AMMONIUM MICA SYNTHESIZED FROM VERMICULITE

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Introduction

The "Action of hydrogen peroxide on weathered mica" was described very recently by Drosdoff and Miles.[1] These investigators noticed that treatment of soil samples with H_2O_2 to destroy organic matter caused the exfoliation of decomposed mica. They ascribed this reaction to the presence of traces of catalytic MnO_2 chiefly, which caused the decomposition of H_2O_2. The liberated oxygen forced the sheets of the mineral apart. They also found that the addition of a few drops of ammonium hydroxide accelerated the reaction considerably. The writer repeated these experiments and extended them to analyzed vermiculites with the idea of introducing between the layers ions which would restore the structure to the original one, which was that of biotite in most cases.

The structures of vermiculite and hydrobiotite (decomposed mica) have been described by the writer.[2] Hendricks and Jefferson[3] have confirmed the correctness of these structures recently. Though their description seems to differ, due to the choice of the *c* axis, it is actually the same, as they have pointed out.[4] They also have shown that the H_2O molecules probably occupy definite positions, and that vermiculite proper may be interstratified with chlorite units which would escape detection in a structure analysis. The present investigation finds strong support for this statement, as will be shown. The writer enjoyed the collaboration of Dr. R. B. Ellestad, who not only carried out the ammonia analyses but also gave much thought and time to the problem. Mr. Lynn Gardiner also assisted the author. The Graduate School of the University of Minnesota generously provided funds.

Experiments

Many experiments were made, of which a limited number will be described. After certain preliminary tests, analyzed specimens of vermiculite were used. These were identical with those described in the structure analysis cited,[5] with one addition. The analyses are repeated here under the same numbers as were used before. Additional information will be found in the paper mentioned. Unfortunately the analyzed

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[1] Drosdoff, M., and Miles, E. F., *Soil Sci.*, **46,** 391–393 (1938).

[2] Gruner, J. W., *Am. Mineral.*, **19,** 557–575 (1934).

[3] Hendricks, S. B., and Jefferson, M. E., *Am. Mineral.*, **23,** 851–862 (1938).

[4] See the last paragraph of their paper.

[5] Gruner, J. W., *op. cit.*

material available was limited in quantity which made an ammonium analysis, for example, of No. 5 (Table 1) impossible.

TABLE 1. ANALYSES OF VERMICULITES BEFORE AND AFTER TREATMENT WITH NH_4OH

	1		4	5	6	V[2]
A. SiO_2	36.12		35.92	36.54	34.92	33.30
TiO_2	0.24				0.60	1.02
Al_2O_3	13.90		10.68	16.96	13.06	14.72
Fe_2O_3	4.24		10.94	2.78	2.74	5.02
FeO	0.68		0.82	0.95	0.54	1.36
NiO	0.28		none	2.32	3.24	2.14
MnO	trace					
MgO	24.84		22.00	19.78	23.92	22.00
CaO	0.18		0.44	0.06	0.24	0.12
K_2O						
Na_2O						
Total H_2O	18.94		19.84	20.40	20.30	19.36
H_2O 110°	(−130°) 8.20		10.50	9.24	9.00	8.56
H_2O 110°–400°	11.6[3]		4.34	3.80	5.00	4.94
H_2O Red heat			5.00	7.36	6.30	5.86
Total	99.42		100.64	99.79	99.56	99.04
B. Spacing of d_{001} before exp.	28.42 Å		28.46	28.38	28.46	28.62
C. Spacing of d_{001} after exp.	20.62		20.43	20.58	20.69	20.51
D. d_{001} after bomb exp.		20.51				
E. Spacing after 48 hours at 300°C.	20.41			20.48		
F. Spacing after 24 hours at 650°C.	18.51			18.49		
Analysis of Alteration Product						
G. NH_4	1.6	2.1	2.4		2.0	2.3
H. H_2O below 300°C.	3.9	1.9	2.4		3.0[1]	2.4
I. Total ignition loss	15.4	13.5	12.3		16.0[1]	13.6
J. Total loss minus NH_4	13.8	11.4	9.9		14.0	11.3
K. Apparent loss of H_2O during experiment	5.1	7.5	9.9		6.4	8.1
L. Indices before exp.		α 1.525 γ 1.545	α 1.532 γ 1.573		α 1.522 γ 1.55	
M. Indices after exp.		α 1.54+ γ 1.57+	α 1.56 α 1.59		α 1.55 γ 1.58	

[1] Only 20 mg. available.

[2] Vermiculite from Webster, N.C., Analysis No. 5; C. S. Ross, E. V. Shannon and F. A. Gonyer: *Econ. Geol.*, **23**, 536 (1928). Also used by Hendricks and Jefferson under #5, *Am. Mineral.*, **23**, 855 (1938).

[3] Loss between room temp. and 300°C.

A small amount (less than 0.2 gram) of material was placed in a beaker and covered with about 5 to 7 cc. of 30% hydrogen peroxide. A few drops of NH_4OH were added. Very soon a vigorous reaction could be observed due to the decomposition of H_2O_2. After some hours exfoliated worm-like aggregates could be seen. After about 10 to 20 hours no more exfoliation was noticeable. Usually the beakers were kept on a warm steam radiator for about 10 per cent of time. Also fresh H_2O_2 and NH_4OH were added each day for 4 days. Then the solutions were decanted and the residues washed three times with distilled water by decantation. Also after filtration they were washed again three times on the filter paper. They were then dried at 50°C.

A number of tests were made for volatile ammonium salts in the residues by heating the treated samples to a temperature of 300°C. for periods varying between 10 to 30 minutes. No appreciable losses could be detected. Three grades of hydrogen peroxide were used. Two of them contained ammonium salts to start with. These did not interfere appreciably. All the experiments of Table 1 were carried out with the purest H_2O_2 obtainable, Merck's "Regent Superoxol," which contained less than 0.001% of "nitrogen compounds as N."

The dried samples were *x*-rayed by the powder method. Unfiltered iron radiation and precision cameras with a radius of 57.3 mm. were used. Though the diagrams are very satisfactory, no attempt is made to reproduce them here as too much detail would be lost in printing the films. It must be pointed out that much similarity exists between certain lines of the powder-diagrams of vermiculites and members of the chlorite group. It is, therefore, possible for appreciable amounts of chlorite to be concealed in vermiculite, especially if interstratification is in almost molecular layers. Some vermiculite lines are very similar to biotite lines, and in the alteration of the mineral to biotite, they might lead to doubtful interpretations. Fortunately the basal reflections of the two minerals are so different that no confusion is possible. Besides, the basal reflections due to the treatment received by the mineral are broader than all the other lines and can be distinguished with ease. In every case, a comparison of the film of the treated material with a film of typical biotite (Mora biotite, Mora, Minnesota[6]), shows their similarity at a glance. Except for the fact that the spacings of the basal planes are slightly greater in the synthetic micas, the structures are unquestionably very similar.

Most of the films show that considerable amounts of the original material are still vermiculite (or possibly chlorite since the two cannot be

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[6] See for example, Gruner, J. W., *Am. Mineral.*, **20,** 701 (1935).

distinguished when present in small amounts). The lines of the unaltered residue are always sharper than the new ones.

One experiment was made at a temperature of 300°C. in a gold-lined bomb of 50 cc. capacity. Powdered vermiculite #1 (0.2 gram), 1 gram $(NH_4)_2CO_3$,[7] and 25 cc. distilled water were put into the bomb, and the space above the solution was filled with CO_2. After four days the results (Table 1) were about the same as in the other experiments conducted at room temperature. Substitution of a concentration of 1:1 ammonium hydroxide instead of a few drops in some experiments produced very similar results. The mineral samples absorbed somewhat less NH_4 under these conditions. Hydrogen peroxide alone exfoliated the vermiculites but did not change their powder diagrams. Blank tests for NH_4 made on the original minerals gave negative results.

Experiments in which hydroxides and salts of potassium and sodium were substituted for NH_4OH did not yield results which were uniform, and in most of these cases mica could not be identified. There were some changes and shifting of lines, but they could not be interpreted with certainty. Mica was produced, however, from vermiculite in a bomb experiment at 300°C. by introducing K ions from a KCl solution, but as this experiment was made in connection with a different problem, it will be reported in another place. Experiments with rubidium and caesium salts are under way at present.

Chemical Considerations

The structural formula of vermiculite is $(OH)_2(Mg,Fe)_3(Al,Si)_4O_{10}\cdot 4H_2O$ as described previously.[8] To become a mica the H_2O molecules between the mica-like layers must be expelled and alkali or NH_4 ions must fill positions between the layers. In this transfer the structure should shrink from about 14 Å thickness per layer to about 10 Å. (A unit cell is two layers high.) It is obvious that the speed and completeness of this reaction depends upon the ease with which the H_2O molecules can leave and the NH_4 ions can enter. This depends largely on the thoroughness with which the hydrogen peroxide can exfoliate the vermiculite. That this exfoliation does not proceed to molecular layer size is evident, among other things from the fact that one still obtains fair powder diagrams.

On the other hand, some specimens, for example, proto-vermiculite, from Magnet Cove, Ark., and nickeliferous vermiculite from Webster, N. C.,[9] exfoliate very little. Neither do they react with NH_4OH to form

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[7] "Baker's analyzed" reagent.

[8] Gruner, J. W., *op. cit.*, p. 574.

[9] See specimens No. 2 and No. 7 respectively. Gruner, J. W., *op. cit.*, p. 558.

mica. Another important factor is the "purity" of the material. If 10 to 20 or more per cent of the biotite layers are interlayered with brucite layers, in other words, are really chlorite in structure, no H_2O molecules are removed nor NH_4 ions introduced in these layers.

Since the NH_4 group is about the size of the K ion (probably slightly larger) the NH_4 mica layer theoretically should be only 10.0 Å thick. If statistically every tenth layer were a chlorite layer the powder diagrams should look about the way they do. In the original vermiculite this chlorite would remain entirely undetected because its unit cell has almost identical dimensions. If every possible alkali position in mica of the composition of Table 1 (disregarding H_2O) were occupied by an NH_4 group, the mica would contain about 4 per cent NH_4. Only about half of the positions seem to be filled according to analyses of row G, Table 1. This discrepancy cannot be explained by the presence of chlorite alone or by only partial alteration, though together they might account for it.

It is noteworthy that the apparent losses of H_2O (Row K, Table 1) are of the same order as the gains in NH_4, as might be expected. The small losses of H_2O (Row H, Table 1) below 300°C. are even more significant. They show that H_2O was removed in considerable amounts from positions in which it was held loosely. Though it is difficult to determine the optical constants on the altered materials, there is a consistent increase in the indices of refraction, noticeable as shown in L and M, Table 1.

A point little understood in this investigation is how charged NH_4 groups can enter between the layers which apparently are neutral. That the groups are charged must be assumed because they are held with great tenacity between the layers. Heating at 300°C. for 48 hours will not expel them (Row E, Table 1). At 650°C. the structure will collapse, however, to talc (Row F) as shown by the spacing of the layers. It is not possible to analyze for ammonia by simply heating the samples in a tube furnace and collecting the gases. Evidently the NH_3 is decomposed under these conditions. The analyses for NH_3 were carried out as described below.[10]

[10] The weighed sample (25 to 50 milligrams) was decomposed by heating in a platinum crucible with a small amount of an HCl-HF mixture. The resulting solution was transferred to a 150 cc. flask, and treated with an excess of NaOH. After distillation, the ammonia content of the distillate was determined in the usual manner, by using Nessler's Reagent, and making colorimetric comparison with standard ammonium chloride solution. Blank determinations were made to correct for any ammonium salts in the reagents used. The decomposition of the sample by HCl-HF mixture may be omitted as equally satisfactory results were obtained by direct treatment with NaOH solution.

There is the possibility that charges exist between the layers of vermiculite, perhaps in the form of hydronium (H_3O) groups. Such an assumption would not necessarily oppose the idea of *two* layers of H_2O molecules between the sheets, as strongly advocated by Hendricks and Jefferson.[11] The following two arguments would be in favor of charges between the layers:

(1). Driving out of half the H_2O does not seem to affect the structure, as may be seen in the powder diagrams.

(2). The spacing of the layers is uniform for all true vermiculites and it has not been possible so far to produce a structure intermediate in spacing between the mineral proper and pyrophyllite to which it collapses when all H_2O is driven out.

In other words, it has not the properties of contraction or expansion which make montmorillonite and nontronite so unique, in spite of apparent great similarity of their layers otherwise.

CONCLUSIONS

Experiments show that NH_4 can enter the structure of vermiculite in such a manner that the mineral becomes an ammonium mica. The replacement of H_2O layers by NH_4 layers is not complete due to the difficulty of access of NH_4 groups between all the layers. Also the probable presence of chlorite units in appreciable amounts between vermiculite units causes apparently incomplete substitution. The introduction of ions of the alkalies Na and K does not seem to produce micas under similar conditions. More work is needed on this phase of the investigation. How charged NH_4 groups can enter apparently neutral layers of vermiculite is not understood. It is suggested that there may exist charges between the layers of vermiculite, possibly in the form of H_3O groups which can be replaced by NH_4 groups.

[11] Hendricks, S. B., and Jefferson, M. E., *Am. Mineral.*, **23**, 863–875 (1938).