The Structure of Chrysotile $H_4Mg_3Si_2O_9$.

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(With 3 figures.)

Summary.

Chrysotile $H_4Mg_3Si_2O_9$ is a member of the serpentine group, occurring in bundles of parallel fibres, with random orientation about the fibre axis. An X-ray pattern from a stationary bundle of fibres gives the equivalent of a rotation photograph, about one of the crystalline axes which we have taken to be the "c" axis. The reflexions are not very numerous, and certain of them are very diffuse. Owing to the random orientation around "c" of the crystals in all specimens of chrysotile, it is not possible to obtain rotation photographs about the other axes. The experimental data are therefore meagre, and the structure we propose is not completely established, though we believe its main features to be correct.

The unit cell is monoclinic, with $a = 14.66$ Å, $b = 18.5$ Å, $c = 5.33$ Å and $\beta = 93°16'$. The space group is probably C_{2h}^3. The structure indicates a formula expressed by doubling the usual molecule $H_4Mg_3Si_2O_9$ and writing it $(OH)_6Mg_6Si_4O_{11}.H_2O$. There are four of these molecules in the unit cell. The projection of the structure on the "ab" plane is found from analogy to the amphiboles, and coordinates x and y are assigned to all atoms. The experimental data are not sufficient to decide between certain alternatives as regards the c coordinates. Calculated structure amplitudes for a number of planes around the "c" zone are in good agreement with the observed intensities.

In the above formula, the hydrogen atoms have been associated with an oxygen atom, which in the structure is found to have a definite position at symmetry centres. However the nature of the structure indicates that there are no water molecules but that each hydrogen atom is shared by two oxygen atoms, $O-H-O$. Each silicon is surrounded by four oxygens tetrahedrally arranged. Part of the oxygens are shared between neighbouring tetrahedra, forming endless chains of silicon-oxygen tetrahedra lying parallel to the "c" axis. The chains have a composition Si_4O_{11}, and are similar to the chains previously found in the amphiboles. Between the sets of chains are sections of Mg and OH arranged as in Brucite. The lateral binding between the chains is weak, being largely due to secondary forces only, and the structure therefore offers a ready explanation of the fibrous nature of chrysotile, and of the fact that the fibres are so flexible and easily separated. A large part of the fibrous asbestos of commerce is chrysotile.

I. Introduction.

Chrysotile $H_4Mg_3Si_2O_9$ is a member of the serpentine group, usually occurring as fine silky fibres, and forming a large part of the fibrous material known as commercial asbestos. Of the various fibrous silicates, chrysotile is probably the most perfectly fibred, the fibres being quite long, flexible, and readily separated. Chrysotile occurs only as a secondary mineral, and single crystals are unknown. It is usually found in blocks of parallel fibres, with the individual fibres microscopically small, and randomly oriented about the fibre axis. Due to the lack of single crystals, the axial ratios and crystal symmetry are unknown.

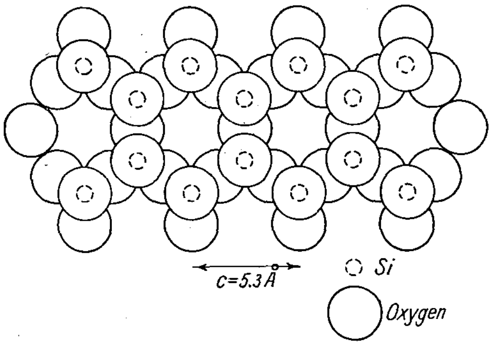

Fig. 1. Silicon-oxygen chain. This type of chain forms the basis of the amphibole and chrysotile structures.

For two other forms of fibrous asbestos, the monoclinic and orthorhombic amphiboles, the crystal structures have already been completely determined[1]).

Each silicon was found to be surrounded by four oxygens arranged at the corners of a tetrahedron. Part of these oxygens of each tetrahedral group are shared with neighboring groups in such a way as to build up endless chains of silicon-oxygen tetrahedra, linked together at their corners by shared oxygens. The silicon-oxygen chain so formed is shown in Fig. 1. In the amphibole structures it was found that these silicon-oxygen chains lay parallel to the "c" axis of the crystal, and consequently parallel to the direction of the fibre, so that the fibrous nature of these substances is readily accounted for in terms of the chains out of which they are built. The physical properties of chrysotile now suggest immediately that here again some sort of silicon-oxygen chain must be responsible for the distinctly fibrous character.

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[1]) B. E. Warren, "The crystal structure and chemical composition of the monoclinic amphiboles". Z. Krist. **72**, 493. 1930. — B. E. Warren and D. I. Modell, "The structure of Anthophylite". Z. Krist. **75**, 161. 1930.

II. X-Ray Determination of Axial Lengths.

In a specimen of chrysotile, the individual fibres are randomly oriented about the fibre axis ("c" axis), so that if a block of fibres is mounted with the fibre axis perpendicular to the direction of the X-ray beam, one obtains what is equivalent to a "c" axis rotation photograph, and without it being necessary to rotate the crystal specimen. Due to the fact that the fibres are already randomly oriented about "c", it is readily seen that only this "c" axis rotation photograph can be obtained, oscillation and rotation photographs about the other axes are impossible.

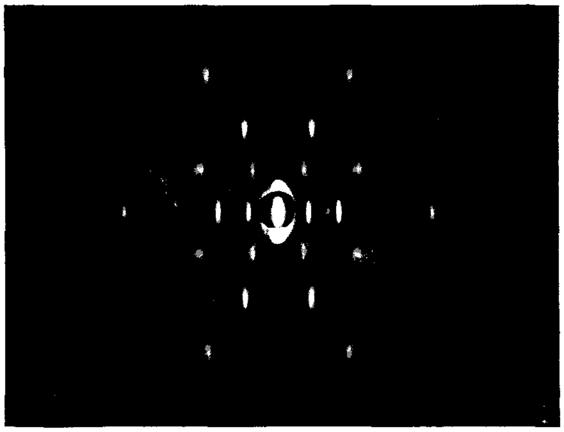

Fig. 2. "c" axis rotation photograph of chrysotile. The specimen was a bundle o parallel fibres with random orientation about the fibre axis, so that rotation of the specimen was not necessary.

The material used was a Chrysotile from the Thetford Mines, Quebec, and consisted of blocks of fine parallel fibres about two inches long. The "c" axis rotation photograph Fig. 2 was made with a slender column of this material about 0.5 mm. cross section, placed perpendicular to the X-ray beam ($K_\alpha Mo$).

From the layer line distances, the length of the "c" axis is calculated in the usual way as $c = 5.33$ Å. Since rotations about the other two axes are impossible to obtain, the lengths of "a" and "b" must be calculated from the various spacings. The "c" axis rotation photograph is too poor in well defined reflexions to lead directly to a determination of the true axial lengths. Only in the later stages of the analysis, after the structure itself has been deduced, can it be determined what indices should be assigned the various reflexions. For simplicity we will anticipate these later results and assign immediately the indices which in the later stages of the analysis are found to be correct.

On the equator there occur six reflexions which are readily found to be the successive orders of a plane with spacing 7.32 Å. Calling these reflexions 200, 400, 600 etc., then $d_{100} = .14.64$ Å. In Table I are given the ξ[1]) values of these six reflections on the equator and of certain reflections on the second layer line.

Table I.

ξ values of hol reflexions.

Equator	.097	.195	.292	.388	.486	.584
1 st L. L.						
2nd L. L.	$\overbrace{.082 \quad .112}$	$\overbrace{.180 \quad .210}$	$\overbrace{.277 \quad .307}$	$\overbrace{.374 \quad .403}$		

To each reflexion on the equator there corresponds a pair of reflections on the second layer line, and differing by $\pm \cdot 015$ in ξ value. These reflexions are accordingly assigned the indices 202, $\bar{2}02$, 402, $\bar{4}02$ etc. From the separation of these pairs of spots on the second layer line, the angle β is readily calculated.

$$\operatorname{ctn} \beta = \frac{-.015}{2c^*} = \frac{-.015}{2 \times 0.132} = -0.057$$

$$\beta = 93^\circ 16'$$

It follows that $a = 14.66$ Å. By taking $b = 18.5$ Å and perpendicular to "a" and "c", five well developed spots take the indices 040, 0120, 061, 0122, and 063. The tentative monoclinic cell has then the following dimensions:

$a = 14.66$ Å
$b = 18.5$ Å
$c = 5.33$ Å $\quad a:b:c = 0.791:1:0.288$
$\beta = 93^\circ 16'$

In the unit cell there are 8 molecules of composition $H_4Mg_3Si_2O_9$.

$$n = \frac{14.7 \times 18.5 \times 5.33 \times 10^{-24} \times 2.5 \times 0.606 \times 10^{24}}{277} = 7.9$$

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[1]) ξ is the radial coordinate of the corresponding reciprocal lattice point. J. D. Bernal, "On the interpretation of X-ray, single crystal, rotation photographs". Pr. Roy. Soc. (A) **113**, 117.

III. Atomic arrangement.

Since the only X-ray data available is the single "c" axis rotation photograph, any straightforward deduction of the atomic arrangement is of course impossible. However, our knowledge of silicate structures, and of the general laws which these structures obey is now sufficiently extensive to allow us to predict with some confidence a possible structure. Having once predicted an atomic arrangement, it is then a simple matter to test its correctness by the available X-ray data.

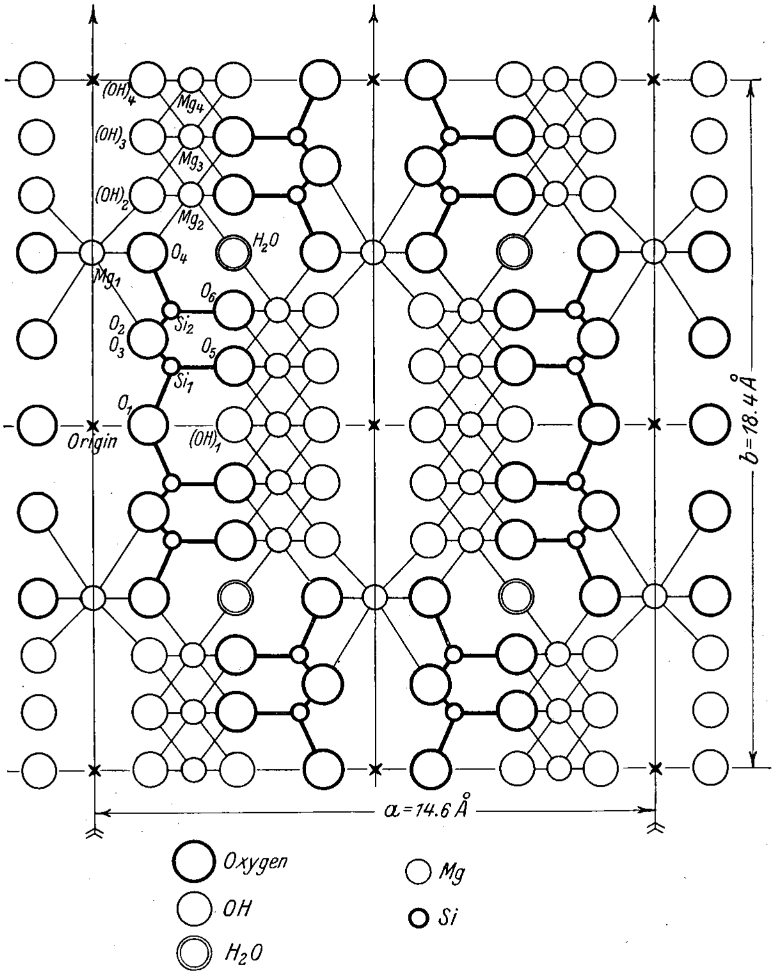

Fig. 3. Projection of the chrysotile structure perpendicular to "c". The heavy lines connecting silicon to oxygen outline the cross section of the silicon oxygen chain.

The accepted chemical composition of chrysotile is $H_4Mg_3Si_2O_9$, and from previous experience with silicate structures one is tempted to write this immediately as $(OH)_4Mg_3Si_2O_5$. A silicon oxygen ratio of 2 to 5 is one in which each silicon-oxygen tetrahedron must share three of its oxygens with neighboring tetrahedra. Such a silicon oxygen ratio should give rise to sheets of coordinated tetrahedra, similar to the Si_2O_5 sheets in the mica structure recently deduced by Pauling1). The fibrous nature of chrysolite is however not at all in agreement with such a sheet structure. The physical properties point to a structure of silicon-oxygen chains, similar to the chains found in the fibrous amphiboles, and the fact that the "c" axis in chrysotile $c = 5.33$ Å is very nearly equal to the "c" axis in the amphiboles 5.26 Å is in agreement with this idea. The composition of the amphibole chains was found to be Si_4O_{11}, and it is now readily seen that by doubling the molecule, and separating one molecule of water, such a silicon oxygen ratio is produced:

$$2\,H_4Mg_3Si_2O_9 = (OH)_6Mg_6Si_4O_{11} \cdot H_2O.$$

There will be 4 of these molecules in the unit cell.

From analogy to the amphibole structures previously determined, the probable atomic arrangement is now immediately suggested. Fig. 3 shows a projection of the structure perpendicular to "c". Parallel to the "a" axis the structure is seen to be pairs of Si_4O_{11} chains placed back to back, and between the pairs of chains are layers of Mg and OH as in the structure of Brucite $Mg(OH)_2$. It is immediately satisfying to note that the "a" and "b" axes of the unit cell are in good agreement with the "a" and "b" lengths which would be calculated from the dimensions in the amphibole and brucite structures. Both the axes and the structure suggest monoclinic symmetry, and from the proposed atomic arrangement the space group is seen to be C_{2h}^3.

From the projection of the structure in Fig. 3 approximate coordinate θ_1 and θ_2 can be assigned the atoms.

Using the tentative coordinates θ_1 and θ_2 in Table II, and the appropriate f values of the atoms, the amplitude contributions F for the reflections $(hk0)$ can now be calculated and compared with the observed intensities of the corresponding spots on the rotation photograph. For the proposed structure the amplitude contribution per unit cell F takes the form;

$$F_{hko} = \sum_m \begin{Bmatrix} 8 \\ 4 \end{Bmatrix} f_m \cos(h\theta_1)\, \cos(k\theta_2)$$

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1) L. Pauling, Pr. Nat. Acad. Sci. **16**, 123. 1930.

Table II.

Atomic coordinates in chrysotile.

The coordinates are given in degrees and in decimal parts of the axial lengths.

Atom	No.	θ_1	θ_2	X	Y
O_1	4	35	0	.10	.00
O_2	8	35	45	.10	.13
O_3	8	35	45	.10	.13
O_4	8	35	90	.10	.25
O_5	8	90	28	.25	.08
O_6	8	90	62	.25	.17
H_2O	4	90	90	.25	.25
$(OH)_1$	4	90	0	.25	.00
$(OH)_2$	8	35	118	.10	.33
$(OH)_3$	8	35	152	.10	.42
$(OH)_4$	4	35	180	.10	.50
Si_1	8	48	28	.13	.08
Si_2	8	48	62	.13	.17
Mg_1	4	0	90	.00	.25
Mg_2	8	64	118	.18	.33
Mg_3	8	64	152	.18	.42
Mg_4	4	64	180	.18	.50

On the "c" axis rotation photograph, the $(hk0)$ reflexions will be found on the equator. For reflexions on the equator, and with $\sin\theta$ small the calculated amplitude contributions F are related to the observed intensities by the following approximate relation:

$$I \propto \frac{F^2}{\sin\theta}$$

In Table III are given the calculated contributions F for 25 reflections $(hk0)$, and a comparison of calculated values of $\frac{F}{(\sin\theta)^{\frac{1}{2}}}$ with the corresponding observed intensities. The agreement is seen to be good for the spectra $(h\,0\,0)$ and $(0\,k\,0)$ and explains the relative weakness of the $(hk0)$ spectra.

In additilon the reflexions 0120 and 063 are both very strong, in keeping with the pseudo hexagonal character of the structure when viewed in the direction of the "a" axis. Although a complete structure determination has not been made, the projection of the structure perpendicular to "c" serves to bring out nearly all of the features of interest. Because of this, we have not attempted to determine the "c" coordinates of the atoms with the very meagre data which is available.

Table III.

Calculated amplitude contributions F for reflexions $(hk0)$ and comparison of calculated $\frac{F}{(\sin\theta)^{\frac{1}{2}}}$ with corresponding observed intensities.

$hk0$	$\sin\theta$	F	$\frac{F}{(\sin\theta)^{\frac{1}{2}}}$	Obs. Int.
200	.0484	188	853	V. S.
400	.0968	282	906	V. S.
600	.1452	59	155	W.
800	.1936	95	215	W.
1000	.2420	82	166	W.
1200	.2904	102	189	W.
1400	.3388	100	172	W.
1600	.3872	60	97	W.
020	.0386	0	0	n. obs.
040	.0772	76	272	W.
060	.1158	0	0	n. obs.
080	.1544	44	110	n. obs.
0100	.1930	0	0	n. obs.
0120	.2316	408	848	V. S.
0140	.2702	0	0	n. obs.
110	.0310	20	113	Weak and too diffuse to be identified
130	.0625	60	230	
150	.0990	76	230	
220	.0620	60	230	
240	.0908	30	99	
260	.1240	16	45	
310	.0752	30	109	
330	.0925	40	130	
350	.1205	48	136	
420	.1042	48	148	

IV. Discussion of structure.

The very interesting physical properties of chrysotile appear to be readily explained in terms of the crystal structure. The structure is built up of silicon-oxygen chains similar to those which were found in the amphiboles. The strong bonds between silicon and oxygen exist only within the chains, and consequently give them a considerable strength along the direction of the chain. The lateral binding between the chains is however very weak, much weaker in fact than in the amphiboles. Inspection of Fig. 3 will show that sections of the structure can be mapped out containing one chain and the five adjacent *Mg* octahedra such that this section is bound by very few and very weak forces to the remainder of the structure. There are certain areas in the structure across which the material is held together only by weak secondary forces. The structure therefore offers a complete explanation of the physical properties of chrysotile, explaining its fibrous nature, and also the fact that the fibres are so very flexible and readily separated. Due to the fact that secondary forces play such an important role in the structure, it is readily understood why single crystal fibres never develop to any appreciable size laterally, and why the material always occurs as bundles of parallel fibres with random orientation about the fibre axis.

The chemical composition has been written in such a way that the unit cell contains 4 molecules; $(OH)_6 Mg_6 Si_4 O_{11} \cdot H_2O$. As is seen by reference to Fig. 3, the four H_2O molecules occupy definite positions in the structure, each H_2O completing two Mg octahedra.

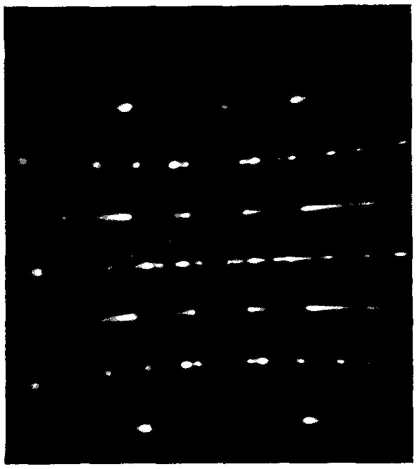

Fig. 4. Photograph of Chrysotile, showing the spreading of the spots along the layer lines (Clark and Aborn).

It is possible that these four units should not be considered as H_2O molecules, but as oxygen atoms sharing two hydrogen atoms with two neighbouring oxygen atoms. These latter are each attached to silicon and two magnesium atoms, and hence (by **Pauling**'s rule) have a residual-valency which a link to hydrogen would compensate.

A striking feature of the photographs is the diffuseness of certain spots as contrasted with the sharpness of others. This is well brought out in Fig. 4[1]). Corresponding spots are diffuse in several varieties which

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[1]) This photograph was taken by Dr. **Aborn**, Massachusetts Institute of Technology, to whom we wish to express our indebtedness.

we have examined, and the effect is also apparent in the photographs of Anderson and Clark[1]). This suggests a variation in the spacing of the corresponding planes. Since the spots are drawn out along the layer lines, which are sharply defined, the "*c*" axis must be very constant in length. It is perhaps significant that the diffuseness is further confined to reflexions by planes for which the index "*k*" is not zero, suggesting that variability in length is limited to the *b* axis. This conclusion is in accord with the structure, for it is possible to picture modifications which would affect the repeat in the "*b*" direction, whereas the lengths of "*c*" and "*a*" are definitely fixed by the general plan.

Chrysotile is seen to be built up by the double silicon-oxygen chains which have been shown to be the structure units characteristic of the amphiboles. In this respect, therefore, chrysotile is very closely related to the amphiboles.

The three forms of commercial asbestos; monoclinic amphibole, orthorhombic amphibole, and chrysotile all have one structural feature in common. All three are built up out of the same form of silicon-oxygen chain, and it is to this fact that they owe their fibrous property.

30th August 1930.

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[1]) H.V. Anderson and G. L. Clark, Industrial Chemistry, **21**, 924. 1929.