58	148
7	—	3.40	0.60	4.0	-0.60	1.01	0.58	—	0.43	—	2.02	-0.40	0.20	0.80	1.00	263
	100	3.78	0.22	4.0	-0.22	—	—	—	—	—	—	-0.37	0.59	—	0.59	152

^a Charge difference between 16 and the sum of charges of the cations. ^b Charge difference between 6 and the sum of charges of the cations.

^c Milliequivalents per 100 g on ignited weight basis. ^d On the basis of 25.35 negative charges (see appendix).

Table 11. *Structural formulas (on a basis of 10 oxygens and 2 hydroxyls) for sodium saturated vermiculite clays associated with montmorillonite*

No.	Mode	Tetrahedral coordination				Octahedral coordination					Interlayered		
		Si	Σ	net ^a charge	Al	Fe ²⁺	Mg	Mn	H	Σ	net ^b charge	coordination Na	meq ^c
8	vermiculite	4.0	4.0	0.0	0.33	0.49	1.26	0.08	0.19	2.22	-0.68	0.68	168
	—	4.0	4.0	0.0	—	0.47	1.91	0.02	0.08	2.44	-0.65	0.65	174
	100	4.0	4.0	0.0	—	0.46	1.88	0.02	0.08	2.36	-0.82	0.82	207
10	—	4.0	4.0	0.0	—	0.49	2.02	0.02	0.08	2.53	-0.45	0.45	130
	68	4.0	4.0	0.0	0.88	0.42	0.66	0.08	0.04	2.06	-0.58	0.58	151
	100	4.0	4.0	0.0	0.88	0.41	0.67	0.08	0.04	2.04	-0.63	0.63	161
11	—	4.0	4.0	0.0	0.90	0.42	0.69	0.08	0.04	2.09	-0.50	0.50	130
	89	4.0	4.0	0.0	—	0.90	1.22	0.03	0.04	2.17	-0.76	0.76	196
	100	4.0	4.0	0.0	—	0.89	1.23	0.03	0.04	2.15	-0.81	0.81	204
—	100	4.0	4.0	0.0	—	0.94	1.30	0.03	0.04	2.27	-0.52	0.52	130

^a Charge difference between 16 and the sum of the charges of the cations. ^b Charge difference between 6 and the sum of the charges of the cations.

^c Milliequivalents per 100 g ignited weight basis.

The vermiculite in the two samples in which chlorite and mica are present, particularly in Yorkville, appear to be intermediate in their tetrahedral composition. This could mean that the vermiculite is either a mixture of the two varieties or because of the difficulty of calculating the chemical composition of the vermiculite in these samples due to the presence of relatively large amounts of mica and chlorite, the average composition of the mixture does not reflect the composition of the vermiculite. If we assume that the vermiculite in these samples is devoid of tetrahedral Al^{3+} and proceed to calculate how much Al^{3+} is present in the tetrahedral positions of the mica or the average for the mica and chlorite we find that it is in the range of values which are normally found in these minerals. The results obtained are as follows:

Neuns Mica

$$Na_{0.2}K_{0.8}(Si_{3.40}Al_{0.60})^{-0.60}(AlFeMgTiH)^{-0.40}$$

Neuns Vermiculite

$$Na_{0.82}(Si_4)(AlFeMgTiH)^{-0.82}$$

Yorkville Mica

$$Na_{0.20}K_{0.80}(Si_{2.64}Al_{1.36})^{-1.36}(AlFeMgTiH)^{+0.36}$$

Yorkville Vermiculite

$$Na_{0.584}(Si_4)(AlFeMgTiH)^{-0.584}$$

This result would tend to suggest that this assumption is correct and that only one species of vermiculite is present in these two samples. It is interesting to report, however, that on the basis of X-ray analysis, while this may be true for Neuns, it is not true for Yorkville. The X-ray results clearly show that in the diffraction pattern of the Yorkville there are d(001) spacings which represent interleaving of vermiculite, mica and chlorite and thereby indicating that at least some of the vermiculite was formed through the alteration of either chlorite or mica or both and therefore its tetrahedral composition would contain aluminium.

(2) The interlayer charge of the two types of vermiculites is of similar order of magnitude and it ranges from about 0.60 to 0.8 equivalents per structural formula or from 150 to 200 meq per 100 g. These values are in the same range of values reported for the coarse-grained vermiculites.

(3) The composition of the octahedral layer of the vermiculite clays can again be divided into two groups: those with either no Al^{3+} or very little Al^{3+} but in which Mg^{2+} and Fe^{3+} are dominant, and those in which the Al^{3+} is the dominant cation. These two groups correspond to the division of the vermiculites on the basis of the tetrahedral Al^{3+} , namely, those with no tetrahedral Al^{3+} are also those which have no Al^{3+} in octahedral layer or are low in it, and those with Al^{3+} in tetrahedral position are also those which have Al^{3+} in octahedral positions. The total number of atoms in the octahedral positions for both groups is in the same range of values, namely, between 2.0 and 2.65. If one omits the H^+ from the vermiculites with Al^{3+} they tend to be generally dioctahedral. Therefore it may be stated that the number of cations in the octahedral position of the vermiculite clays differ from most coarse-grained vermiculites in tending to be dioctahedral rather than trioctahedral.

(4) As to the origin of the positive interlayer charge, the vermiculite clays can again be divided into two groups: those in which the charge originates entirely from a deficiency in positive charge in the tetrahedral layer and those in which it originates from a deficiency of a positive charge in the octahedral layer. These two groups obviously correspond to the previously indicated groupings. Furthermore, the vermiculite clays in which the negative charge originates in the tetrahedral layer have also a positive charge in the octahedral layer (in other word, the negative charge in the tetrahedral position is compensated partially by octahedral excess positive charge and partially by the interlayer cations), whereas the other group of vermiculite have a negative octahedral charge.

(5) From the data on potassium and ammonium fixation measurements and X-ray analysis (both will be reported in detail in a separate paper), two other conclusions regarding the structural formulas of vermiculites may be reported here: The first conclusion is that the structural formulas of the vermiculite clays as reported in this study are most likely average formulas of at least two or more species of vermiculite; one species with an interlayer charge large enough to cause K^+ fixation in the wet state and resulting in a contraction of the $d(001)$ spacings from 14 to 10 Å, and another species with a much lower charge in which K^+ "fixation" results only upon drying, so that upon K^+ saturation they do not show any contraction of their crystal lattice in the wet state but do so upon drying. The second conclusion is that the octahedral iron in most of the vermiculite clays studied can readily be reduced or oxidized by chemical means resulting in a definite change in the interlayer charge of the minerals.

II. Similarities to and Differences from Other 2:1 Clay Minerals

(1) *The Wide Range of Chemical Composition.* The results of this study have shown that vermiculite clays possess a unique character among the 2:1 minerals, that is, their wide range of chemical composition. On the one hand some of the species resemble the illites in having large amounts of Al^{3+} in tetrahedral positions and on the other hand some of the species resemble most of the montmorillonites in having only Si^{4+} in tetrahedral positions. Furthermore, on the basis of the octahedral composition, they seem to resemble a mixture of nontronites, saponites, and montmorillonites. Those vermiculite clay species with only silica in the tetrahedral layer may be considered as an extension to the various montmorillonite species but having a higher interlayer charge, while those vermiculite clay species with Al^{3+} in their tetrahedral layer may be considered as an extension to the various beidellite species but again having a higher interlayer charge.

(2) *The Wide Range of Interlayer Charge.* Another unique feature of these vermiculite clays, particularly when the species in which the Fe^{3+} is reduced to Fe^{2+} are included, is their wide range of interlayer charge. This varies from 0.55 to 1.0 equivalent per structural formula, which is a much wider range than for any other group. This is in agreement with WALKER (1961) and BARSHAD (1960, 1965) who reported a wide range of interlayer charge for vermiculites. However, this result is contrary to the assumption of ALEXIADES and JACKSON (1965) who assigned a small range of values to all vermiculites.

(3) *The Vermiculite Continuum.* It is important to emphasize that the structural formulas calculated in this study represent average formulas for two or more

species of vermiculite of a varying magnitude of layer charge. This conclusion was made on the basis of the data obtained on potassium and ammonium fixation in the wet state and after drying and as related to the interlayer expansion. A varying interlayer charge also imposes a varying composition on the octahedral layer. Thus, if the *relative* ion composition is assumed to be alike for all species, then the higher the interlayer charge the smaller is the number of octahedral ions.

Another interesting result of the discovery of the two distinct types of vermiculite clays is that it offered for the first time the opportunity to verify whether or not the origin for the interlayer charge affects the ability of a clay mineral to "fix" K^+ or NH_4^+ using Barshad's definition of fixation: "the extent to which adsorbed K^+ is not replaceable by NH_4^+ and vice versa". The results of this study will be reported in a separate paper.

(4) *Behavior of the Vermiculite Clays with Regard to their d(001) Spacing.* It was mentioned before that the structural formula given for a vermiculite clay is actually an average formula for more than one species. This conclusion was made on the basis of the K^+ fixation and NH_4^+ fixation data and corresponding X-ray analysis. From the X-ray data it was established that all vermiculite species have an interlayer d(001) spacing in water ranging from 14.5 to 15.0 Å when Na^+ saturated. This common property distinguishes them from all montmorillonites which expand in water to spacings ranging from 100 to 200 Å.

On the basis of interlayer expansion in glycerol in their Na^+ saturated state, the vermiculite clays differ from montmorillonites in the same way as the coarse-grained vermiculites, namely, they expand to a thickness of a single layer of glycerol, whereas montmorillonite expands to a thickness of two layers. In their K^+ saturated forms, however, their interlayer expansion with glycerol varies greatly, depending on the species present. Thus, among the K^+ vermiculite clays when wetted with glycerol from the water wet state some species exhibit a 10 Å while others remain expanded to 14 Å. But if the vermiculite clays are wetted with glycerol from their dehydrated K^+ state *all* the vermiculite species studied remain essentially contracted.

Among the montmorillonite clays some of the K^+ saturated species exhibit a 14 Å d(001) spacing upon expansion in glycerol from the water wet state, a spacing similar to that of vermiculite, but other montmorillonite species do not exhibit such a spacing and instead they exhibit an 18 Å d(001) spacing which does not occur in the vermiculite clays. The K^+ montmorillonite 14 Å spacing contracts to 10 Å upon heating, but it reexpands almost immediately upon rehydration in contrast to the stable 10 Å line obtained by dehydrated K^+ vermiculites.

III. The Occurrence of the Two Types of Vermiculite Clays

It is of interest to point out that all the vermiculite clays in which there is no Al^{3+} in tetrahedral positions occur in soils derived from basic or metamorphised basic igneous rocks, whereas the vermiculite clays in which there is Al^{3+} in tetrahedral positions occur in soils derived from acid igneous rocks or from sedimentary rocks of acid-igneous sediments. The fact that the latter clays are associated with micas and that the degree of isomorphous substitution of Al^{3+} for Si^{4+} is similar to that found in the micas would suggest strongly that the vermiculite

in these samples has altered from mica. In the two samples which are high in mica, the Taiwan and the Masterson samples, the occurrence in their X-ray diagrams of $d(001)$ spacing caused by interleaving of 10 and 14 Å material confirms this conclusion.

The samples without tetrahedral Al^{3+} are believed to be products of synthesis from primary oxides and hydroxides rather than products of alteration from micas or other minerals. Since it is difficult to conceive a mechanism by which minerals like feldspars, pyroxenes, amphiboles and olivines could alter directly to vermiculite it is necessary to conclude that the vermiculites in soils derived from basic igneous rocks are products of synthesis.

The absence of tetrahedral Al^{3+} in these vermiculites confirms BARSHAD's (1955 and 1964) prediction that Al^{3+} should not be present in tetrahedral positions in clay minerals forming in a normal soil environment.

Accordingly, it may be suggested that vermiculite species which have considerably less than 1.0 Al^{3+} in four tetrahedra, as in those species from Yorkville and Neuns, are a mixture of the two forms of the vermiculite clays — synthetic and altered.

IV. Chemical Changes in the Process of Vermiculitization of Micas

If we compare the "average" structural formulas of the samples analyzed, as seen in Table 9, with those of normal formulas of micas, these two differences appear: (1) the interlayer charge is considerably less than 1.0, and therefore, it may be said that there was a considerable loss in charge in this position; (2) for the type of composition that is found in these samples, the number of cations in octahedral positions is less than in fresh micas, and therefore, it may be said that the octahedral positions become empty in the course of weathering. If one assumes that the mica fraction of the "average" sample, that is, the residual mica, has retained the original charge of 1.0 per structural formula, then the loss in charge in the course of vermiculitization is even larger than indicated by the average formula (this change is indicated in the tables) and similarly, the loss in octahedral ions is greater during vermiculitization.

It has been suggested by many investigators (BARSHAD, 1955; FOSTER, 1963; RAMAN and JACKSON, 1966) that for micas containing Fe^{2+} iron, a loss of charge on the interlayer surface can result from the oxidation of Fe^{2+} to Fe^{3+} . In recent years such a change has been confirmed experimentally by several workers (RAMAN and JACKSON, 1966; NEWMAN and BROWN, 1966; BARSHAD and ISMAIL, 1966 — unpublished).

The incorporation of H^+ in the crystal lattice of the vermiculite clays is believed due primarily to the interchange reaction (BARSHAD, 1960b) and is partially responsible for the reduction in the number of metallic cations present in the octahedral positions.

V. The Vermiculite-Montmorillonite Continuum

It may be pointed out that in the vermiculite clays formed in soils derived from basic igneous rocks, the dominant cations in octahedral position are Mg^{2+} and Fe^{3+} and not Al^{3+} and that they are associated with montmorillonite. It is

believed that in these samples the vermiculite and montmorillonite form a continuous series distinguishable only by their cation-exchange capacity. Furthermore, it was found experimentally that some of the montmorillonite species in these samples can be altered to the vermiculite species by reducing the Fe^{3+} to Fe^{2+} as will be discussed in a later paper.

It may be of interest to note that low temperature synthesis of clay minerals in the laboratory was found by several workers (DE KIMPE, GASTUCHE, and BRINDLEY, 1961) to occur much easier and with a higher yield for the magnesium silicates than for the aluminium silicates. This is in agreement with the above observation for natural clays.

Summary

By determining the total chemical and mineralogical composition of eleven soil clays containing large amounts of vermiculite clay, it was possible to ascertain structural formulas of the vermiculite species in these clays.

Two types of structural formulas were discovered: one type in which Al^{3+} substitutes for Si^{4+} in tetrahedral positions in the same order of magnitude as in the mica minerals and another type in which only Si^{4+} occupies the tetrahedral positions as in kaolinite and as in most montmorillonites.

The total interlayer charge is in the same order of magnitude as in the coarse-grained vermiculites ranging from 0.6 to 0.8 per structural formula. In some of the samples it was found possible to increase experimentally the value to 1.0 charge by reducing the octahedral Fe^{3+} to Fe^{2+} iron.

The total octahedral number of ions in both types of vermiculites tends to be nearer to dioctahedral than to trioctahedral. However, in those vermiculites having tetrahedral aluminium, Al^{3+} also tends to be the dominant cation in the octahedral position, whereas in the other type of vermiculite Mg^{2+} tends to be the dominant cation. Cation-exchange and fixation studies together with X-ray analysis indicate that the structural formulas are only "average" formulas representing species of varying amount of interlayer charge and a varying number of octahedral ions.

The vermiculite clay type with tetrahedral Al^{3+} was found to occur in soils derived from acid igneous rocks or in sedimentary rocks from acid igneous sediments and is usually associated with mica clay, whereas the vermiculite clay type which contains only Si^{4+} in tetrahedral positions was found to occur in soils derived from basic igneous rocks. This type may or may not be associated with mica and chlorite depending on whether or not the parent rock contains mica and/or chlorites.

Because of the close association of the two types of vermiculite clay with their parent materials it is believed that the vermiculite type with Al^{3+} in tetrahedral positions is a product of alteration of mica, whereas the vermiculite type with only Si^{4+} in tetrahedral position is believed to be a product of synthesis from primary oxides of silica, alumina, iron, and magnesium.

The process of the alteration of mica to vermiculite is depicted as resulting from the replacement of K^+ with Ca^{2+} , Mg^{2+} , Na^+ and Al^{3+} and oxidation of Fe^{2+} to Fe^{3+} causing loss in the interlayer charge and a loss of octahedral cations.

Associated with vermiculitization is the interchange reaction which further reduces the number of the original metallic octahedral cations by their replacement with H^+ .

Appendix

I. Calculation of the Chemical Composition of Vermiculite

The chemical composition of the vermiculites which are associated with mica was calculated differently from those without mica, and that of vermiculites associated with chlorite was calculated differently from those with or without mica. The calculations were made as follows:

(1) *Samples without Mica or Chlorite* (No. 8 to 11). The SiO_2 content was determined by subtracting from the total SiO_2 the amounts associated with the kaolinite or halloysite, the feldspars, the quartz, and the amount of alkali soluble SiO_2 in excess of a SiO_2/Al_2O_3 ratio of 2.0. The Al_2O_3 content was determined by subtracting from the total Al_2O_3 the amounts associated with kaolinite or halloysite, the feldspars, the gibbsite, if any, and the amount of alkali-soluble Al_2O_3 in excess of SiO_2/Al_2O_3 ratio of 2.0. The nonexchangeable Na_2O and CaO were completely subtracted since they were part of the feldspars. The Fe_2O_3 content was determined by subtracting from the total Fe_2O_3 the free Fe_2O_3 determined directly and also an amount assumed to be associated with all the TiO_2 as in ilmenite ($FeTiO_3$). All of the TiO_2 was subtracted on the assumption that it is present as ilmenite. All of the MgO was assumed to belong to the vermiculite since exchangeable MgO was replaced during sample preparation. The remaining elements were allocated to vermiculite and montmorillonite and expressed on the basis of 100.

(2) *Samples of Vermiculite Containing Mica*. The SiO_2 and Al_2O_3 content for the vermiculite and mica was determined as in (1); the Fe_2O_3 was determined by subtracting only the free Fe_2O_3 . All of the MgO , K_2O and TiO_2 were assigned to the vermiculite and mica; an amount of H_2O (crystal structure water) was added to the other oxides equal to the nonexchangeable aluminium as determined by the increase in the cation-exchange capacity upon treatment with 0.5 N $NaCl + 0.2$ N $NaOH$. (This addition of the crystal structure H_2O was necessary so that the calculation of the structural formula could be made correctly as will be discussed later). The interlayer cation content — as measured by the Na_2O content in vermiculite and the $(Na_2O + K_2O)$ content for the vermiculite and mica — was assumed to equal the amount of exchangeable Na^+ after the removal of "fixed" aluminium rather than the total Na_2O content as determined in the sample which was analyzed for total chemical analysis. The exchangeable Na^+ belonging to the other minerals present in the sample was subtracted from the total exchangeable Na^+ (see Table 3).

(3) *Samples of Vermiculites Associated with Chlorite and Mica* (No. 6 and 7). The chemical composition of vermiculite was calculated by subtracting from the sample as a whole the elemental oxides of a chlorite and a mica having a composition with a ratio of Mg^{2+} to $(Fe^{2+} + Fe^{3+})$ similar to that of the sample as a whole, and the feldspars, quartz, and free oxides as indicated previously. To the elemental oxides thus assigned to the vermiculite, an amount

of exchangeable Na_2O was added which was equal to the cation-exchange capacity of the vermiculite after the "fixed" adsorbed exchangeable aluminium was removed. The crystal structure water equal to the degree of unsaturation as determined by the increase in cation-exchange capacity after the removal of "fixed" aluminium is also added to the other oxides.

II. Calculation of the Structural Formula of Vermiculite

General Consideration. To calculate the structural formula for vermiculite clay, it is necessary to assume that the total negative charge for the minimum unit cell is 22 — which is equal to 10 O^- and 2 OH^- . Because of the difficulty of determining experimentally the exact amount of crystal structure water, the chemical analysis is always calculated on the ignition basis assuming that the normal OH^- content is present in the mineral. Since in recent years it has been established that the H^+ adsorbed by the silicate surfaces in the course of weathering disappears from the surface and is replaced by crystal structure Al^{3+} and Mg^{2+} by the interchange reaction (Barshad, 1960 b) and that this H^+ becomes incorporated in the O^- framework and since upon analysis, it is lost as H_2O , it is no longer possible to assume that only 2 OH^- ions are present per minimum unit cell. The amount of OH^- in excess of 2 must be known so that 22 negative charges can be assigned to the structural formula. In the present study it was assumed that this excess OH^- was equal to the degree of base unsaturation as determined by the increase in cation-exchange capacity after removal of adsorbed complex aluminium. Thus, if the increase, for example, is equal to 20 meq per 100 g (on the ignition basis) then an amount of 10 millimole of H_2O is added to the other elemental oxides. Preliminary calculations of the Structural formulas of the samples associated with montmorillonite indicated that the amount of Si^{4+} and Al^{3+} per 22 negative charges was insufficient to fill the 4 required tetrahedra in a structural formula. To fill 4 tetrahedra it would have been necessary to assign Fe^{3+} or Ti^{4+} to that position. Since these ions are too large to be present in tetrahedral positions, it was decided that in view of the chemistry of Ti^{4+} there is little likelihood it would become incorporated in the crystal structure of vermiculite in the course of its formation and that the Ti^{4+} which is present in the sample is ilmenite (TiO_2FeO). Therefore, for the purpose of calculating the structural formula, all the TiO_2 was eliminated from the analysis together with enough Fe_2O_3 as present in ilmenite. Jackson and Mackenzie (1964) concur with this conclusion. The elements allocated to vermiculite were the SiO_2 , Al_2O_3 , Fe_2O_3 , MgO and Na_2O .

Structural Formulas. Summarizing the foregoing discussion it is seen that the data needed to calculate the structural formula are: total chemical composition of the sample on an ignition weight basis; mineralogical composition of sample on an ignition weight basis which includes "free" Fe_2O_3 , Al_2O_3 and SiO_2 ; the cation-exchange capacity of the Na-saturated sample as analyzed and the C.E.C. after the removal of fixed aluminium; a list of the chemical composition of the feldspars, kaolinite, halloysite and gibbsite (Barshad, 1965), chlorite, and micas (Deer, Howie and Zussman, 1965).

Samples of Vermiculite Associated with Mica. Because of the uncertainty of assigning a "known" chemical composition to the mica fraction of a clay it was

decided to calculate an "average" formula for the mica and the vermiculite and then distribute the "interlayer" cations and charge between them on the basis that the mica contains the "normal" 1.0 unit charge per 10 O⁻ and 2 OH⁻ and then calculate the interlayer charge for the vermiculite.

The total elemental oxides belonging to the vermiculite and mica are calculated as indicated previously. The total weight of these oxides should equal the percent of vermiculite plus mica as given in the Table 5 — mineralogical composition. For the purpose of calculating the structural formula it is not necessary to convert the amount of the oxides to a 100 per cent mineral (vermiculite + mica) basis. Instead each oxide is divided by its formula weight, multiplied by the number of cation atoms in the formula and then by the number of charges per atom. The total charges of the cations are added and then divided into 22 to obtain the "factore" by which the cation atoms must be multiplied to yield their number in the structural formula. By multiplying the total weight of the oxides by the "factor" one obtains the molecular weight of the clay. The distribution of the cations is made by standard procedures as follows: All the Si⁴⁺ is placed in tetrahedral positions and enough Al³⁺ is added to the position to fill *four* tetrahedra. The remaining Al³⁺ together with all the other cations except K⁺ and Na⁺ are placed in the octahedral position. These should not exceed three. The K⁺ and Na⁺ are placed in the interlayer position. If the calculation were made correctly the charge on the tetrahedral layer should equal the sum of the charges of the octahedral and the interlayer positions. It was not possible to ascertain the variations which may exist in the composition of the tetrahedral and octahedral layers of the vermiculite and mica. If one assumes that the tetrahedral composition of the two is alike, it is obvious that the differences which cause them to have different amounts of interlayer cations must exist in their octahedral composition. The results of the calculations are reported in Table 9.

Samples of Vermiculite Associated with Mica and Chlorite (No. 6 and 7). As indicated previously, one method of calculating the chemical composition and the structural formula of vermiculite is to assume a definite chemical composition for the mica and chlorite and then subtract their elemental oxides from the total sample along with those of the feldspars and free oxides. The results of such a calculation are given in Tables 7 and 10.

If one does not exclude the elemental oxides belonging to the chlorite and mica, it is necessary then to calculate an "average" structural formula for all the three minerals: vermiculite, chlorite and mica. To do so it is necessary to calculate an "average" negative charge for the "mixture" as follows: Since vermiculite and mica both have 22 negative charges in their structural formula one multiplies 22 by their sum as given in Table 5, namely 53.90 for No. 7 and 42.73 for No. 6 and thus obtaining 11.86 and 9.40 respectively. Since the chlorite formula contains 28 negative charges one multiplies 28 by the chlorite content which is 29.18 for No. 7 and 12.0 for No. 6, and thus obtaining 9.17 and 3.36 respectively. The "average" negative charge of the mixture per 100 g of sample is equal to $\frac{21.03}{83.08} \times 100 = 25.35$ for No. 7 and $\frac{12.73}{54.73} \times 100 = 22.90$ for No. 6. The structural formula on this basis for No. 7 is given in Table 10.

Still another method for calculating the structural formula of such samples is to assume as "known" a chemical composition for the chlorite alone and subtract its elemental oxides from the samples and then calculate an average structural formula for vermiculite and mica as was done for the samples in group (1). The results of such a calculation are included in Table 10 for samples No. 6 and 7.

Samples of Vermiculite Associated with no Mica or Chlorite but which May Contain Montmorillonite. This group of samples contain no mica or chlorite [some may contain only a negligible amount of (< 5%) mica]. After subtracting from the total elemental oxides those belonging to minerals other than vermiculite, feldspars, quartz, gibbsite, etc. the "free" oxides and ilmenite, the remaining oxides which belong to the vermiculite are then used to calculate the structural formula directly without recalculating their amounts on a 100 percent basis (their sum should be equal to the per cent vermiculite in the sample). As for the previous samples the Na_2O content corresponding to the total C.E.C. (after the removal of "fixed" aluminium) is used for determining the interlayer charge rather than that found in the directly analyzed sample. The molecular weight of the clay is determined by multiplying the "factor" by the sum of the elemental oxides. The C.E.C. in equivalents per 100 g vermiculite can be calculated by merely dividing the exchangeable Na^+ in moles by the sum of the oxides belonging to the vermiculite and multiplying by 100 or [(weight of Na^+ atoms/Formula weight of the clay) \times 100]. The theoretical crystal structure water in vermiculite can be calculated by dividing 18 (M.W. of H_2O) by the molecular weight of the sample.

Justification for excluding TiO_2 , and amount of Fe^{3+} as found in illminite, is seen in the nature of the structural formulae obtained without this exclusion. Thus for No. 11 it is $(\text{S}_{3.750}\text{Ti}_{0.25})(\text{Fe}_{0.936}\text{Mg}_{1.165}\text{Mn}_{0.025})\text{Na}_{0.71}$ and for No. 9 it is $(\text{Si}_{3.814}\text{Ti}_{0.186})(\text{Fe}_{0.546}\text{Mg}_{0.186}\text{Mn}_{0.02})\text{Na}_{0.63}$. It is necessary to allocate Fe^{3+} or Ti^{4+} to tetrahedral positions to complete four tetrahedra. Such an allocation is unjustifiable since the ionic radii of these two ions are too large to fit into a tetrahedral position. (Ionic radius of $\text{Fe}^{3+} = 0.67 \text{ \AA}$ and $\text{Ti}^{4+} = 0.68 \text{ \AA}$ but the radius of the cavity of the tetrahedral position is only 0.31 \AA .) Three of the samples of this group contain appreciable amounts of montmorillonite associated with vermiculite. To calculate the structural formula in this case it was necessary to obtain an "average" formula for the vermiculite and montmorillonite "mixture" and then distribute the ions between the two minerals to obtain the structural formula of each. To do so, it is necessary to assume that their tetrahedral compositions are alike and that the *relative* content of the octahedral ions is also alike except for the total amount, and that this amount should account for the difference in the interlayer charge. The "average" formula for the mixture is obtained as described before and then to obtain the formula of each mineral separately, the following steps are made: (a) To distribute the interlayer cations between vermiculite and montmorillonite it is assumed that the charge of montmorillonite is equal to 130 meq/100 g [based on the finding that the 18 \AA line of the Na^+ — saturated form changes to 14 \AA upon K^+ saturation (Barshad, 1960a)] and therefore that of the vermiculite can be calculated. For example, in the Auburn sample the sum of interlayer charge of vermiculite and montmorillonite was determined to be 72.0 meq per 46.0 g. Since the sample contains

15 g of montmorillonite with a cation exchange capacity of 130 meq 100 g, the amount of interlayer charge for the montmorillonite is equal to 19.5 meq and therefore 52.5 meq is for the vermiculite. Upon multiplying these quantities by the "factor" one obtains their amount per 22 negative charges, namely, 0.16 and 0.42 equivalent for montmorillonite and vermiculite, respectively, or 0.58 in the average structural formula. This amounts to 0.50 for montmorillonite and 0.63 for vermiculite when calculated on a 100 percent basis (32% mont + 68% vermiculite). (b) The distribution of the octahedral ions between the vermiculite and montmorillonite can be made by assuming that the *relative* composition in the two minerals is alike and therefore the total number must be such that they would account for the difference in the interlayer charge. The steps involved are: (1) To calculate percent of cation charge of each cation in the average formula; thus for Auburn:

Cation charges in octahedron of the average formula	Percent of cation charge in octahedron of the average formula
$\text{Al}^{3+} = 3 \times 0.882 = 2.646$	$\text{Al}^{3+}\% = 48.9$
$\text{Fe}^{3+} = 3 \times 0.416 = 1.248$	$\text{Fe}^{3+}\% = 23.0$
$\text{Mn}^{2+} = 2 \times 0.082 = 0.164$	$\text{Mn}^{2+}\% = 3.0$
$\text{Mg}^{2+} = 2 \times 0.680 = 1.360$	$\text{Mg}^{2+}\% = 25.1$
<u>5.418</u>	<u>100.0</u>

(2) To calculate the positive charge in the octahedral position for the vermiculite and the montmorillonite, thus for Auburn it is $6.000 - 0.623 = 5.377$ for vermiculite and $6.00 - 0.479 = 5.521$ for montmorillonite.

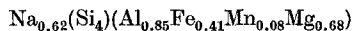
(3) By multiplying the percentages of the cation composition found in (1) by 5.377 one obtains the composition of vermiculite and by 5.521 one obtains the composition of montmorillonite. It is necessary then to divide the atomic charges by the valence of the cation to obtain the composition in terms of atoms. Thus for Auburn:

	<i>Vermiculite</i>		<i>Montmorillonite</i>	
	charges	atoms	charges	atoms
Al^{3+}	2.635	0.878	2.700	0.900
Fe^{3+}	1.230	0.412	1.270	0.423
Mn^{2+}	0.162	0.081	0.166	0.083
Mg^{2+}	1.350	0.675	1.385	0.692
	<u>5.377</u>	<u>2.046</u>	<u>5.521</u>	<u>2.098</u>

Therefore the average formulas, after rounding of the results to hundredths, are:



and for vermiculite



and for montmorillonite



The structural formulas of this group of samples are presented in Table 11.

References

- ALEXIADIS, C. A., JACKSON, M. L.: Quantitative determination of vermiculite in soils. *Soil Sci. Soc. Am. Proc.* **29**, 522—527 (1965).
- Quantitative clay mineralogical analysis of soils and sediments. *Clays Clay Minerals Proc. Natl. Conf.* **14** (1965), 35—52 (1966).
- BARSHAD, I.: Vermiculite and its relation to biotite as revealed by base exchange reactions, X-ray analyses, d. t. a. curves and water content. *Am. Mineralogist* **33**, 655—678 (1948).
- The effect of interlayer cations on the expansion of the mica type of crystal lattice. *Am. Mineralogist* **35**, 225—238 (1950).
- Significance of the presence of exchangeable magnesium ions in acidified clays. *Science* **131**, 988—990 (1960b).
- X-ray analysis of soil colloids by a modified salted paste method. In: *Clays Clay Minerals, Proc. Natl. Conf.* **7** (1959, 350—364) (1960a).
- Chemistry of soil development. In: *Chemistry of the Soil*, ed. by F. E. Bear. New York: Reinhold Publ. 1955, 1964.
- Thermal analysis techniques for mineral identification and mineralogical composition. In: *Methods of Soil Analysis*, ed. by C. A. Black, Monograph No. 9. American Society of Agronomy, Madison, Wisconsin 1965.
- The effect of a variation in precipitation on the nature of clay minerals formation in soils from acid and basic igneous rocks. *Proc. of Int'l Clay Cong. 1966, Jerusalem, Israel*, vol. 1, 167—173. Israel Program for Scientific Translations, Jerusalem 1966.
- BOETTCHER, A. L.: Vermiculite, hydrobiotite and biotite in the Rainy Creek Igneous Complex near Libby, Montana. *Clay Minerals* **6**, 283—296 (1966).
- COOK, M. G., RICH, C. I.: Negative charge of dioctahedral micas as related to weathering. *Clays and Clay Minerals, Proc. Natl. Conf.* **11** (1962), 47—64 (1963).
- DEER, W. A., HOWIE, R. A., ZUSSMAN, J.: *Rock forming minerals*, vol. 3. (Sheet Silicates). New York: John Wiley & Sons 1965.
- DEKIMPE, C., GASTUCHE, M. C., BRINDLEY, G. W.: Ionic Coordination in aluminosilicic gels in relation to clay mineral formation. *Am. Mineralogist* **46**, 1370—1381 (1961).
- FOSTER, M. D.: Interpretations of the composition of vermiculites and hydrobiotites. *Clays and Clay Minerals, Proc. Natl. Conf.* **10** (1961), 70—89 (1963).
- JACKSON, M. L., MACKENZIE, R. C.: Chemical analysis in the quantitative mineralogical examination of clays. In: C. I. RICH and G. W. KUNZE (ed.), *Soil clay mineralogy*, p. 313—330. Chapel Hill: University of North Carolina Press 1964.
- NEWMAN, A. C., BROWN, G. W.: Chemical changes during the alteration of micas. *Clay Minerals* **6**, 297—310 (1966).
- RAMAN, K. V., JACKSON, M. L.: Layer charge relations in clay minerals of micaceous soils and sediments. *Clays and Clay Minerals, Proc. Natl. Conf.* **14** (1965) 53—67 (1966).
- SAWHNEY, B. L., JACKSON, M. L.: Soil montmorillonite formulas. *Soil Sci. Soc. Am. Proc.* **22**, 115—118 (1958).
- WALKER, G. F.: Distinction of vermiculite, chlorite and montmorillonite in clays. *Nature* **164**, 577 (1949).
- Vermiculite minerals. In: *X-ray identification and crystal structure of clay minerals*. 1951, Ch. VII, p. 199—223. (G. W. BRINDLEY, ed.). 1961, Ch. VII, 297—324 (G. BROWN, ed.). London: Mineralogical Society 1951, 1961.
- Differentiation of vermiculites and smectites. *Clay Minerals Bull.* **3**, 154—163 (1957).

Dr. ISAAC BARSHAD
Department of Soils and plant Nutrition
University of California
Berkeley, California, U.S.A.

Dr. FAWZY M. KISKH
Department of Soils
College of Agriculture
University of Alexandria
Alexandria, U.A.R.