

THE STRUCTURE OF STILPNOMELANE REEXAMINED

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ABSTRACT

New x-ray data show the distribution of ions normal to the basal cleavage in the layer silicate stilpnomelane. Since it is similar to talc and biotite a structure consistent with its properties can be proposed. It explains satisfactorily the behavior of the mineral including its base exchange of K for Tl. Stilpnomelane is an important essential constituent of certain iron formations.

INTRODUCTION

The writer (1) made an attempt in 1937 to determine the composition and crystal structure of stilpnomelane. At that time the mineral had been reported from the quartz veins in iron formations and from the chlorite-epidote-albite schists in New Zealand (8 and 11). Recently it has been identified in large amounts in the iron formations of the Cuyuna and Mesabi ranges of Minnesota. There it is one of the three principal iron silicates, iron talc, to be described in detail shortly, being the second and greenalite the third.

As was pointed out previously, (1, p. 912) stilpnomelane may readily be mistaken for biotite under the microscope. Like biotite it is negative with a small optic angle and has similar pleochroism. In the hand specimen it resembles either biotite or chlorite, but is much more brittle. Its cleavage is excellent. Basal sections with partially developed hexagonal outlines have been observed. These properties and the discussion that follows make it certain that stilpnomelane has a layer structure and is related to the micas and chlorites.

CHEMICAL COMPOSITION

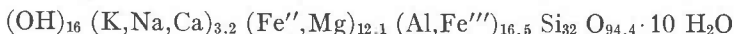
Nothing essentially new can be added with regard to the chemical composition of stilpnomelane. As a constituent of the iron formations it is so fine-grained and intergrown with other minerals that it cannot be separated for analysis. But there is no reason to believe that it differs materially from published analyses (1), to which the reader is referred. Table 1 is copied partly from the original paper, but with some additions calculated from new analyses by Hutton (11). The number of positive ions in the table have been recalculated from the chemical analyses on the basis of 32 Si ions per unit cell. This represents the largest number of Si ions possible in a talc-like layer structure in which all tetrahedral positions are occupied by Si, and leads to an average comparative formula: $\text{OH}_{16} (\text{K}, \text{Na}, \text{Ca})_2 (\text{Fe}, \text{Mg}, \text{Al})_{29} \text{Si}_{32} \text{O}_{93} \cdot 13 \text{H}_2\text{O}$.

The positive charges necessary to satisfy the O and OH charges are also shown in Table 1. It is quite evident that they are greatly in excess of those needed for a talc structure containing 32 Si, which would be 80 O and 16 (OH) = 176 negative charges. Also, the number of cation positions in such a talc structure does not exceed 24 while the actual numbers in the table range from 30.0 to 32.

Based on the size of the unit cell assumed at that time and the specific gravity, it was calculated in the original paper (1, p. 915) that the total content of the unit cell could be reduced to the following formula for No. 4 of Table 1:



It has been found since, as will be shown below, that the unit cell is actually about 6% larger and that for sample No. 4 of Table 1, its formula is very close to:



Since the highest total number of cations is 64, one may conclude with some assurance that this is the maximum number of positions available in the structure. In some stilpnomelanes with relatively low specific gravities the 32 Si positions may not be all occupied by Si, but also by Al, as was assumed in the earlier paper. In No. 5, for example, 31 positions would be occupied by Si instead of 32, provided the observed specific gravity and theoretical density are correct. At no time would it be possible, however, to have just simple mica or talc layers without additional structure elements in the cell as Hutton (11, p. 191) apparently tried to assume. Besides leading to disagreements of intensities of reflections, the density of such a structure would scarcely reach 2.50. For No. 8 in Table 1 it would be 2.4, for example. The condition of H₂O in the structure is only partially explained by the dehydration curves shown in the papers by Gruner (1) and Hutton (11, p. 190). It is certain that part of the water is present as (OH) ions. Hutton shows that at least 3% of the H₂O of No. 9 in Table 1 can be removed over concentrated H₂SO₄. This water is entirely regained upon exposure to the atmosphere for eight hours. The channels in the structure described below plausibly explain this behavior.

X-RAY DATA

Stilpnomelanes Nos. 3 and 4 gave excellent powder photographs with iron radiation and precision cameras of 57.3 mm. radius. These have already been published (1, p. 919). Films of samples Nos. 6 and 7, while still distinct, were poorer in quality. Even in the hand specimens they appeared somewhat altered as indicated by their brownish colors. X-ray photographs obtained from the microscopically fine-grained stilpnome-

TABLE 1. NUMBER OF IONS IN A UNIT VOLUME CONTAINING 32 SI IONS

	1	2	3	4	5	6	7	8	9
Si	32.0	32.0	32.0	32.0	32.0	32.0	32.0	32.0	32.0
Al	3.4	4.4	4.0	5.3	5.5	4.1	5.2	5.6	6.2
Fe'''	7.3	8.8	6.3	11.2	12.3	2.9	12.6	13.5	11.3
Fe''	15.2	9.0	12.2	7.7	9.6	14.2	3.5	2.0	8.4
Mg	2.2	6.3	6.2	4.3	1.5	9.0	9.9	8.1	3.0
Mn	0.0	0.7	0.2	0.1	0.3	0.5	0.0	0.4	0.0
Ca	0.3	0.0	0.7	0.1	0.4	0.0	0.0	1.5	0.4
Na	1.0	1.2	0.4	0.1	0.0	?	0.0	0.0	0.0
K	2.0	1.6	1.9	3.0	0.4	?	0.0	1.5	1.9
H+	32.0	34.0	28.0	26.9	31.0	53.1	} 43.0	31.7	30.8
H-	9.5	8.7	8.7	9.3	12.6	10.7		3.6	6.5
Al+Fe'''	10.7	13.2	10.3	16.5	17.9	7.0	17.8	19.1	17.5
Al+Fe+Mg+Mn	28.1	29.2	28.9	28.6	29.2	30.7	31.2	29.6	28.9
∑ cations without H and Si	31.4	32.0	31.9	31.8	30.0	30.7	31.2	31.8	31.2
∑ +charges without H	195	202	200	205	206	196	208	211	206
Mol. Weight	4374	4300	4243	4294	4410	4356	4235	4250	4313
Sp. Gr.	2.82		2.82	2.88	2.85			2.78	2.84
Theor. Density	2.94	2.89	2.85	2.89	2.96	2.93	2.85	2.85	2.90

1. Theodor Mine. Described by Holzner (2).

2. Mont Chemin. Described by Jakob (7).

3. Genoa Mine of the Mesabi range. Described by Grout and Thiel (6). This material contained a little quartz. The original analysis was recalculated on the assumption that 3% of the reported SiO₂ was present as quartz.

4. Baern (Sternberg-Bennisch), Moravia. Described by Gruner (1).

5. North Wales. Described by Hallimond (5).

6. Westfield, Mass. Average of two analyses. Described by Shannon (3).

7. Lambertville, N. J. Described by Shannon (4) as chalcodite.

8. Otago, New Zealand. Described by Hutton (11).

9. Zuckmantel, Silesia. Described by Hutton (11).

lane in the iron formations mentioned were of fair quality. No x-ray photographs were available of stilpnomelanes Nos. 1, 2, 5, 8, and 9. Fankuchen (11, p. 201) has made oscillation photographs of portions of stilpnomelane crystals which are rather complicated. Based on very weak reflections he concludes that the mineral has a superlattice of about the following dimensions: $a_0 = 22.0 \text{ \AA}$, $b_0 = 38.0 \text{ \AA}$, $c_0 = 36.2 - 37.9 \text{ \AA}$. In other words, his unit cell would be about 48 times the author's and would contain over 2000 ions. Apparently this is a similar case to that de-

scribed for the micas by Hendricks (12, p. 770). Fankuchen's observations do not conflict essentially with the present ones. He does not advance a structure scheme of his own. What astonishes the writer are the considerable fluctuations in the lengths of the c axes, as given by Fankuchen. In the present investigation the thicknesses of the layers varied from 12.07 to 12.18 Å. His range apparently from 12.07 to 12.63 Å, differences much greater in proportion than any encountered so far in any layer silicates, not excluding the chlorites. Fankuchen lists no x -ray powder photographs. In those of the writer's not more than four basal reflections could be indexed with certainty. More recently the writer has obtained rotation photographs from small flakes of Nos. 3 and 4 and was able to measure basal reflections including the 11th order. Their intensities are listed in Table 2. Also, by selecting thicker basal sections and trimming them to about 1 mm. diameter, measured in the plane of the base, it was possible to obtain and index reflections of planes 060, 200, and 400. Based on these new data the volume of the smallest unit cell was increased from 578 Å³ to 614 Å³.

TABLE 2. THEORETICAL AND OBSERVED INTENSITIES OF BASAL REFLECTIONS OF STILPNOMELANE. FE RADIATION

Indices	001	002	003	004	005	006	007	008	009	0010	0011
Theoret. I	200	0.3	12	16	0	0.2	0.05	2.0	0.6	0.8	0.5
Observed I Powder Sample 7	10+	0	3	3	0	0	0	1	0.5	0	0
Observed I Powder Sample 4	10+	faint	5	5	0	0	0	2	0.5	0.5	?
Observed I Rotation Sample 4	very strong	1	15	15	0	0	doubt- ful	2-3	0.5	1	faint

The dimensions for No. 4 are: $001 = 12.12$ Å, $b_0 = 9.40$ Å, $100 = 5.39$ Å. The dimensions for 100 and b_0 are similar to those of cronstedtite (9) and other layer silicates high in iron. This gives us a workable unit cell as compared with Fankuchen's, though slight changes may be necessary in it at some future date.

The theoretical intensities of the basal reflections were calculated as follows:

The bulk of the ions is distributed as in the individual talc layers. As-

suming monoclinic symmetry a plane of symmetry lies in the plane of the *a* and *c* axes. Atoms in this plane are shown in Fig. 1. Their positions with respect to a basal plane of reference are given in the figure. The distribu-

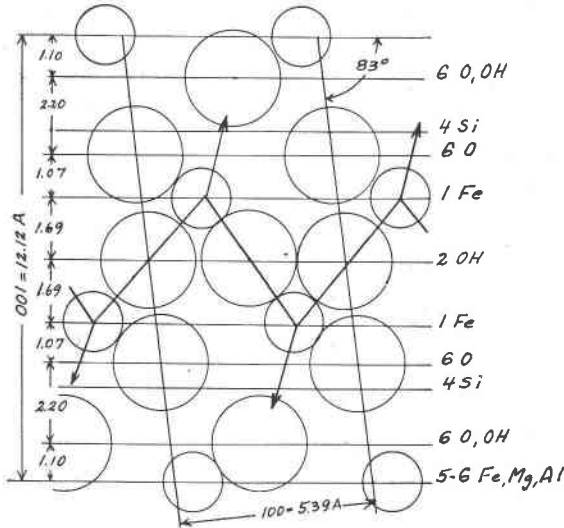


FIG. 1. Distribution of ions in the plane of symmetry. All positions shown are in this plane. Small circles are Fe, Al, or Mg.

tion of the atoms in the plane half way between the talc layers is shown in Fig. 2. In computing the structure factor it was assumed that Fe, Mg, and Al are distributed statistically over the available positions. The mean

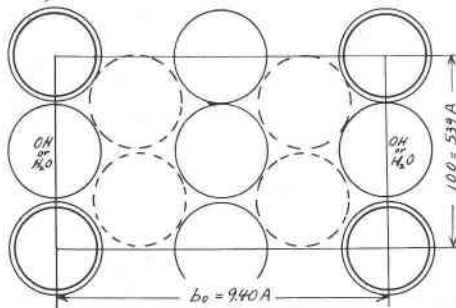


FIG. 2. Distribution of atoms in a plane halfway between talc layers. OH and O ions full rings. K ions double rings. H₂O broken line rings.

of the scattering power of each of these positions was taken to be the same and calculated from the chemical compositions. There is no doubt that this method introduces considerable errors to which must be attributed

some of the disagreements in Table 2. For example, if two Mg ions filled the two cation positions between the talc layers leaving more Fe'' ions for the octahedral positions, theoretical and observed intensities would be in very good agreement. It was not possible to determine how much more intense the reflection 001 is than 003, but it is certain that it is several times as great, and possibly as much as 15 to 20 times.

STRUCTURE

The significant feature of the structure is that 12.12 Å is the simplest x -ray period, with indices 001. There is not the slightest indication in the films that the indices of the basal reflections given in Table 2 need to be doubled and that other basal reflections might occur between them. This means that the structure must be simpler than a combination of any known layers. The periods of such combinations would be multiples of 12.12 Å, and would all have several reflections at such distances as 24/3, 24/5, 24/7, 24/9 Å, etc. They were discussed before (1, p. 918). There are, however, other possibilities for interpreting the chemical composition of the mineral. For example: (a) Instead of having one octahedral gibbsite layer between two tetrahedral layers, two such layers could occur between tetrahedral layers. The thickness of a layer would be about 11.5 Å. The formula would be about $(\text{OH})_4\text{M}_8 (\text{SiAl})_8\text{O}_{26}$. If K or H₂O were between the layers the thickness would be about 12.2 Å. (b) The serpentine structure proposed by Bragg which is 14.6 Å in thickness can be simplified with the result that it would be only 12.2 Å thick and have a layer structure. (c) A layer consisting entirely of two tetrahedral SiO₄ layers facing each other, 7.2 Å thick, combined with a nearly neutral gibbsite layer 4.9 Å in thickness. Its formula would be $(\text{OH})_{12}\text{M}_{4-6} (\text{SiAl})_4\text{O}_{16}$. Theoretically, there seems to be no objection to such a combination.

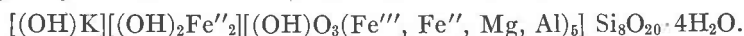
All these possibilities were thoroughly tested but had to be rejected. The only structure that will fit the observed intensities is similar to the one proposed earlier (1), but it is now possible to fix the ions with considerable assurance.

It is fundamentally a talc structure. There is just sufficient room between the layers for (OH) or O ions to slip in between the nearest oxygens of the talc. The layers are stacked in such a manner that the hexagonal rings more or less fit on each other as in micas. There are 2 (OH) ions halfway between two unit layers or, what is more probable, one O ion and one (OH). They probably lie at the intersections of alternate planes of symmetry and theoretical cleavage planes, that is, parallel to the a axis. Two cations of Fe'', Mg, or Ca are held by the O and (OH) ions as indicated in Fig. 1.* Some of the valences of the cations are bound by the

* There are also other O ions in contact with the Fe''.

(OH) positions of the octahedral layers. The (OH) in these positions are replaced in part by O which also explains why so many trivalent ions are found in the octahedral positions of the talc layers. The ferrous ions outside of these layers would obey Pauling's rule by having three bonds of 1, $\frac{1}{2}$ and $\frac{1}{2}$ valences. It would be chiefly by these $\frac{1}{2}$ valence bonds to the octahedral layers that the structure would be held together. It is quite possible that these bonds might have a strength of one depending upon the numbers and kinds of cations in the octahedral layers. In that case all of the O positions between the layers would be filled by (OH).

The K ions fit easily into the rows of large spaces left between the chains of (OH) and Fe, (Fig. 2). They lie in the theoretical cleavage planes. Their charges are probably partially satisfied by the O ions in the octahedral OH positions. There is, however, a distinct possibility that (OH) ions are in the positions indicated. There are 5 positions available for H₂O unless one of them is filled by OH as just mentioned. The smallest completely filled unit cell would then contain:



The brackets indicate the ions which belong together structurally. This formula has 50 negative charges which is in good agreement with the + charges of Table 1. By converting the only remaining (OH) in the octahedral layer to O a maximum of 51 charges may be reached.

DISCUSSION

The proposed structure must be able to explain the peculiar properties of the mineral. The mineral is remarkably stable, being found in schists and slates. The thickness of the layers is very uniform regardless of changes in composition. The uniformity of the radii of O and (OH) between the talc layers accounts for both of these properties and for the fact that no breakdown occurs below 550° C. in an atmosphere of CO₂ as does in nontronite (10) and vermiculite.

As was pointed out previously (1, p. 922) thallium readily replaces K. The arrangement of the K ions in wide channels in the structure easily explains this rapid substitution. Boiling in HCl or H₂SO₄ produces identical sheets of amorphous silica so well known in similar experiments with biotites. This also suggests their similarity. Experiments in which talc-like structures were produced in bombs are also significant as already discussed (1, p. 923).

While the amount of Al in the structure is not large, no reliable stilpnomelane analyses have been reported without several per cent of Al₂O₃. As a matter of fact, most of the Al₂O₃ found in the iron formations of the Cuyuna and Mesabi ranges seems to be in the mineral stilpnomelane

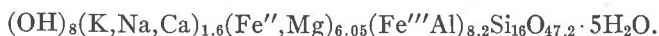
as discovered recently. Also Mg is never absent. The writer believes that these two elements are essential to the formation and particularly to the stability of this otherwise unusual structure. It is, of course, probable that small amounts of the Al ions substitute for Si. Chemical analyses suggest that not all available positions are necessarily filled in the structure, a property characteristic of many layer silicates. The spaces available for OH and H₂O are slightly more than sufficient to accommodate them. The dehydration curves of stilpnomelane (1, p. 916) are in excellent agreement with the distribution of OH and H₂O.

CONCLUSIONS

Based on the new data it is found that the unit cell of stilpnomelane is about 6% greater than published previously.

$$001 = 12.12 \text{ \AA}, b_0 = 9.40 \text{ \AA}, 100 = 9.39 \text{ \AA}.$$

New basal reflection calculations lead to an unusual type of layer structure related to biotite and iron talc (a mineral to be described shortly). The formula for the stilpnomelane (No. 4) for which the most complete data are at hand is for two smallest unit cells:



Simplified to a structural formula of one cell it is:



The structure contains channels parallel to the *a* axis in which K ions may be situated. These may be replaced by thallium and probably other ions of suitable dimensions or H₂O. Between the channels are chains of Fe-OH-Fe-O ions which hold the main layers apart. Mg and Al are thought to be essential to the structure. Without them probably quartz and magnetite would have resulted. This is the impression one receives in studying the iron formations of the Mesabi and Cuyuna ranges in which stilpnomelane occurs in very large amounts as an essential constituent.

REFERENCES

1. GRUNER, J. W., *Am. Mineral.*, **22**, 912-925 (1937).
2. HOLZNER, JULIUS, *Neues Jahrb. Min., Beilage Bd.* **66, A**, 213-222 (1933).
3. SHANNON, E. V., *Proc. U. S. Nat. Mus. Wash.*, **57**, 397-403 (1921).
4. SHANNON, E. V., *Ibid.*, **58**, 451-453 (1921).
5. HALLIMOND, A. F., *Mineral. Mag.*, **20**, 193-197 (1924).
6. GROUT, F. F., AND THIEL, G. A., *Am. Mineral.*, **9**, 228-231 (1924).
7. JAKOB, JOHANN, *Schweiz. Min. and Petr. Mitt.*, **7**, 311-313 (1927).
8. TURNER, F. J., AND HUTTON, C. O., *Geol. Mag.*, **72**, 1-8 (1935).
9. HENDRICKS, S. B., *Am. Mineral.*, **24**, 529-539 (1939).
10. GRUNER, J. W., *Am. Mineral.*, **20**, 475-483 (1935).
11. HUTTON, C. O. (WITH I. FANKUCHEN), *Mineral. Mag.*, **25**, 172-206 (1938).
12. HENDRICKS, S. B., *Am. Mineral.*, **24**, 729-771 (1939).