

# THE CRYSTAL STRUCTURE OF STILPNOMELANE

## PART I. THE SUBCELL

by

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### ABSTRACT

FERRIC-IRON stilpnomelane is triclinic, space group  $Pl$ ,  $a = 21.724 \text{ \AA}$ ,  $b = 21.724 \text{ \AA}$ ,  $c = 17.740 \text{ \AA}$ ,  $\alpha = 124.14^\circ$ ,  $\beta = 95.86^\circ$ ,  $\gamma = 120.0^\circ$ ,  $Z = 16$ . The structure is dominated by a subcell for which  $a_s = \frac{1}{2}a$ ,  $b_s = \frac{1}{2}b$ ,  $c_s = \frac{1}{2}c$ ,  $\alpha_s = \alpha$ ,  $\beta_s = \beta$ ,  $\gamma_s = \gamma$ . The subcell reflections have  $h-k = 3n$ , and have a trigonal intensity distribution. The structure was determined from Patterson projections and by trial and error. Three-dimensional refinement by least squares gave an  $R$  factor of 14.4 per cent for 296 reflections.

Stilpnomelane is a layer structure, having five anion and five cation planes parallel to (001). An iron-rich octahedral sheet is flanked by two tetrahedral sheets. The tetrahedral sheets differ from those found in the common layer silicates in that adjacent tetrahedra point in opposite directions. Each tetrahedral sheet has 1.25 tetrahedra pointing toward the octahedral sheet, and 0.75 tetrahedra pointing away. Detail in the tetrahedral sheet cannot be determined from the subcell reflections only.

### INTRODUCTION

STILPNOMELANE is an iron silicate of micaceous habit found in low grade metamorphic rocks. It was first described by Glocker (1828). An investigation of the properties and composition of stilpnomelane by Gruner (1937) showed that a group of minerals rather than a single species is involved. Gruner's work culminated in a structural analysis: the structure proposed was that of talc-like sheets joined by  $FeOH$ . Hutton (1938) made an extensive study of the composition and optics of stilpnomelane and showed the existence of a continuous series between ferrous and ferric iron-bearing stilpnomelanes.

Stilpnomelane develops as radiating tufts in the very first stages of reconstitution of greywackes and other iron-aluminum-bearing sediments and persists through the greenschist facies, where it may be associated with quartz-chlorite-epidote-spessartite. As the metamorphic grade increases, stilpnomelane commonly becomes segregated into veins. Hutton (1938) notes this in the higher grade metamorphic stages of the greenschists of Otago, New Zealand. The same thing is shown by the stilpnomelane of the Lake Superior iron formations. In the Mesabi Range, stilpnomelane occurs as small radiating bundles associated with greenalite-chlorite-carbonate-chert. In the higher grade rocks of the Upper Peninsula of Michigan, coarse stilpno-

melane occurs in veins associated with quartz and carbonate, commonly concentrated in the noses of minor folds. In the Crystal Falls district, well-crystallized stilpnomelane occurs in quartz-feldspar veins.

## PHYSICAL PROPERTIES

### *Unit Cell*

Gruner (1937) determined the unit cell of stilpnomelane by powder methods (Table 1) and gave the space group  $C2/m$ . Fankuchen (1938) used single crystal rotation photographs to show that Gruner's cell was actually a subcell, and that the true unit cell contained forty-eight such subcells.

Single crystal precession photographs of material from Crystal Falls, Michigan, show three types of reflections. Reflections of the first type, T1, are strong, sharp reflections and lie on a reciprocal lattice that is consistent with the C-centered monoclinic unit cell found by Gruner.

Reflections of types 2 and 3 are much weaker than the T1 reflections, and they lie on a triclinic reciprocal net. The true unit cell of stilpnomelane is thus triclinic; the parameters are given in column 3 of Table 1.

The relation between the true unit cell and Gruner's monoclinic cell are (Fig. 1):

Gruner	This Study
<i>a</i>	$[\bar{1}\bar{1}0]$
<i>b</i>	$[\bar{1}\bar{1}0]$
<i>c</i>	$[231]$

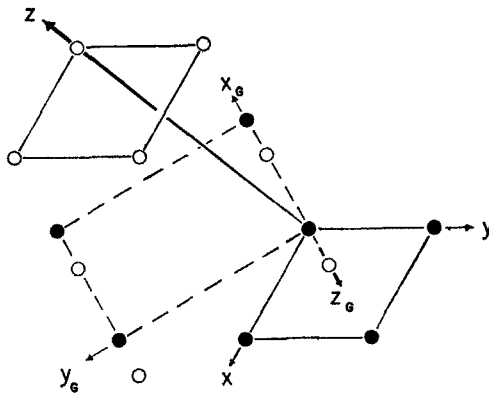


FIG. 1.—Relation between Gruner's monoclinic unit cell and the triclinic subcell of stilpnomelane.

Full circles: lattice points at  $z = 0$ .  
 Open circles: lattice points at  $z = 1$ .

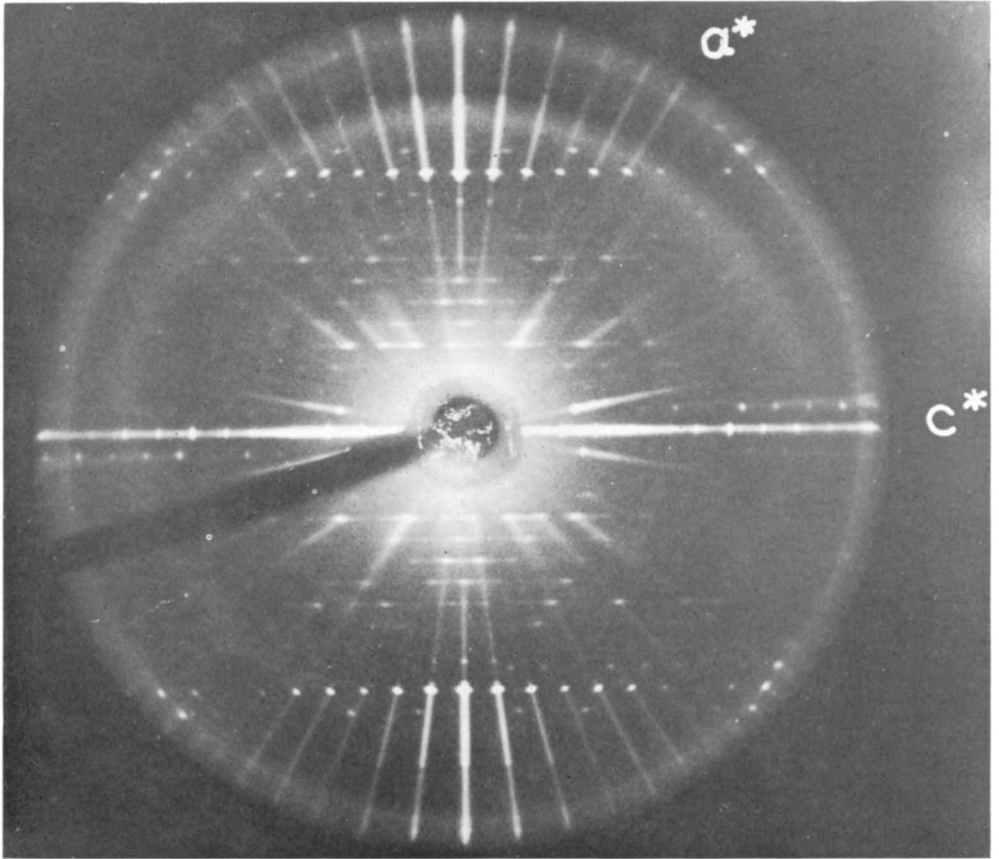


PLATE 1.— $h0l$  Precession photograph of stilpnomelane.

The strong sharp spots are T1 reflections.

The weak sharp reflections on each side of the rows of T1 reflections are T3 reflections.

The T2 reflections occur between the rows of T1 reflections and are rather diffuse.

TABLE 1.—COMPARATIVE STILPNOMELANE CELL DIMENSIONS

	Gruner monoclinic	Hutton, orthohexagonal	This study, triclinic
<i>a</i>	5.45 Å	22.1 Å	21.6 Å
<i>b</i>	9.40 Å	38.1 Å	21.6 Å
<i>c</i>	12.2 Å	36.2 Å	17.7 Å
<i>α</i>	90°	90°	124°
<i>β</i>	98°	90°	96°
<i>γ</i>	90°	90°	120°

Single crystal photographs show that the T1 reflections are related by a three-fold axis of symmetry normal to (001). The T2 and T3 reflections do not conform to this symmetry. The T1 reflections could be indexed on a trigonal subcell with  $a' = 3.1\text{Å} \left( = \frac{\sqrt{3}}{12} a \right)$ ,  $c' = (12.4 \times 3)\text{Å}$ . Such a definition of the subcell is of little value. Instead the subcell was defined so that its axes coincided with those of the true cell, but with  $a$  and  $b = \frac{1}{4}a_0$  and  $\frac{1}{4}b_0$  respectively. Thus the subcell has 1/16 the volume of the true cell.

The following threefold equivalences hold for the subcell:

$$(hkl) \sim (hkl) \cdot T \sim (hkl) \cdot T^{-1}$$

$$\text{Where } T = \begin{vmatrix} 0 & -1 & 13/3 \\ 1 & -1 & 11/3 \\ 0 & 0 & 1 \end{vmatrix}, TT = T^{-1}$$

$$(xyz) \sim (xyz) \cdot V \sim (xyz) \cdot V^{-1}$$

$$\text{Where } V = (T^{-1}), = \begin{vmatrix} -1 & -1 & 0 \\ 1 & 0 & 0 \\ 2/3 & 13/3 & 1 \end{vmatrix}, V^{-1} = T^T \text{ (T transpose)}$$

When the subcell is so defined, the T1 reflections have indices such that  $h-k = 3n$ . In addition there are three mirror planes perpendicular to (001) and to X, Y and [110] respectively.

The presence or absence of a center of symmetry in the subcell was determined by the statistical test of Howells, Phillips and Rogers (1950), the  $N(z)$  test. Fig. 2 shows the theoretical cumulative curves for the centrosymmetric and noncentrosymmetric situations. The values for the stilpnomelane subcell, shown as circles, were determined from 130 observed and unobserved general reflections. The subcell of stilpnomelane is noncentrosymmetric, space group P1.

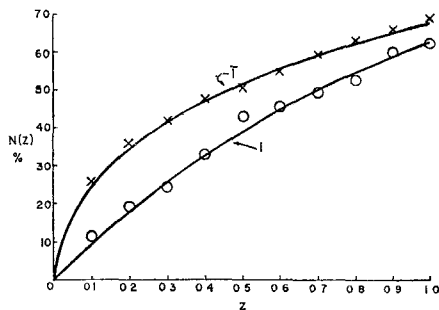


FIG. 2.— $N(z)$  test for centrosymmetry.

Circles: T1 reflections.

Crosses: T2 and T3 reflections.

### *Order-Disorder in Stilpnomelane*

As already noted, the T1 reflections can be indexed on the basis of a trigonal cell with  $a = 3.1 \text{ \AA}$ ,  $c = 37 \text{ \AA}$ . The T1 reflections are so much stronger than the T2 and T3 reflections that it is evident that the trigonal subcell they define forms the framework of the stilpnomelane structure. If at any plane in the crystal parallel to (001) there occurs a shift of atoms equal to  $1/3(2a_s + b_s)$ ,  $1/3(a_s + 2b_s)$  or  $1/3(a_s - b_s)$ , the T1 reflections will remain unaffected, for such a shift is equivalent to no shift. However, if random  $1/3$  shifts in the  $[210]$ ,  $[120]$ , and  $[1\bar{1}0]$  directions occur, the periodicity of the true cell in the  $Z$  direction is lost, and the T2 reflections degenerate into continuous rods in reciprocal space. Stilpnomelane crystals have this one dimensional disorder: of 400 examined, only one was periodic in the  $Z$  direction.

Whereas the T2 reflections are continuous for disordered crystals, the T3 reflections remain sharp. The T3 reflections occur in rows parallel to  $Z^*$  on either side of the T1 reflections and have indices  $12n \pm 1$ ,  $12n \pm 1$ ,  $l$ .  $n = 0, 1, 2, \dots$

### *Powder Pattern*

The powder pattern of stilpnomelane is dominated by the trigonal T1 reflections; thus, referred to the true unit cell, most of the observable lines have three sets of indices. A few weak T2 and T3 reflections can be detected at low  $\theta$ . Table 2 lists the powder pattern for stilpnomelane from Crystal Falls with the lines labeled according to reflection type. Very few samples give sharp reflections at  $\theta > 45^\circ$ , hence indexing beyond this point is not possible.

### *Composition and Cell Content*

A structural formula for stilpnomelane was given by Gruner (1944) and also by Hutton (1938, 1956). Gruner's formula was calculated to a total Si

content of 8, whereas Hutton calculated to a total  $O + OH + H_2O$  of 30. Gruner's formula for ideal stilpnomelane is:  $2[Si_4(Fe, Mg, Al)_{3.5-4.0}(K, Na, Ca)_{0.0-0.5}(OH)_2O_{11.5-12.0} \cdot 2H_2O]$ . Hutton's (1956) formula is:  $2[(Si, Al)_4(Fe, Mg, Mn, Ti, Al)_{3.6}(Na, Ca, K)_{0.25}(O, OH)_{15}]$ . Hutton (1938) points out a relation between the ferrous : ferric iron ratio and total water in stilpnomelane analyses, the water content decreasing with increase in ferric iron.

The specific gravity and the volume of the unit cell were determined for stilpnomelane from Crystal Falls and for an analysed stilpnomelane from Cobar, New South Wales (Raynor, 1961). The content of the unit cell was determined by the method of Hey (1954), with the following results:

Stilpnomelane	Anions	Cations
Crystal Falls	15.6	7.68
Cobar	15.2	7.72

The ideal anion content was therefore taken as  $15(O + OH)$ .

The analyses of stilpnomelane available in the literature do not reveal how much, if any, of the aluminum substitutes for silicon. When reduced to  $15(O + OH)$  most of the analyses show less than 4Si. Aluminum is always present in stilpnomelane, but the distinction between the structural formulas  $(Si, Al)_4(R^{2+}, R^{3+})_{3.7}(Na, Ca, K)_{0.25}(O, OH)_{15}$  and  $Si_{3.7}(R^{2+}, R^{3+})_4(Na, Ca, K)_{0.25}(O, OH)_{15}$  requires a structure determination.

### SAMPLE

The crystal used in this study was from a stilpnomelane sample from Crystal Falls, Michigan. Stilpnomelane from this locality was described by Ayres (1940). The stilpnomelane occurs in veins in Upper Huronian slates, with quartz and K-feldspar. It is dark brown with a resinous luster and a curved platy habit.

The density of the stilpnomelane was determined by displacement of water from a 25 g pycnometer using 1.1 g of separated crystals,  $D_m = 2.827$ .

The refractive indices were determined by double variation on a five-axis universal stage using a crystal from the same sample.

This crystal has:

$$\alpha = 1.623 \pm 0.002$$

$$\beta = 1.735 \pm 0.002$$

$$\gamma = 1.735 \pm 0.002$$

These refractive indices are slightly different from those determined by Hutton (1944) on stilpnomelane from the same locality, but the 1.623  $\alpha$ -index plots closer to Hutton's curve of  $\alpha$  vs. composition than does Hutton's 1.634 value. The refractive indices, therefore, show that Ayre's analysis

applies to the material used in this study, even though our sample was collected at a later date.

The cell dimensions of the stilpnomelane from Crystal Falls were determined from a powder photograph taken with Fe radiation, camera diameter 114.6 mm.  $\text{PbNO}_3$  was used as an internal standard; the value used for the cell edge was 7.8568 Å (Swanson, Gilfrich, and Ugrinic, 1955).

The stronger lines of the stilpnomelane pattern were measured, and the cell parameters adjusted to give the best "least squares" fit. The least-squares cycles were performed on the University of Wisconsin Control Data Corporation 1604 computer. The measured and calculated  $d$  values used in the least-squares refinement of cell parameters are indicated by an asterisk in Table 2. The resultant cell dimensions are:  $a = 21.724 \pm 0.004$  Å,  $b = 21.724 \pm 0.004$  Å,  $c = 17.740 \pm 0.004$  Å,  $\alpha = 124.14^\circ \pm 0.015^\circ$ ,  $\beta = 95.86^\circ \pm 0.023^\circ$ ,  $\gamma = 120.00^\circ \pm 0.02^\circ$ .

The subcell content of this stilpnomelane was determined from Ayres' analysis, the subcell volume and the measured density. The composition, calculated to a total O + OH of 15 is  $\text{Si}_{3.7}\text{Al}_{0.7}\text{Mg}_{0.7}\text{Fe}_{2.2}^{3+}\text{O}_{10}(\text{OH})_5$ . Thus the sample is dominantly ferric stilpnomelane.

## EXPERIMENTAL

A crystal was found for which the T2 reflections were not continuous, but formed discrete, slightly elongate spots, indicating that the crystal was considerably ordered. This crystal has the shape of a rectangular prism with dimensions  $0.21 \times 0.14 \times 0.09$  mm. Intensity data were collected on a Buerger precession camera using filtered Mo radiation. The quality of the crystal was such that reflections beyond the recording limit of the precession camera were too diffuse to be photographed by a Weissenberg camera.

Photographs were taken of the six major levels around the  $Z^*$  axis,  $0kl$ ,  $h0l$ ,  $\bar{h}hl$ ,  $2hhl$ ,  $\bar{h}2hl$ , and  $hhl$ , as well as certain upper levels. For each level a sequence of exposures was made, the exposure time being doubled for successive photographs. Intensities were visually estimated by comparison with a standard film. The observed intensities were corrected for Lorentz and polarization factors using the expression given by Waser (1951) and were also corrected for the absorption by a rectangular prism.

## STRUCTURE DETERMINATION

Stilpnomelane is similar to the layer silicates in habit, cleavage, hardness, specific gravity and optical properties. The subcell, when redefined as a C-centered orthohexagonal cell has  $a = 5.4$  Å,  $b = 9.5$  Å, as do the layer silicates. However, the  $d_{001}$  spacing of stilpnomelane is 12 Å, unlike that of any layer silicate. A comparison of the layer silicate basal spacings is given in Table 3.

TABLE 2.—POWDER PATTERN OF CRYSTAL FALLS STILPNOMELANE Fe RADIATION, 114.6 mm. DIAMETER

INT	$d$ -obs	$d$ -calc	$h$	$k$	$l$	$h$	$k$	$l$	TYPE
10+	12.3	12.4	0	0	1				T1
2	7.14	7.2	1	0	-2				T3
5	6.26	6.21	0	0	2				T1
4	5.42	5.42	2	2	-2				T2
4	4.68	4.68	0	4	-3	4	-4	1	T2
2	4.36	4.20	0	4	-4	4	0	-3	T2
10	4.16	4.14	0	0	3				T1
1	3.78	3.74	-1	1	3				T3
4B	3.61	3.61	1	0	3	0	1	-4	T3
3	3.36	3.33	1	0	-4	0	1	3	T3
6	3.12	3.10	0	0	4				T1
1	2.98			Many					T2
7	2.686	2.687	4	4	-5				T1
10	2.547	2.551	4	4	-6				T1
2	2.48	2.483	0	0	5				T1
5	2.345	2.346	4	4	-7				T1
3	2.192	2.194	4	4	-1				T1
4	2.1173	2.1183	4	4	-8			*	T1
2	2.02			Many					T2
2	1.9716	1.9708	4	4	0			*	T1
5	1.8999	1.9003	4	4	-9			*	T1
1	1.828			Many					T2
2	1.778	1.774	0	0	7				T1
1B	1.734			Many					T2
4	1.7039	1.7050	4	4	-10			*	T1
1	1.636	1.634	9	5	-6				T2
2	1.591	1.589	4	4	2				T1
6	1.5677	1.5679	12	0	-5			*	T1
4	1.5540	1.5555	12	0	-4	12	0	-6	* T1
2	1.5364	1.5357	4	4	-11			*	T1
2	1.5210	1.5201	12	0	-3	12	0	-7	* T1
2	1.468	1.466	12	0	-2	12	0	-8	T1
3	1.4361	1.4365	4	4	3			*	T1
2B	1.427			Many					T2
2	1.3539	1.3542	8	8	-8			*	T1
1	1.3356	1.3358	8	8	-7			*	T1
3	1.3058	1.3060	4	4	4			*	T1
1	1.276	1.275	8	8	-12				T1
1	1.261	1.260	8	8	-5				T1
1	1.210	1.209	8	8	-4				T1
4	1.1549	1.1541	8	8	-3			*	T1
2B	1.098	1.097	8	8	-2				T1
3	1.058	1.060	8	8	-16				T1
2	1.037	1.036	12	0	-14	12	0	4	T1
2	1.024	1.025	20	-16	3				T1
3B	1.016	1.017	20	-16	4				T1
2B	1.002	1.002	20	-16	5				T1

\* Used in least-squares parameter refinement.

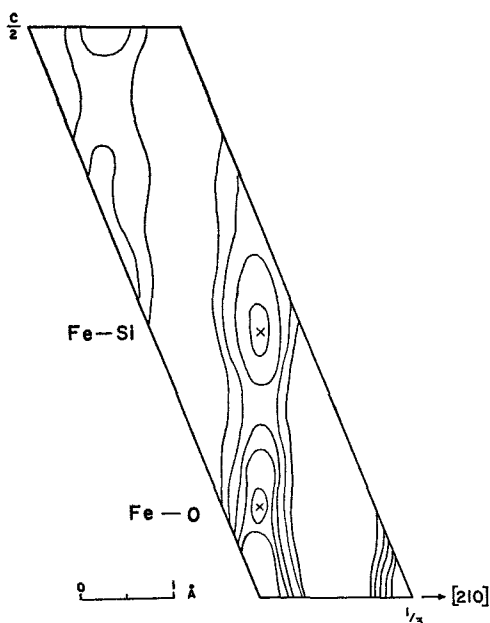
B Broad reflection.



TABLE 3.—LAYER SILICATE BASAL SPACINGS

Kaolin	7Å	3 anion planes
Talc	9Å	4 anion planes
Mica	10Å	4 anion planes expanded by K
Stilpnomelane	12Å	
Chlorite	14Å	6 anion planes

The similarities between the layer silicates and stilpnomelane indicate that the stilpnomelane structure is based on the layer silicate structure, as Gruner (1937) pointed out.

FIG. 3.— $hhl$  Patterson projection of stilpnomelane.

The positions of the silicon atoms were determined from  $\bar{h}hl$  and  $hhl$  sharpened Patterson projections (Figs. 3 and 4). The positions of the oxygens of the basal triad were deduced from packing considerations and by trial and error. The atomic parameters were refined using a full-matrix least-squares program written at the Los Alamos Scientific Laboratory and modified for use on the 1604 computer. An empirical weighting scheme was used; very strong reflections were weighted at 0.2 and those for which the  $L_p$  correction was large, at 0.5. A total of 296 reflections was used in the refinement, of which 10 were unobserved and given zero weight.

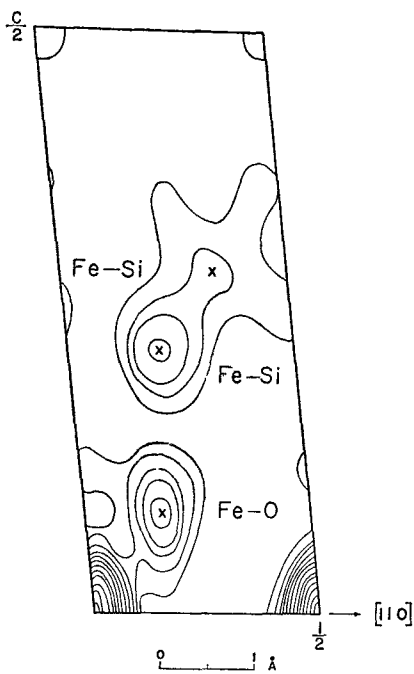


FIG. 4.— $hhl$  Patterson projection of stilpnomelane.

Because the subcell structure is an average structure, the refined sites give the mean positions of the atoms averaged over all the sixteen subcells in the unit cell. As a result, the refined temperature factors are extremely large, and this introduces uncertainty into the proposed model for the subcell structure. Six models were refined by least squares, differing from each other only in the positions of certain oxygen atoms. Each of these six models converged under least-squares refinement to give an  $R$  factor between 12 and 16 per cent. The model proposed was selected on the basis of steady and consistent temperature factors and tolerable interatomic distances. Because of the uncertainty of the oxygen positions, only temperature and scale factors were varied in the final two cycles of refinement, the atoms being held in the ideal sites indicated by previous cycles. The final  $R$  factor was 14.4 per cent overall, 13.4 per cent weighted.

#### DESCRIPTION OF THE STRUCTURE

The final subcell structure (Table 4, Fig. 5) has an atom content slightly less than that determined from analysis, cell volume and density, and is  $(\text{Si}_{3.5}\text{Al}_{0.5}) (\text{Fe}_{2.1}^{3+} \text{Al}_{0.13}^2) (\text{Fe}_{0.03}^{2+} \text{Mg}_{0.63})\text{O}_{9.5}(\text{OH})_{4.5}$ . This composition was

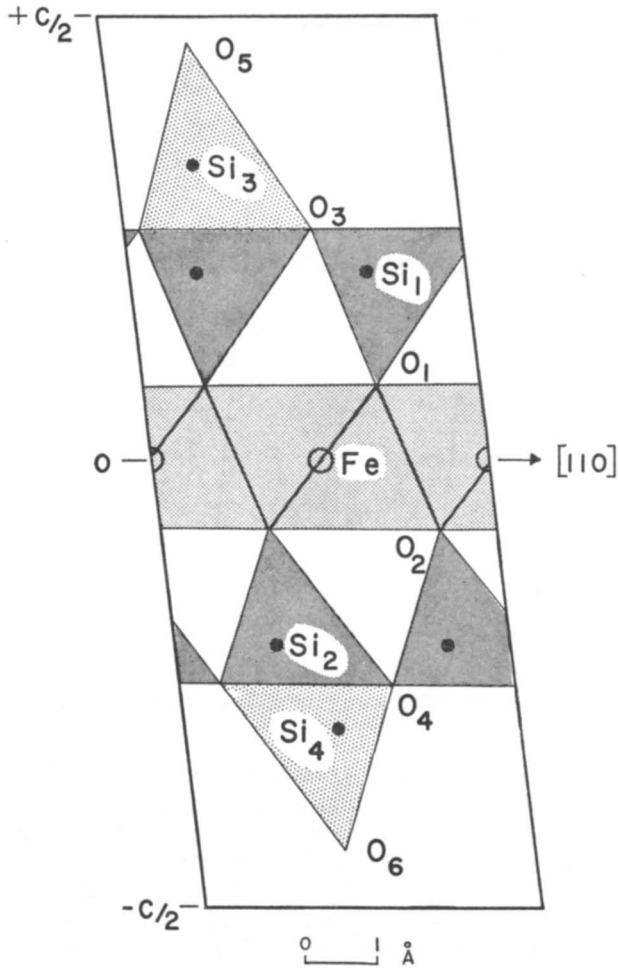


FIG. 5.—Diagram of the stilpnomelane subcell structure.

adopted to satisfy the stacking requirements of oxygens O<sub>5</sub> and O<sub>6</sub>, for at the level of these atoms only two oxygens per subcell can be accommodated. In addition, a total content of three oxygens in O<sub>5</sub> and O<sub>6</sub> caused the temperature factors of these atoms to increase indefinitely under least-squares refinement, whereas a reduction to two oxygens made them stable.

The stilpnomelane structure has an octahedral sheet containing 2.23 (Fe,Al) + 0.66(Fe,Mg,Mn), which is flanked by two tetrahedral sheets. Each tetrahedral sheet has 1.25 tetrahedra pointing toward the octahedral sheet and co-ordinated to the octahedral anions, and 0.75 tetrahedra pointing away.

In most layer silicates the total octahedral cation charge is + 6, and there are four tetrahedral cations co-ordinated to the octahedra. In stilpnomelane a higher charge on the octahedral cations (+ 8) is possible because only 2.5 Si co-ordinate to the octahedra, permitting 3.5 anions to be co-ordinated to the octahedral cations alone. Because there are six basal oxygens in the tetrahedral sheet, and 9.5 oxygens altogether, the octahedral sheet can contain at the most 3.5 oxygens, leaving a residual charge of + 1 on the sheet. The remainder of the hydroxyls are probably in the positions labelled  $O_5$  and  $O_6$ , 1.5 are co-ordinated to  $Si_3$  and  $Si_4$  as apical anions, and 0.5 hydroxyl is unco-ordinated. The tetrahedral sheets thus have a charge of  $-1/2$  each, balancing the charge on the octahedral sheet.

The final co-ordinates of the basal oxygens of the tetrahedral sheet are those of the close-packed sites relative to the octahedral anions. Such positions give an oxygen—oxygen bond distance of 3.13 Å, very much larger than the theoretical distance of 2.64 Å (Brown and Bailey, 1963). It must, therefore, be assumed that the positions of these oxygens differ between subcells, with the close-packed sites as their mean position. This assumption is consistent with the large temperature factors found for  $O_3$  and  $O_4$ .

### Bond Lengths

Oxygens  $O_3$ ,  $O_4$ ,  $O_5$  and  $O_6$  are all in average sites, hence bond lengths involving these atoms are of little significance and are not given in Table 5. Standard deviations are not given for the bond lengths listed, since the average nature of the subcell and the anisotropy of the oxygens lead to an average value for the bond lengths.

TABLE 4.—FINAL ATOMIC PARAMETERS

Atom	<i>x</i>	<i>y</i>	<i>z</i>	B		
Fe	0	0	0	anisotropic		
Si <sub>1</sub>	0.360	0.909	0.216	2.3		
Si <sub>2</sub>	0.297	0.425	0.793	8.5		
Si <sub>3</sub>	0.557	0.224	0.334	5.2		
Si <sub>4</sub>	0.500	0.200	0.700	12.1		
O <sub>1</sub>	0.143	0.562	0.086	anisotropic		
O <sub>2</sub>	0.540	0.797	0.924	anisotropic		
O <sub>3</sub>	0.433	0.693	0.260	32		
O <sub>4</sub>	0.125	0.875	0.750	34		
O <sub>5</sub>	0.783	0.586	0.470	19		
O <sub>6</sub>	0.293	0.857	0.564	16		
	<i>b</i> <sub>11</sub>	<i>b</i> <sub>22</sub>	<i>b</i> <sub>33</sub>	<i>b</i> <sub>12</sub>	<i>b</i> <sub>13</sub>	<i>b</i> <sub>23</sub>
Fe	0.073	0.047	0.019	-0.013	0.023	0.039
O <sub>1</sub>	0.126	0.030	0.000	-0.051	0.000	0.000
O <sub>2</sub>	0.236	0.076	0.023	-0.108	0.031	0.042

*Tetrahedral Sheet*

The ideal silicon-oxygen distance for a pure silicon tetrahedron in a layer silicate is about 1.62 Å, and this distance increases with increased substitution of aluminum for silicon. The average Si—O apical distance for the tetrahedra pointing toward the octahedra is 1.62 Å, whereas the distance in the tetrahedra pointing away is about 1.69 Å, suggesting that the bulk of the aluminum is concentrated in the latter tetrahedra, Si<sub>3</sub> and Si<sub>4</sub>.

TABLE 5.—BOND LENGTHS

Octahedral distances (Å)		Tetrahedral distances (Å)	
Fe—O <sub>1</sub>	2.10	Si <sub>1</sub> —O <sub>1</sub>	1.61
Fe—O <sub>2</sub>	2.04	Si <sub>2</sub> —O <sub>2</sub>	1.63
O <sub>1</sub> —O <sub>1</sub>	3.14		
O <sub>2</sub> —O <sub>2</sub>	3.14		
O <sub>1</sub> —O <sub>2</sub>	2.71		

The distance between the coplanar oxygens in the stilpnomelane octahedra is about 3.13 Å, and an ideal hexagonal tetrahedral sheet having these anions as apical oxygens would have a basal oxygen—oxygen separation of 2.72 Å. This separation is much greater than the theoretical oxygen—oxygen distances of 2.64 for a tetrahedral sheet with the composition Si<sub>3.5</sub>Al<sub>0.5</sub> as given by Brown and Bailey (1963). The misfit between octahedral and tetrahedral layers could be compensated in three ways. If some of the silicon tetrahedra were replaced by ferric iron tetrahedra, the larger iron tetrahedra would cause an expansion of the sheet and permit registry with the octahedral sheet. Actually, the structure determination gives no indication that this occurs. Indeed, the observed intensities require that all the iron be concentrated in the octahedral sheet and that the total scattering power of the tetrahedral cations do not exceed that of four silicons.

A second method of compensation involves changing the nature of the tetrahedral sheet from the normal hexagonal-layer silicate arrangement. Inversion of some of the tetrahedra in a sheet so that they point away from the octahedral sheet removes some of the restrictions on the orientation of the tetrahedra and permits local warping to achieve a fit. Overall, the tetrahedral sheet cannot expand and still remain a continuous sheet. In order to achieve the necessary expansion, discontinuities in the sheet would have to occur. Such faults in the tetrahedral sheet, occurring at regular intervals, could well give rise to the observed T3 reflections.

Further evidence that something of this nature occurs in stilpnomelane is given by the co-ordinates and temperature factors of the basal oxygens. The least-squares refinement showed no tendency to move the basal oxygens away from the close-packed sites relative to the octahedral oxygens. If the tetrahedral sheet were regular and continuous, as would be the case if iron substituted for silicon, the basal oxygens would be displaced systematically

from the close-packed positions, and least-squares refinement should reveal this. In fact, initial positions, suitably displaced, tended to move back to the close-packed sites under least-squares refinement.

The basal triads of a tetrahedral sheet can be superimposed on an octahedral sheet in two orientations  $60^\circ$  apart. If it is assumed that both orientations are present in the supercell, with faults at the change in tetrahedron orientation, then the oxygen would appear to be distributed over nine sites in the subcell. These nine sites are in three groups of three, each group being centered over one of the close-packed sites relative to the octahedral anions. The atoms of each group are equidistant from the close-packed site and disposed in three directions at  $120^\circ$  to each other. In the average structure each of the three groups would appear as a single atom at the mean point of the displacements but with a large temperature factor, as was observed.

A third method of compensation for the differences between the tetrahedral and octahedral sheets is indicated by some of the least-squares cycles. In certain models tested,  $\text{Si}_4$  tended to move into the plane of its basal oxygens ( $\text{O}_4$ ). Although other inconsistencies in the models suggest that this arrangement is unreal, it may be that the aluminum is in a fivefold site, co-ordinated to an upper octahedral anion, three oxygens of the tetrahedral sheet, and to an anion below, rather than in a tetrahedron pointing away from the octahedra. Andalusite (Burnham and Buerger, 1961) contains a five-co-ordinated aluminum, the greatest oxygen—oxygen distance of which is  $2.9 \text{ \AA}$ . If it is assumed that one five-co-ordinated Al is present for every seven silicon tetrahedra, the tetrahedral sheet can be expanded to  $5.37 \text{ \AA}$  in a subcell. However, this is still somewhat less than the observed value for the subcell edge of  $5.43 \text{ \AA}$ .

The apical oxygens of the tetrahedra pointing away from the octahedra do not link the two tetrahedral sheets. Packing considerations show that if twelve anions in each supercell are in site  $\text{O}_6$  co-ordinated to  $\text{Si}_3$ , and twelve more in site  $\text{O}_6$  co-ordinated to  $\text{Si}_4$ , then there are vacancies between the two sheets large enough to accommodate a further twelve anions of like size. Each of the tetrahedral sheets proposed have twelve tetrahedra with apices at this level; however, the twenty-four apical anions do not satisfy the charge on the tetrahedral sheets. The residual charge may be balanced by a further eight OH, positioned midway between the two sheets. These hydroxyls would serve to hold the tetrahedral sheets together.

#### *Presence of Alkalis in Stilpnomelane*

Many analyses of stilpnomelane show a small amount of alkalis, amounting to a few atoms per supercell. At the level of  $\text{O}_5$  and  $\text{O}_6$  there are only thirty-two anions, while there is room for at least thirty-six ions of the size of oxygen. The alkalis can thus be accommodated in the vacancies at this level. However, because the sample studied contained no alkalis, this location of them cannot be proved.

*Formation of Stilpnomelane*

Hutton (1938) suggested that stilpnomelane forms as the ferrous iron variety and is later oxidized to form ferric stilpnomelane. The structure proposed here for ferric stilpnomelane is consistent with this proposition. The ferrous iron cation, being larger than the ferric, requires a larger octahedron to accommodate it. This larger octahedron would have even more tendency to force the inversion of some tetrahedra. If it is assumed that 2.5 silicons coordinate to the octahedra, as in the sample studied, then there must be at least 2.5 oxygens in the octahedra. Therefore the octahedral sheet of the pure ferrous stilpnomelane would contain 2.5 oxygens and 3.5 hydroxyls, giving a net charge of zero. The theoretical subcell composition becomes  $(\text{Fe}^{2+}, \text{Mg})_3 (\text{Si}, \text{Al})_4 \text{O}_8 (\text{OH})_6$ . Hutton (1938) gives an analysis for ferro-stilpnomelane, which, recalculated to  $14 \text{O} + \text{OH}$ , is  $(\text{Fe}^{2+}, \text{Mg})_{2.8} \text{Fe}_{0.2}^{3+} (\text{Si}, \text{Al})_4 \text{O}_{8.1} (\text{OH})_{5.9}$ . Oxidation of the ferrous iron can be accomplished with concomitant reduction of hydroxyl to oxygen without major rearrangement of the structure. However, this does not necessarily imply that all ferric iron stilpnomelane initially formed as the ferrous variety.

The average structure proposed still leaves some questions unanswered. The unit cell content determined from the chemical analysis, cell volume and density is greater than that found by the structure determination. The actual cell content may well be between the two values. The role of magnesium, recorded in most stilpnomelane analyses, has not been determined. If stilpnomelane forms as ferro-stilpnomelane, the magnesium may be accepted in the octahedral sheet together with the iron. Oxidation of a ferro-stilpnomelane containing no magnesium would produce such a high charge on the octahedral sheet that the structure might break down, thus explaining the lack of magnesium-free ferric iron stilpnomelanes.

It is hoped that these problems will be at least partly solved by the analysis of the superstructure at present in progress.

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