COMPOSITION AND STRUCTURE OF STILPNOMELANE

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INTRODUCTION

Stilpnomelane is an iron silicate which has been described from a number of iron mining districts where it occurs usually as a vein mineral, in iron formations, or in iron ore. Lately, however, it has been described from Western Otago, New Zealand (8), as a constituent of chlorite-epidote-albite schists in which it seems to be quite common. It is quite possible that stilpnomelane is much more widely distributed than is generally believed because only very close inspection under the microscope will distinguish it from biotite in fine grained material. This optical resemblance has been emphasized a number of times. In the hand specimens it occurs as curved bladed and micaceous aggregates showing perfect basal cleavage. In color it varies from pitch black through greenish to brownish black. The almost golden brown varieties have been called chalcodite, though structurally they are stilpnomelane, as will be shown. In hardness the mineral resembles the chlorites, though it is much more brittle, possessing no toughness as mica or chlorite. Occasionally "hexagonal" platy basal sections are seen under the microscope. All these properties make it certain that stilpnomelane is a close relative of the chlorites and micas, and therefore, possesses a layer structure. Some doubt was cast on the correctness of some of the layer structures as proposed by the writer by the work of Ksanda and Barth[1] on dickite. Hendricks,[2] however, has confirmed the writer's structure of kaolinite. He also finds[3] that the space group of dickite given by the writer is correct though the structure of the individual layer does not seem to be "quite correct." The structure of vermiculite has also been recalculated once more by the writer and found as published in 1934 (13). It must be admitted, however, that the structure of stilpnomelane is more difficult of interpretation and is solved only in part. Since it contains some very unusual features its publication seems desirable at this time. The writer is indebted to Dr. W. F. Foshag for analyzed samples and to Dr. R. B. Ellestad and Dr. Samuel Goldich for many suggestions in connection with the chemistry of stilpnomelane. The liberal grants of the Graduate School of the University of Minnesota have made this study possible.

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[1] Ksanda, C. J., and Barth, T. F. W., Note on the structure of dickite and other clay minerals: *Am. Mineral.*, vol. **20**, p. 634, 1935.

[2] Hendricks, S. B., Concerning the crystal structure of kaolinite, $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, and the composition of anauxite: *Zeits. Krist.*, vol. **95**, pp. 247–252, 1936.

[3] Personal communication.

TABLE 1. ANALYSES OF STILPNOMELANES AND THEIR AVERAGE COMPOSITION

	1. Theodor Mine	2. Mont Chemin	3. Genoa Mine	4. Baern	5. North Wales	6. West-field	7. Lambert-ville	8. Molecular Ratios	9. No. of Oxide "Molecules"*	10. Total Molecular Weight	11. No. of Positive Ions	12.
SiO_2	44.08	44.70	46.85	44.77	43.74	44.08	45.12	0.7453	32.000	1921.9	32	
Al_2O_3	3.94	5.16	4.64	6.32	6.36	4.74	6.29	0.0525	2.254	229.8	4.5	13.2
Fe_2O_3	13.33	16.38	11.60	20.79	22.47	5.27	23.67	0.1015	4.358	695.9	8.7	
FeO	25.08	15.08	20.00	12.83	15.74	23.31	5.93	0.2346	10.730	770.8	10.1	16.0
MgO	2.00	5.88	5.75	4.01	1.43	8.36	9.36	0.1303	5.595	225.6	5.6	
MnO	0.05	1.15	0.33	0.21	0.50	0.87	tr.	0.0063	0.270	19.1	0.3	
CaO	0.40	0.00	0.94	0.10	0.53	tr.	tr.	0.0050	0.215	12.1	0.2	1.9
Na_2O	0.67	0.84	0.27	0.07			tr.	0.0042	0.180	11.2	0.4	
K_2O	2.20	1.79	2.07	3.31	0.75		tr.	0.0153	0.657	61.9	1.3	
TiO_2	0.05	0.18	0.15	0.04								
H_2O+	6.63	7.17	5.77	5.64	6.36	10.97	9.12	0.3934	16.891	304.4	33.8 H	
H_2O-	1.96	1.83	1.80	1.96	2.59	2.21		0.1142	4.903	88.3	9.8 H	
	100.39	100.23	100.17	100.05	100.47	99.81	99.49					
Gr.	2.823		2.81	2.89	2.85							
Molecular Weight	4374	4300	4101	4294	4419	4356	4235			4341		

* These calculations are based on the assumption that 32 SiO_2 "molecules" are distributed over 4 unit cells.

1. From Theodor Mine. Described in great detail by Holzner (1).
2. From Mont Chemin. Described by Jakob (7).
3. From Genoa Mine of the Mesabi range. Described by Grout and Thiel (6). This occurrence was discovered by the present author in 1921 and the analyzed material was available for the present investigation.
4. From Baern (Sternberg-Bennisch), Moravia. Museum specimen No. 3208 of University of Minnesota. Black color, pitchy to glassy luster. Light greenish brown streak. $\alpha=1.58\pm.01$, $\gamma=1.677\pm.004$, 2 V very small. Analyzed by S. Goldich in the Rock Analysis Laboratory of the University of Minnesota for the present investigation. Originally described by Kretschmer (9).
5. From North Wales. Described by Hallimond (5).
6. From Westfield, Mass. Average of two analyses. Described by Shannon (3). The original analyzed sample No. 93438 of the U. S. National Museum was used in the present investigation.
7. From Lambertville, N.J. Described by Shannon (4) as chalcodite. The original analyzed samples No. 84735 and 84736 of U. S. National Museum were used in this investigation.
8. From a vein at Crystal Falls, Michigan. Unanalyzed material. Kindly furnished by Dr. V. L. Ayres of Houghton, Mich.

CHEMICAL COMPOSITION

Only the most reliable analyses were selected from the literature for the determination of the chemical composition of stilpnomelane. A new analysis was made of the mineral from Baern bringing the total used in this paper to seven. They are recorded in Table 1 and the specimens are described in the accompanying paragraphs.

It will be noticed that the SiO_2 content is remarkably constant, but enormous fluctuations occur in the ratios of Fe_2O_3:FeO. It was this fact which had caused a former division into stilpnomelane and chalcodite, the latter being "oxidized" stilpnomelane. Such a division is untenable on structural grounds. Besides, in a single specimen of apparently homogeneous material this oxide ratio will vary considerably. There has also been discussion as to whether the alkalies are essential constituents. Table 1 shows that they are not necessary though commonly present. CaO structurally is included in the alkalies. Their total average content in the first five analyses is only about one fourth of that which is commonly found in micas. The amount of H_2O, with the exception of No. 6, is fairly uniform. To arrive at a chemical formula for the mineral the molecular ratios were computed for each occurrence. From these the number of oxide molecules were calculated on the basis of 32 SiO_2 for a unit volume. This number was chosen because it represents an approximation to the largest possible number of SiO_2 in four unit cells as will be shown. Also the theoretical proportional molecular weights for these unit volumes were computed and are found in the bottom row of Table 1. Table 2 lists the proportional numbers and kinds of positive ions in unit volumes containing these molecular weights. In the second part of Table 1 average values are given for the seven analyses. By dividing the molecular ratio of SiO_2 by 32, a number is obtained by which each molecular ratio is divided. The quotients represent the oxide molecules given in column 9 (Table 1). These are multiplied by the molecular weights of the oxides to arrive at the total average molecular weights in column 10. Columns 11 and 12 show the average number of positive ions in a unit volume.

TABLE 2. NUMBER OF POSITIVE IONS IN A UNIT VOLUME CONTAINING 32 Si IONS

	1	2	3	4	5	6	7	Avg.	*Actual No. in No. 4
Si	32.0	32.0	32.0	32.0	32.0	32.0	32.0		30.3
Al	3.4	4.4	3.7	5.3	5.6	4.1	5.2	29.2	5.0
Fe'''	7.3	8.8	6.0	11.2	12.3	2.9	12.6		10.6
Fe''	15.2	9.0	11.4	7.7	9.6	14.2	3.5		7.3
Mg	2.2	6.3	5.8	4.3	1.5	9.0	9.9		4.0
Mn	0.0	0.7	0.2	0.1	0.3	0.5	0.0		0.1
Ca	0.3	0.0	0.7	0.1	0.4	0.0	0.0	1.9	0.1
Na	1.0	1.2	0.4	0.1	0.0	0.0	0.0		0.1
K	2.0	1.6	1.8	3.0	0.4	0.0	0.0		2.9
H+	32.0	34.0	26.2	26.9	31.0	53.1	43.0		25.4
H−	9.5	8.7	8.2	9.3	12.6	10.7			8.8

* Actual number of ions in four unit cells of specimen No. 4 based on a theoretical density of 2.90.

On account of the great differences in the oxidation of the iron no significant formula is obtained unless the di- and trivalent ions are added. Then it is discovered that this number is close to 29 in each stilpnomelane.

The average comparative formula may then be written:

$$(K_2, Na_2, Ca)O \cdot 16(Fe, Mg)O \cdot 6\text{–}7(Al, Fe)_2O_3 \cdot 32\ SiO_2 \cdot 21\ H_2O$$

or

$$(OH)_{16}(K, Na, Ca)_2\ (Fe, Mg, Al)_{29}Si_{32}O_{93} \cdot 13\ H_2O$$

The total H_2O was reduced by $\frac{1}{2}$ H_2O on account of the unusually high H_2O in analysis No. 6.

DEHYDRATION OF STILPNOMELANE

The formula just given does not indicate the distribution of H_2O in the structure. Jakob (7, p. 312), for example, thought that the 20 per cent of total H_2O which he obtained below 105°C in analysis No. 2

should be separated structurally. That he was mistaken is evident from the inspection of the two dehydration curves in Fig. 1. Mr. L. C. Armstrong, at the suggestion of the writer, dehydrated samples No. 3 and No. 4 in vacuo with a tensi-eudiometer as described by Hüttig (16). The two curves are quite similar and show a gradual rise to 500°C. No. 4 from Baern reaches this point, however, after a somewhat greater loss of water than No. 3. The difference may be due to the fact that sample No. 4 was much more finely divided than No. 3. Several investigators including L. C. Armstrong[4] have noticed that the physical nature, especially grain size (in other words exposed surface), influences the results somewhat as indicated. The water given off above 500°C most likely is (OH) in the structure and comprises from $\frac{2}{5}$ to $\frac{1}{3}$ of the total. It is for this and structural reasons that $(OH)_{16}$ appears in the last formula above. This also explains why stilpnomelane is stable to a temperature of 560°C, but starts to collapse in every case above this temperature. The residues taken from the tensi-eudiometer after complete dehydration were magnetic in spots, but there had been no oxidation of FeO at the expense of H_2O as was ascertained by two analyses on sample No. 3.

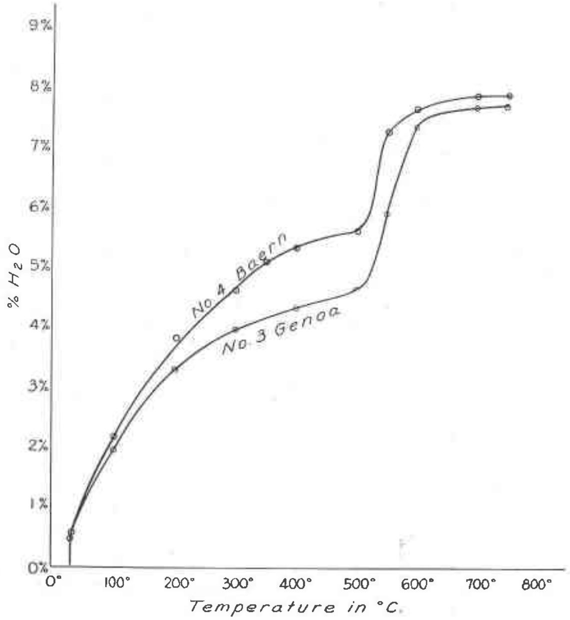

FIG. 1. Dehydration of stilpnomelane carried out in vacuo with a tensi-eudiometer.

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[4] Unpublished data.

Density Determinations

Unless the density of a mineral is known it is, of course, impossible to assign the proper number of "molecules" to the unit cell. Accurate density determinations encounter unusual obstacles in stilpnomelane. The mineral is extremely porous between layers so that it is almost impossible to remove all gases. Also it is probable that physical reactions produce colloidal solutions on boiling in distilled water. It was noticed for example that such solutions became opalescent and remained in that state indefinitely. Filtering through dense papers had no effect on them.

Three different methods of density determination were tried, but no two of them produced concordant results. Centrifuging in heavy liquids produced worthless results. Bromoform diluted with alcohol was used. In several trials with apparently homogeneous material from Baern the first fraction to come down had a gravity of 2.67 while the last one settled after dilution to 2.58. The samples of No. 3 and No. 7 behaved in a similar manner but showed still lower values. The reasons for such low results can only be guessed at present. Apparently the gases were not replaced by the liquids. Determinations with the Jolly balance or chemical balance, without any attempts to remove air bubbles, gave higher values than these by one in the first decimal place. The highest values were obtained with the pycnometer and water. A silica glass pycnometer was used. The water was boiled under reduced pressure intermittently for 15 minutes to remove any air from the samples. In this way No. 4 gave 2.87 and 2.89[5] in two determinations. No. 3 has a density close to 2.81.[5] The sample No. 7 has such a peculiar texture that the writer agrees with Shannon (4) that its density cannot be determined by present methods.

One pycnometer weighing was made on a 2.4 gram sample of No. 4 with tetrahydronaphthalene (Spec. Grav. 0.967 at 25°C.). This liquid is especially reliable with clay minerals according to Nutting (18). The sample covered with the liquid was subjected to a partial vacuum for over an hour to extract the air. The specific gravity corrected to 4°C was 2.842. It is believed that the true density of No. 4 is probably close to 2.89, the highest value obtained by any of the methods. Holzner's determination of 2.823 on No. 1 seems to the writer somewhat too low for a stilpnomelane with the highest total iron content of the seven. This may also be the case to a lesser extent with No. 5 which Hallimond determined as 2.85.

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[5] Both corrected to 4°C.

X-RAY DATA

It is evident that no idea of the structure of such a complicated mineral as stilpnomelane can be obtained without *x*-ray data. Holzner (2), however, attempted it and thought that it probably was an interstratification of mica and chlorite units. Very recently he (10, p. 448) discarded this idea and mentioned units of kaolinite and mica instead. Such combinations had been investigated two years ago by the writer when he began this *x*-ray study and had been found impossible.

The following materials were investigated by the powder method: Nos. 3, 4, 6, 7, and 8, an unanalyzed stilpnomelane. No suitable specimens for any other method of *x*-ray analysis were discovered. Unfiltered iron radiation was used. Very good diagrams were obtained with the type of camera described by Buerger.[6] The general scattering and darkening near the zero beam was reduced to such an extent that a faint line No. 3 at 6 Å was found which with older equipment had escaped detection. Table 3 contains the interplanar distances and intensities of a number of air dried and specially treated specimens. Other samples give practically identical patterns.

The conspicuous features in the films are always the lines Nos. 1, 2, 3, 5, 7, 9, and 10 which are very sharp and definite. They are undoubtedly reflections from the basal plane with the indices as recorded. It is possible that they need to be doubled as the unit cell may be twice as high as assumed. The reflection No. 2 at 12.1 Å[7] is several to many times as intense as any other reflection. This, coupled with the fact that no other reflections occur between No. 3 and No. 9 (except those indicated), especially no medium to strong ones at about 4.8 Å and 3.45 Å, is of greatest significance. Calculations of theoretical basal reflections show that certain layer structure combinations which are possibilities on the basis of the chemical formula are out of the question structurally. For example, the following are impossible:

1. Interstratification of mica and chlorite units with $d_{001}=24.2$ Å. (For the structure of chlorite see reference 15.)

2. Interstratification of mica and kaolinite layers with a spacing of $d_{001}=24.2$ Å. The kaolinite layers could be all pointing in one direction or could be facing each other as shown in (11, Figs. 2 and 3).

3. Interstratification of mica and vermiculite units (13) with a spacing of 24.2 Å. This combination is also impossible for other reasons, because on heating to 600°C, and even at much lower temperatures, a collapse to 19.5 Å would occur.

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[6] *Am. Mineral.*, vol. **21**, p. 11, 1936.

[7] This spacing is calculated on the basis of the average of the other basal reflections which are much more reliable, being farther away from the zero beam.

TABLE 3. POWDER PHOTOGRAPHS OF STILPNOMELANE
Unfiltered Fe radiation. Camera Radius—57.3 mm.

No.	4.		3.		4.+Tl		4.+$MgCl_2$		Indices
	*d*Å	*I*	*d*Å	*I*	*d*Å	*I*	*d*Å	*I*	
1	12.9	7	13.0	6	13.1	5	13.1	6	β001
2	11.9	10	11.9	10	12.0	10	11.8	10	001
3	6.03	0.5	6.06	0.5	6.06	1			
4	4.74	0.5	4.74	0.5			4.704	0.5	
5	4.476	1	4.446	1			4.440	0.5	β003
6	4.138	0.5					4.138	0.5	
7	4.045	5	4.035	5	4.059	3	4.016	3	003
8	3.566	1b	3.555	1b	3.570	1b	3.522	1b	
9	3.349	1	3.339	1			3.332	0.5	β004
10	3.036	4	3.026	4	3.044	3	3.013	3	004
11	2.831	1	2.818	1	2.815	1	2.831	0.5	β
12	2.693	2	2.702	2	2.689	2	2.708	1	
13	2.549	4	2.560	4	2.557	4	2.562	3	
14	2.481	i	2.508	i			2.513	0.5	
15	2.418	0.5	2.421	0.5			2.426	0.5	
16	2.341	3	2.341	3	2.343	3	2.347	2	
17	2.188	0.5	2.187	0.5			2.191	0.5	
18	2.109	2	2.105	2	2.112	2	2.110	1	
19	1.964	0.5	1.955	0.5			1.955	0.5	
20	1.888	2	1.886	1	1.888	1	1.886	1	
21	1.739	0.5	1.732	0.5			1.729	0.5	β
22	1.686	2	1.686	1	1.692	1	1.686	2	
23	1.576	3	1.577	3	1.575	3	1.586	2	
24	1.561	3	1.563	3	1.560	2	1.570	2	
24a							1.535	0.5	
25	1.519	2	1.517	2	1.522	2	1.513	2	060
25a							1.454	i	
26	1.416	1	1.416	1	1.421	0.5	1.415	1	
27	1.397	0.5	1.399	0.5	1.398	0.5	1.405	0.5	
28	1.359	0.5	1.351	0.5	1.357	0.5	1.368	0.5	
29	1.339	1	1.341	0.5	1.339	0.5	1.346	0.5	
30	1.322	0.5	1.323	0.5			1.327	0.5	
31	1.305	0.5	1.309	0.5			1.310	0.5	
32	1.287	0.5			1.290	0.5	1.282	1	
33			1.229	0.5					
34	1.151	0.5	1.150	0.5			1.153	0.5	
35			1.093	0.5					
Averaged $d_{(001)}$	=12.13		=12.11		=12.18		=12.07		

i = indistinct.
b = broad.

4. Interstratification of mica and nontronite layers (14) with a spacing of 24.2 Å. The collapse mentioned under 3 would also occur.

A number of other combinations of spacings of 12.1 Å and multiples of them were tried but always with results disagreeing entirely with observed intensity measurements. In this way it was finally discovered that the structure could possess an x-ray period of only 12.1 Å, and not a multiple of it. Also almost all the ions would need to be concentrated in three-fourths of the space of the unit cell, leaving an almost vacant layer—as far as ions or atoms with reflecting power are concerned—between densely populated layers. Such a condition would exist if the pyrophyllite or talc units were spaced properly. Unit layers of these have a thickness of about 9.2 Å (12, p. 416). Since stilpnomelane is 12.1 Å thick a vacancy of 2.9 Å is left which could contain some ions or atoms not adaptable to the pyrophyllite layers proper.

The other dimensions of the unit cell are given by line No. 25 which is the reflection of (060). A corresponding line occurs in a very similar position in measured biotites. One other possibility for (060) might have been No. 24 but this would have made the b axis somewhat longer than found in any other similar structure. Besides in the structure treated with $MgCl_2$ this line No. 24 has shifted to a position which would make the b axis entirely too long. With $b_0 = 9.10$ Å on the assumption that the structure is pseudohexagonal, $a_0 = 5.25$ Å. A monoclinic structure with these dimensions and $d_{001} = 12.12$ Å has a unit cell volume of 578 Å^3. If we place in this volume the molecular weight of No. 4 we have the theoretical density:

$$d = \frac{4294 \times 1.65}{4 \times 578} = 3.064$$

This is evidently too high a value. Taking 2.90 as the correct one, the number of all ions in the unit cell is reduced in the ratio of 3.06:2.90. The actual numbers become those recorded in the last column of Table 2.

1.7 ions of Al will be needed to completely fill the 32 available Si positions in four pyrophyllite layers. The actual formula divided by 2 for convenience becomes then:

$$(OH)_8(K, Na, Ca)_{1.5}(Fe, Mg, Al)_{12.6}(Si, Al)_{16}O_{44.5} \cdot 4.5\ H_2O.$$

That of stilpnomelane No. 3 adjusted on the basis of density = 2.81 is:

$$(OH)_8(K, Na, Ca)_{1.5}(Fe, Mg, Al)_{12.3}(Si, Al)_{16}O_{43} \cdot 4.25\ H_2O.$$

Stilpnomelane No. 5 has the adjusted formula:

$$(OH)_8(K, Na, Ca)_{.5}(Fe, Mg, Al)_{11.8}(Si, Al)_{16}O_{42.5} \cdot 5.75\ H_2O.$$

One half of this must be accommodated in the unit cell described. How this may be done is shown diagrammatically in Fig. 2. There is nothing new as far as the pyrophyllite layers are concerned. It is probable that as the ratio of Fe″:Fe‴ increases, some of the (OH) positions become occupied by O, while the hydroxyls may move between the layers to dotted positions to satisfy the Fe ions there (Fig. 2). How far this process can be carried out is a matter of conjecture at present.

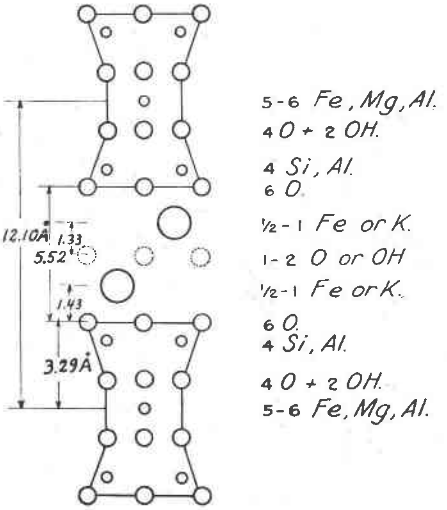

FIG. 2. Proposed structure of the stilpnomelane. Part of the (OH) in the pyrophyllite probably may be replaced by O as Fe″:Fe‴ increases.

The difficulty which confronts one is the location of the (Fe, Mg) and K ions between the layers. It seems reasonable that they occupy the positions held by K in mica, or Ca in brittle micas, only not centered between the layers (Fig. 2). There is room for four such ions in the cell, but only 2 will be needed at the most. The other two may be partially filled by H_2O. The following possibilities are considered for these ions:

1) They are all in random positions. The structure becomes a defect structure (17). Intensities of theoretical basal reflections are recorded under 1, Table 4.
2) The Fe ions are in positions 0.6 Å distant from the oxygen layers of the SiO_4 sheets. A corresponding number of O or (OH) ions are half way between sheets. Case 2, Table 4. The somewhat different position of K is not considered separately in this case.
3) The Fe and K ions are 1.43 Å distant from the oxygen layers of the SiO_4 sheets (Fig. 2). This is about the distance of Ca ions in brittle micas. A corresponding number of O or (OH) ions are distributed at random in this instance. Case 3, Table 4.
4) The positive ions are distributed as in 3 but the O or (OH) ions are half way between sheets. Dotted circles in Fig. 2.

TABLE 4. THEORETICAL AND OBSERVED INTENSITIES OF BASAL REFLECTIONS OF STILPNOMELANE

Indices	001	002	003	004	005	006	007	008	009	0010
1	116	$\frac{1}{2}$	3	5	0	0	0	0	0	0
2	104	$\frac{1}{2}$	6	6	0	0	0	0	0	0
3	83	$\frac{1}{2}$	4	3	0	$\frac{1}{2}$	0	$\frac{1}{2}$	0	0
4	64	0	3	4	0	0	0	$\frac{1}{2}$	0	$\frac{1}{2}$
Observed Intensities	>10	$0-\frac{1}{2}$	4	3	0	0	0	?	0	0

Case 1 does not fit the observed intensities. It is, however, difficult to choose between the other three. In either of the three possibilities there would be just enough room left between the layers to take care of the water molecules. This might be an explanation for the relative constancy of H_2O. In any case the structure may be considered a new type.

EXPERIMENTS ON BASE EXCHANGE AND STABILITY

Holzner[8] was the first to point out the fact that thallium easily replaces potassium in stilpnomelane. The writer boiled sample No. 4 four hours in a solution of $TlNO_3$. The analyses of the alkalies afterwards were $Tl_2O = 6.25$, $K_2O = 0.29$, $Na_2O = 0.15$. The specific gravity had increased to 3.00. Theoretically it should have been 3.014. The *x*-ray data for this treated material are recorded in Table 3. There are no appreciable changes in the positions and intensities of the lines, indicating, therefore, possibly random positions for the heavy Tl ions.

Other experiments dealt with the replacement of Fe by Mg for a possible clue to the structure of stilpnomelane. The mineral No. 4 was heated in gold-lined bombs in strong solutions of $MgCl_2$ for 4 days at 300°C. The atmosphere in the bomb was CO_2. There was found considerable Fe in solution. Also the mineral had become reddish brown in color. The *x*-ray results are listed in Table 3, 4th column. While there is some evidence of slight shrinkage in the direction normal to the layers and of some slight changes in intensities, the writer hesitates to interpret these results.

Bomb experiments were also made with weak hydrochloric acid to see whether possible amorphous portions between layers could be removed due to their lesser stability. A 0.03 *N* HCl solution at 300°C did not harm

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[8] It may be pointed out that Holzner's specific gravity of 3.068 for the thallium-treated sample is higher than it should be when compared with 2.823 of the natural material. Probably the figure for the latter is too low.

the structure in seven days, except that it dissolved ferrous iron and caused a shrinkage from 12.13 Å to 11.91 Å.

Surprising results were obtained in two experiments in which the concentration of HCl had been increased to 0.1 normal. With No. 4 and No. 7 stilpnomelane a pyrophyllite structure resulted. All the lines in the films agree with those of pyrophyllite. There are considerable differences in sharpness and intensities of the lines but they do not detract from the reality of the structures. It is of interest to note that the same pyrophyllite structure resulted when the writer heated nontronites to a temperature of 575°C (14, p. 476). As a matter of fact these films cannot be differentiated from those obtained in the present experiments, so great is their similarity.

The important question about these experiments is whether the pyrophyllite structure is the original structure of stilpnomelane as assumed above, or whether it is an entirely new development. In the first case, the material between the pyrophyllite layers would have been actually dissolved by the acid causing a collapse to 9.5 ± Å. In the second one the ions liberated by the breaking up of stilpnomelane would have combined to form a new structure. The material is white in color and under the microscope shows fibrous and platy aggregates which, however, are not uniform in behavior. The indices are much lower than would be expected, reaching below 1.48 for α. The birefringence is considerable. Interference figures on large enough plates are almost uniaxial. This phase of experimental work is being continued.

The stability of all the stilpnomelane samples was investigated. It was surprisingly great. In an atmosphere of CO_2 no break-down was noticeable in the structures at 550°C after 24 hours heating. At 600°C the collapse was well underway, and after heating at 640°C new but very poor x-ray patterns were obtained. Apparently the structures shrink in the direction normal to the layers from 12.1 Å to about 11 Å, for the most prominent and strongest line in the new pattern occurs at this spacing.

CONCLUSIONS

A number of stilpnomelanes were investigated. A comparison of the best available analyses gives a formula: $(OH)_{16}(K,Na,Ca)_{0-2}(Fe,Mg,Al)_{29}Si_{32}O_{93}\cdot 13\ H_2O$. It is not feasible to separate the trivalent from the bivalent elements in this mineral on account of the great fluctuations in the state of oxidation of the iron. If all the oxides of Fe, Mg and Al are added it is found, however, that the formula of each stilpnomelane approaches closely the one above. Alkalies are not necessary for the structure of the mineral. Chalcodite is not different from stilpnomelane structurally or chemically, except for the state of oxidation of the iron. Dehydration in vacuo shows that from $\frac{1}{3}$ to $\frac{2}{5}$ of the total H_2O is present in the mineral as (OH). This is not given off until a temperature of 500°C is reached. Dehydration becomes complete at 750°C. Iron is not oxidized in the process of dehydration at high temperature. After about half of the hydroxyl has been lost the structure begins to collapse. This collapse is complete between 600° and 650°C.

X-ray powder photographs of five stilpnomelanes give the following unit cell dimensions based on the assumption that the mineral is pseudohexagonal like other layer structures: $d_{(001)} = 12.07–12.18$ Å, $b_0 = 9.08–9.12$ Å, $a_0 = 5.23–5.27$ Å.

Density determinations of stilpnomelane were carried out only with a great deal of difficulty due to the peculiar physical nature of the mineral. Older values seem to be lower than justified. Pycnometer determinations with water gave the highest values. These were used in determining the number of ions contained in the unit cell of the dimensions given above. By this procedure we obtain the actual formula for an analyzed specimen whose unit cell is known, which is for stilpnomelane from the Genoa Mine of the Mesabi range, namely: $(OH)_8(K,Na,Ca)_{1.5}(Fe,Mg,Al)_{12.3}(Si,Al)_{16}O_{43} \cdot 4.25\ H_2O$.

There exist very good reasons to believe that the structure consists of pyrophyllite-talc layers which are spaced 12.1 Å apart. The space between them contains the ions of Fe, Mg and K which cannot be accommodated in these layers. Also a corresponding number of O or (OH) ions must be present between the layers. The result is a defect structure in which ions may even be in random positions. This is therefore a new type of structure.

The partial replacement of potassium by thallium is described which is indirect confirmation of the proposed structure since it could not take place if the K ions were as closely confined and held as in mica. Experiments in gold-lined bombs at 300°C show that stilpnomelane goes to a true pyrophyllite structure in 0.1 *N* HCl solutions. This phase of the work is being investigated further.

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