

## VERMICULITE AND HYDROBIOTITE

ROBERT F. RUTHRUFF,<sup>1</sup>

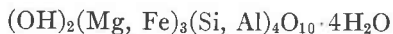
*Chempats Incorporated, Wilmington, Delaware.*

### ABSTRACT

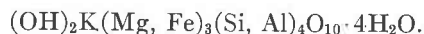
An analysis of hydrobiotite tends to confirm the findings of Gruner<sup>2</sup> that this mineral consists of interstratified layers of vermiculite and biotite. The indications are that the layers of the two minerals are present in a 1:1 ratio although by using somewhat less reasonable assumptions a ratio of 3 vermiculite : 2 biotite is obtained.

On heating with dilute sulfuric acid all oxides, with the exception of silica, are removed from vermiculite, the final silica being obtained in the form of white plates. The complete removal of oxides other than silica from hydrobiotite by similar treatment is much more difficult. Hydrobiotite saturated with concentrated sulfuric acid and then exposed to air over a considerable period, or steamed for a shorter time, exfoliates greatly, a behavior not shown by vermiculite.

While the vermiculites have long been recognized as complex minerals of rather indefinite composition (the sixth edition of *Dana* lists no less than 14 varieties), Gruner<sup>2</sup> was the first to distinguish clearly between true vermiculite,



and hydrobiotite which consists of interstratified layers of true vermiculite and biotite,



Vermiculite and hydrobiotite differ markedly in several respects. Since the present major source of supply (Libby, Montana) of minerals of this type furnishes hydrobiotite and as the differences between vermiculite and hydrobiotite have not been generally recognized,<sup>3</sup> the following observations with respect to these two minerals may be of interest.

A large sample of hydrobiotite (Libby, Montana) was successively quartered and then analyzed, the results being shown in Table 1. For comparison, the average of seven vermiculite analyses collected by Gruner<sup>2</sup> is also shown (Column 2). If it is assumed that structurally a calcium ion is equivalent to an alkali metal ion in hydrobiotite, then the atom distribution is approximately as follows:

<sup>1</sup> Present address, 1711 West 100th Street, Chicago, Illinois.

<sup>2</sup> Gruner, *Am. Mineral.*, **19**, 557-575 (1935).

<sup>3</sup> For example, Hansen, Samuel and Forni, Sorption of water vapor by vermiculite and its silica: *Ind. Eng. Chem.*, **32**, 116-118 (1940). In this work hydrobiotite was investigated although the vermiculite composition and structural formula was used throughout.

Silicon	11.2	}	17.05	}	27.90
Aluminum	5.85				
Iron	1.45	}	10.85		
Magnesium	9.4				
Potassium plus Calcium	2.0				

The above, after rounding off and transferring one atom of aluminum from tetrahedral to octahedral coordination becomes:

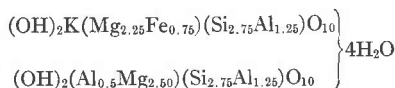
TABLE 1. ANALYSES OF VERMICULITES AND HYDROBIOTITES

Column	1	2	3	4
SiO <sub>2</sub>	43.3	46.0	42.3	43.5
Al <sub>2</sub> O <sub>3</sub>	19.0	17.7	19.5	18.4
Fe <sub>2</sub> O <sub>3</sub>	7.4	5.5	7.7	8.2
MgO	24.0	30.8	24.5	} 25.0
CaO	1.6		} 6.0	
K <sub>2</sub> O	4.7			
Total	100.0	100.0	100.0	100.0
Loss on ignition	11.0	20.1	12.1	10.8

1. Analysis of hydrobiotite. (True total, 99.15%, corrected to 100%.)
2. Average of seven vermiculite analyses collected by Gruner,<sup>2</sup> reduced to water free basis.
3. Calculated analysis of hydrobiotite assuming vermiculite and biotite sheets in 1:1 ratio.
4. Calculated analysis of hydrobiotite assuming vermiculite and biotite sheets in 3:2 ratio.

Silicon	11.0	}	16
Aluminum	5.0		
Iron	1.5	}	12
Magnesium	9.5		
Aluminum	1.0		

which reduces to



equivalent to alternating layers of vermiculite and biotite. The calculated analysis of this complex is given in Column 3, Table 1.

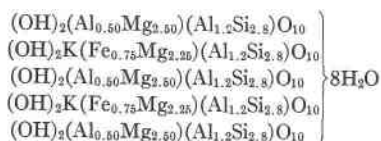
While isomorphic substitution of a calcium ion for an alkali metal ion, particularly a sodium ion is extremely common, it is possible for a calcium ion to occur in octahedral coordination. If it is assumed that a calcium ion is structurally equivalent to magnesium in hydrobiotite, then the atom distribution is approximately as follows:

Silicon	14.4	} 21.9	} 36.25
Aluminum	7.5		
Iron	1.85	} 14.35	
Mg+Ca	12.5		
Potassium	2.0		

Again rounding off these values and transferring 1.5 aluminum atoms from tetrahedral to octahedral positions there results:

Silicon	14.0	} 20
Aluminum	6.0	
Iron	1.5	} 15
Aluminum	1.5	
Magnesium	12.0	

which reduces to:



Here the configuration of biotite and vermiculite layers is *VBVBV*. The calculated analysis of this complex is given in Column 4 of Table 1. For reasons already given, it is believed that the structure represented by biotite and vermiculite layers in 1:1 ratio is the more likely of the two alternatives.

When hydrobiotite is treated with hot dilute sulfuric acid more or less pure silica lamellae (lamisilite) result.<sup>3,4</sup> In a study of the suitability of silica lamellae from both vermiculite and hydrobiotite as substrates for catalysts, the behavior of these two minerals when treated with acids was examined intensively. Data obtained during the treatment of true vermiculite from the Georgia-Carolinas mineral district are presented in Table 2.

In the first pair of experiments of Table 2, the mineral (through 4 mesh) was refluxed for 3 hours with a 1:2 mixture (by weight) of sulfuric acid and water, 1.1 parts by weight of acid being used per 1.0 part by weight of mineral. This amount of acid is that theoretically required to remove all oxides (except silica) as the normal sulfates. After the reaction was ended the product was thoroughly washed and dried at 110°C. About 43g. of quite pure silica was obtained. It has been stated<sup>5</sup> that hydrogen peroxide exfoliates vermiculite in the cold. Groves<sup>6</sup> found that other oxidizing agents act similarly, but not as energetically. For certain reasons

<sup>4</sup> Guthrie and Wilbor, U. S. Patent 1,898,774. February 21, 1933.

<sup>5</sup> Gruner, *Am. Mineral.*, **24**, 428-433 (1934).

<sup>6</sup> Groves, *Nature*, **144**, 554 (1939).

TABLE 2. ACID TREATMENT OF VERMICULITE

Exp. No.	Verm. g.	H <sub>2</sub> SO <sub>4</sub> g.	H <sub>2</sub> O g.	CrO <sub>3</sub> g.	Time hrs.	Dry Wt. g.
1	100	110	220	—	3	43.4
2	100	110	220	—	3	42.9
3	100	110	220	10	3	42.4
4	100	275	550	—	3	45.0
5	100	234	468	—	3	39.4

Experiment 1. On exposure to air, weight increases to 50.35g. (16% increase).

Experiment 2. Apparent density of the product, 0.477.

Experiment 3. Apparent density of product 0.471. Product colored with chromate ion even after thorough washing.

Experiment 4. Partially exfoliated material employed. 100g. exfoliated charge equivalent to 117.7g. raw mineral. 45.0g. product from 100g. exfoliated = 117.7g. raw mineral equivalent to 38.2g. product from 100g. raw mineral. Also, proportions are equivalent to 100g. raw mineral : 234g. acid : 468g. water. Compare with Experiment 5.

Experiment 5. Compare with Experiments 1 and 2.

the action of chromium trioxide was of interest. Accordingly, 100g. of vermiculite was soaked in a solution containing 10g. of this strong oxidizing agent in 220g. of water. No reaction was observed over a period of several days so the usual amount of acid was added and the mixture was refluxed for 3 hours. The product weighed 42.4g. (Experiment 3, Table 2). The use of chromium trioxide gave rise to no exfoliation and had little if any effect on the progress of the leaching reaction.

In Experiment 4 (Table 2) partially exfoliated vermiculite was leached. Due to the large bulk of the exfoliated charge, a much larger volume of the acid-water mixture than usual was required but the acid concentration was kept constant. The product weighed 45.0g., equivalent to 38.2g. per 100g. of raw (unexfoliated) mineral. To determine whether the more complete cleanup resulted from the use of exfoliated mineral, or from the large excess acid employed, Experiment 5 was run in which raw mineral was refluxed with the usual 1:2 acid-water mixture in an amount equivalent to that employed in Experiment 4. The product weighed 39.4g. indicating that exfoliation has little if any effect on the leaching process but that a large excess of acid gives an appreciably better cleanup. A large number of experiments that need not be considered in detail indicated that very pure silica lamellae are obtained using 1.0 raw vermiculite, 2.2 acid and 2.5 water (all parts by weight) and refluxing for three hours.

It is interesting to note that vermiculite when soaked in concentrated sulfuric acid (1g. mineral per 1.1g. acid) and then exposed to air effloresces greatly with the elimination of salts, but undergoes no additional change. This is in striking contrast to the behavior of hydrobiotite when treated similarly (see below).

The silica lamellae obtained from vermiculite by acid leaching are themselves of high purity but are mixed with a small amount of granular, heavy greenish material which is easily separated from a suspension of the silica plates by settling. The thus purified silica formed an excellent catalyst substrate.

A somewhat similar series of experiments was run with hydrobiotite, the results being presented in Table 3. When refluxed with the 1:2 (by weight) sulfuric acid-water mixture, using 1g. mineral per 1.1g. sulfuric

TABLE 3. ACID TREATMENT OF HYDROBIOTITE

Exp. No.	Hydro-biotite g.	H <sub>2</sub> SO <sub>4</sub> g.	H <sub>2</sub> O g.	CrO <sub>3</sub> g.	Time hrs.	Dry Wt. g.
1	100	110	220	—	3	60.0
2	100	110	220	10	3	58.1
3	100	275	550	—	3	56.0
4	100	110	220	—	6	51.4
5	100	110	440	—	6	64.1
6	100	110	440	—	6	53.6
7	100	110	220	—	5	50.6

Experiment 1. Apparent density of product 0.261.

Experiment 2. Apparent density of product 0.264. Final product colored with chromate ion.

Experiment 3. Compare with Experiment 1.

Experiment 4. Compare with Experiments 1 and 3. Weight of product after exposure to air, 57.2g. (11% increase).

Experiment 5. Soaked in the concentrated acid 48 hours, exposed to air 72 hours. Volume increase tenfold. Weight after exposure to air, 238g. 238g. - 210g. = 28g. water absorbed from air. 440g. - 28g. = 412g. water added before refluxing.

Experiment 6. Compare with Experiments 4 and 5.

Experiment 7. Soaked in concentrated acid 24 hours, steamed 1 hour, then sufficient water added to give 430g. total before refluxing for five hours.

acid, the final product weighed 60g., the cleanup being much less complete than with vermiculite (Experiment 1). The product from hydrobiotite consists of lamellae of silica mixed with a considerable amount of darker colored plates. Hydrobiotite exfoliates markedly when boiled with the diluted acid giving a final product weighing about 0.25g. per cc. which however undergoes additional exfoliation on heating. True vermiculite does not visibly exfoliate during refluxing and the resulting product does not exfoliate on heating. Hydrobiotite does not exfoliate in a cold solution of chromium trioxide, and when acid is added and the mixture is refluxed, removal of oxides other than silica is little better than in the absence of the oxidizing agent as Experiment 2 shows.

While vermiculite theoretically requires about 1.1g. acid per gram to

unite with all oxides, except silica, to form normal sulfates, hydrobiotite requires in the neighborhood of 1.2g. per gram. Accordingly, in Experiment 3, a large excess of acid, 2.75g. per gram of hydrobiotite, was employed and while an improvement is noticeable it is not commensurate with the large additional amount of acid used. On the other hand, on returning to the standard 1.1g. acid per gram of mineral but increasing the treating time from three to six hours a marked improvement in the leaching process followed as Experiment 4 testifies.

Hydrobiotite, when soaked in concentrated sulfuric acid and then exposed to air behaves in a most striking manner. After soaking 100g. hydrobiotite in 110g. concentrated sulfuric acid for 48 hours, the resulting mixture is exposed to air in a thin layer which is turned occasionally. After 24 hours' exposure exfoliation is noticeable and at the end of 2 to 3 days, depending upon humidity conditions, it is complete, the volume increase being as much as ten fold. During exposure to air the mineral gradually becomes white due to the separation of salts. Many investigators<sup>7</sup> have stated or implied that the exfoliation of vermiculite is due to the expulsion of water on heating. Obviously, this is not necessarily true for otherwise exfoliation would be an exceedingly common phenomenon. Groves<sup>6</sup> pointed out that the cold exfoliation of vermiculite in hydrogen peroxide made this theory untenable and the exfoliation of acid soaked hydrobiotite when exposed to air is another case in point. In the present instance, the exfoliation is attributed to the forcing apart of lamellae by sulfate crystals formed between them. When a cork of heat exfoliated vermiculite or hydrobiotite is pinched between the fingers it easily compresses to approximately the original size of the mineral particle from which it was obtained, and the resulting compressed mass forms a coherent whole. Acid exfoliated hydrobiotite, on the other hand, resists compression to a small but noticeable degree, and after compression the resulting material tends to disintegrate into a number of lamellae. During compression of such material the destruction of the sulfate crystals is felt distinctly. Even if this explanation of acid exfoliation of hydrobiotite is correct the question as to the mechanism of thermal exfoliation remains.

Some hydrobiotite, exfoliated with acid as above described, was treated with water and then refluxed (Experiment 5). Because of the exfoliation, twice the normal amount of water was required to give a fluid reaction mixture. The cleanup was very poor, the final product containing considerable insoluble basic aluminum sulfate. To determine if the unusually dilute acid employed was responsible for the formation of this insoluble

<sup>7</sup> For example, Crouse, *Eng. Mining Jour.*, **128**, 923 (1929).

Kriegel, *Bull. Am. Ceram. Soc.*, **19**, 94-97 (1940).

Pardie and Larson, *U. S. Geol. Sur. Bull.*, **805B** (1928).

basic salt, Experiment 6 was run similar to Experiment 4 in all respects with exception of the concentration of the acid employed. The cleanup was almost normal.

When raw hydrobiotite is steamed for one hour there is no change in the appearance or apparent volume of the mineral. On the other hand, if acid soaked hydrobiotite is steamed for one hour considerable exfoliation occurs. The resulting product, when treated with the standard amount of water and refluxed gives the expected amount of cleanup.

While it is comparatively easy to obtain a pure silica from vermiculite by an acid leach, this was impossible when using raw hydrobiotite. The product from the latter mineral was invariably contaminated with dark flakes believed to be biotite.

#### ACKNOWLEDGMENT

The author wishes to acknowledge the invaluable aid rendered by Mr. D. Rein during the progress of this work.