An X-ray study of the crystal-structure of antigorite.

(With Plate V.)

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ANTIGORITE is a lamellar variety of serpentine, and is supposed to be a dimorphous form of chrysotile, which is finely fibrous. Its chemical composition is approximately $H_4Mg_3Si_2O_9$, which is taken as the basis of calculations here.

This study was undertaken primarily because it was hoped that knowledge of the structure of antigorite would throw some light on that of chrysotile. Certain similarities between the two structures have been established, namely in the $c(7\cdot3kX$ or $14\cdot6kX)$, and $b(9\cdot2kX)$ directions.[1] There are two main differences, however. Firstly, imperfections which cause line broadening in the X-ray pattern of chrysotile, are absent in antigorite (apart from certain 'streaks'). Secondly, the $a(43\cdot4kX)$ axis of antigorite is approximately eight times longer than the corresponding axis in chrysotile. A complete determination of the structure has not been achieved, but the X-ray pattern has been described, and some suggestions made as to the explanation of the peculiarities observed. A further study of the outstanding questions is in progress.

There is some disagreement in the nomenclature of serpentines (cf. Dana,[2] Selfridge,[3] Caillère[4]). This X-ray study is limited to three specimens obtained through the courtesy of Prof. C. E. Tilley, and labelled as antigorite from: (1) Antigorio valley, Piedmont;[5] (2) Griffin range, Hokitika, New Zealand (no. 19343);[6] (3) Cropp river, Mikonui, New Zealand (no. 11566). Only the last sample is coarse enough to give small flakes suitable for single-crystal photographs. Except when otherwise stated, in this work 'antigorite' stands for the material from Mikonui. Powder photographs of the three minerals are compared in section 6.

The previous X-ray work on antigorite (Winchell,[7] Gruner,[8] Selfridge, and Caillère, both loc. cit.) has been confined solely to the powder method for mineral identification purposes. Gruner, however, has compared the powder patterns of antigorite and chrysotile, finding that the unit cells are comparable, and that the two structures are closely similar as regards the $c(14\cdot6kX)$ direction.

[1] 1kX = 1000 X-units, as defined by Siegbahn. $1kX = 1\cdot00203 \times 10^{-8}$ cm., according to the up-to-date value of Avogadro's number, $6\cdot0228 \times 10^{-23}$ per mole. Cf. H. Lipson and D. P. Riley, Nature, 1943, vol. 151, p. 250, and A. J. C. Wilson, ibid., p. 562. [M.A. 9-39.]

[2] Dana, Descriptive mineralogy, 6th edition, New York, 1892.

[3] G. C. Selfridge, Amer. Min., 1936, vol. 21, pp. 463-503. [M.A. 6-476.]

[4] S. Caillère, Bull. Soc. Franç. Min., 1936, vol. 59, pp. 163-326. [M.A. 6-475.]

[5] For a description and occurrence see T. G. Bonney, Quart. Journ. Geol. Soc. London, 1908, vol. 64, pp. 152-170.

[6] The specimen numbers given are those of the Department of Mineralogy and Petrology, Cambridge University.

[7] A. N. Winchell, Amer. Min., 1928, vol. 13, pp. 161-170. [M.A. 4-206.]

[8] J. W. Gruner, Amer. Min., 1937, vol. 22, pp. 97-103. [M.A. 7-93.]

E. ARUJA ON

Dana, Selfridge, and Caillère quote a number of optical and chemical data on antigorite. According to Mineralogical Abstracts, extensive data about antigorite may be found in a monograph on serpentine minerals by Lodochnikov.[1]

1. The unit cell.

Small flakes of antigorite from Mikonui, about 0·1 mm. thick, and 1 mm. long, which showed moderately clear isogyres under a polarizing microscope, were also suitable for single-crystal photographs. The adjustment of the specimens was performed by X-ray methods, because there was nothing to indicate the crystallographic directions in the specimen except that the flakes are approximately parallel to the (001) plane, and the short fibrous fragments which make up the flake are approximately parallel to the $b(9\cdot2kX)$ axis. Oscillation crystal photographs were taken about all three crystallographic axes. Weissenberg photographs were taken of the equatorial and the third layers of the b-axis, and also Laue photographs with X-rays parallel to the $c(7\cdot3kX)$ and $a(43\cdot4kX)$ directions respectively.

Except for Laue photographs, Cu–Kα radiation, filtered through a nickel foil, was used in this work. The camera employed was 60·0 mm. in diameter, and had a collimator of 0·7 mm. bore, 40 mm. long.

Oscillation and Laue photographs reveal only one symmetry plane, that perpendicular to the $b(9\cdot2kX)$ axis. Rotation and oscillation photographs about the three crystallographic directions agree with a monoclinic unit cell (cf. tables I, II, and III) of: a 43·39, b 9·238, c 7·265kX, β 91·40°.

The probable error in the determination of the axial lengths should be less than 0·1%. Of the inter-axial angles $\alpha = 90°$ with a high accuracy (cf. table II). The angle γ (90°) is not determined with the same accuracy (cf. table I). The monoclinic symmetry, however, is revealed by the observation of a plane of symmetry.

TABLE I. Antigorite from Mikonui, New Zealand. The equator of the c-axis rotation photograph. Cu–Kα (filtered) radiation, camera 60 mm. in diameter. Intensities are estimated visually. A stroke / in the column of intensities indicates that the reflection is a vertical streak. The calculations are for a monoclinic unit cell a 43·39, b 9·238, c 7·265kX, β 91·40°. $\Delta = 4\sin^2\theta_{obs} - 4\sin^2\theta_{calc}$.

$4\sin^2\theta_{obs}$	Intens.	hkl.	$\Delta \times 10^4$.	$4\sin^2\theta_{obs}$	Intens.	hkl.	$\Delta \times 10^4$.
0·1098	4/	020	−13	1·3634	5	17 6 0	− 1
		810	+14			33 0 0	−77
0·1300	3/	910	+2	1·4534	3	34 0 0	−20
0·3530	3	930	+11	2·2648	1	40 3 0	+5
0·3633	4	17 0 0	−6	2·3650	2	41 3 0	−13
0·8056	1/	17 4 0	−26			33 6 0	−57
0·9749	10	24 3 0	−3	2·9004	3	48 0 0	−3
1·0004	8	060	+8	2·9781	4	24 9 0	+38
1·0960	1	26 3 0	−51	3·8932*	3	48 6 0	− 7

* Observed a resolved Cu–Kα_1 line; for all other calculations a weighted mean wave-length, 1·53867kX, is used.

[1] V. N. Lodochnikov, Serpentine and serpentinite . . . Trans. Centr. Geol. Prosp. Inst. Leningrad, 1936, no. 38. (Russian, with German summary.) [M.A. 7-1.] Also E. S. Simpson, Journ. Roy. Soc. W. Australia, 1938, vol. 24, pp. 107–122. [M.A. 7-340.] T. Du Rietz, Geol. För. Förh. Stockholm, 1935, vol. 57, pp. 133–260. [M.A. 6-216.] B. P. Krotov, Mem. Soc. Naturalists Imp. Kazan Univ., 1915, vol. 47, no. 1. [M.A. 2-170.]

TABLE II. Antigorite from Mikonui, New Zealand. The equator of the $a(43\cdot39\text{kX})$ axis rotation photograph. Dots, or streaks, in the column of intensities indicate a row of spots, or horizontal streaks, respectively. Other details as for table I.

$4\sin^2\theta_{obs}$	Intens.	hkl.	$\Delta \times 10^4$.	$4\sin^2\theta_{obs}$.	Intens.	hkl.	$\Delta \times 10^4$.
0·0453	8 :	001	+4	1·0456	6 .	061	+11
0·1122	8 —	020	+11	1·1218	4 :	005	+2
0·1562	4 =	021	+2	1·1790	4 :	062	−1
0·1810	8 :	002	+15	1·4044	4 :	063	+10
0·2945	2 =	022	+39	1·6160	3 :	006	+9
0·4046	4 :	003	+8	1·7204	1 :	064	+30
0·4484	2 —	040	+41	2·1268	3 :	065	+46
0·4892	4 —	041	0	2·1968	2 :	007	−15
0·6248	3 =	042	+10	2·6178	3 :	066	+29
0·7184	4 :	004	+6	2·8712	2 :	008	−1
0·8192	1 =	024	−103	3·1992	2 :	067	+13
0·8508	1 =	043	+27	3·8634*	4	068	−9
0·9984	10 .	060	−12	3·8848*	2	068	+11

* Resolved Cu-Kα doublet.

TABLE III. Antigorite from Mikonui, New Zealand. Some reflections of the $a(43\cdot39\text{kX})$ axis photograph, showing the agreement of the monoclinic angle. Details as for table I.

$4\sin^2\theta_{obs}$	hkl.	$\Delta \times 10^4$.	$4\sin^2\theta_{obs}$.	hkl.	$\Delta \times 10^4$.
0·0897	710	+2	0·3524	73$\bar{1}$	−17
0·1090	810	+1	0·3728	83$\bar{1}$	+3
0·1313	910	+15	0·3935	93$\bar{1}$	0
0·1509	81$\bar{1}$	+5	0·7058	73$\bar{3}$	−19
0·1774	911	−2	0·7461	93$\bar{3}$	+7
0·3515	930	−4			

Density.—A 'molecule' of $H_4Mg_3Si_2O_9$ weighs $277\cdot1 \times 1\cdot650 \times 10^{-24}$ g. Assuming sixteen such molecules in a unit cell of dimensions given above, the density calculated by X-ray methods would be 2·51 g./cm.³ This is 3·5% smaller than the observed density of antigorite, 2·60 g./cm.³, obtained by flotation. The reasons for this discrepancy cannot be discussed before an analysis of the specimen used is obtainable. An isomorphous substitution by heavier atoms, for instance, may take place, as in chrysotile, where the contents of the unit cell actually weigh 1% more than would be in accordance with the ideal composition.

2. Special features of the X-ray pattern of antigorite.

The notable features of the X-ray pattern of antigorite are the streaks parallel to the c^* direction [an asterisk signifies the corresponding reciprocal axis], the variation of intensities of the spots in the a^* row-lines, and additional spots, on oscillation photographs, and radial streaks on Laue photographs. These features will be discussed separately.

(i) Streaks, instead of sharp reflections, parallel to the c^*-axis appear whenever the index k is not a multiple of three. These streaks are of maximum intensity at the reciprocal plane of the index l an integer, but they extend at least half-way between these reciprocal layers, possibly until the next integral value of l. A point of unknown significance is a picturesque bicycle-chain-like formation of streaks (pl. V, fig. 1): though the streaks may link up through consecutive layer-lines on the c-axis oscillation photographs, for the same h and k values there are never more than two consecutive layers thus bound with an unbroken streak.

This reveals the asymmetry of the streaks about the integer lattice point. Possible explanations for the streaks will be discussed in section 4.

(ii) The variation of the intensities of the reflections in the a^* row-lines resembles the phenomenon of beats in acoustics. Because of the length of the $a(43\cdot4kX)$ axis, the a^* row-lines are very prominent. The observed spots in every a^* row cluster, about certain h values, which are apparently a multiple of eight, including zero. This clustering is particularly evident on rotation, and on Weissenberg photographs, where not more than six spots appear in a cluster (pl. V, fig. 3). Occasionally, however, there appear on the oscillation photographs all the reflections in a row-line for every consecutive h value over a considerable range (pl. V, fig. 2). The average distance between the centres of gravity of such clusters in any row is sixteen, in units of the index h. Incidentally, the centre reflection itself at $h = n \times 8$ of such clusters may be occasionally of zero intensity. For instance, the $h02$ row (the fourth reflection from the centre, of fig. 3), where the reflection 002 is obviously missing. Other peculiarities are the rows $h20$, $h40$, and $h60$, for which the only reflections observed are those with $h = 0$, 17, and $\overline{17}$; higher orders in h are not in the range of reflection. An interval of seventeen in the h values between the strongest spots (as distinct from the distance between the apparent centres of gravity of clusters) in a row-line is observed also in some other rows, notably the $h11$ and $h1\overline{1}$ rows. (An average distance of seventeen in the h values of the centres of the clusters does not agree with the observations.) This grouping of spots in the row-lines is taken to indicate the presence of a kind of superlattice (cf. section 3).

(iii) Some additional spots appear on the oscillation photographs, notably on those about the b and c axes (pl. V, figs. 1 and 2). It seems, however, that all these spots can be accounted for by assuming the specimen to consist of several small fragments, each maladjusted by a turning movement of a few degrees of arc about the common $a(43\cdot4kX)$ direction. This dislocation may have been brought about when splitting the flake from the hand-specimen.

(iv) Laue photographs of antigorite show no conventional Laue spots, but spotty radial streaks: one streak every 60° approximately, when taken with X-rays parallel to the $c(7\cdot3kX)$ axis, and more irregular when the X-rays were parallel to the $a(43\cdot4kX)$ axis. The smearing-out of Laue spots into radial streaks could be explained either by the presence of a cross-grating structure, or by an imperfect alinement of the fragments in the specimen.[1] An imperfect alinement of the fragments has been observed on oscillation photographs, as described in the preceding subsection. On the other hand, there is evidence of, at least partial, scattering of thin lamellae (cf. the streaks parallel to the c^* direction, subsection (i)), which should also result in a cross-grating Laue photograph. Apparently, both of these causes contribute to the smearing-out of Laue spots of antigorite.

3. The sub-unit cell.

The clustering of spots at regular intervals along the a^* rows gives reason to assume a sub-unit cell of antigorite with an a-axis eight times shorter than that measured from the identity period in the a^* row-lines. [A symbol a' will be used to indicate this shorter axis.] Exactly how these sub-unit cells of $a' = 5\cdot4kX$ are

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[1] Cf. W. L. Bragg, Nature, 1929, vol. 124, p. 125.

piled up to make a unit cell of $a = 43.4$kX, cannot be said at present. It seems that there exists a distortion of one kind or another which makes the space-group of the crystal as a whole somewhat different from that of the sub-unit cell.

In describing the X-ray pattern of antigorite in terms of the sub-unit cell (with b, c, and β the same, but $a' = a/8 = 5.42$kX), we regard each cluster of spots as a single reflection (with a certain 'fine structure') and we obtain an index H for the whole cluster. A cluster with the indices Hkl is counted as a 'missing reflection' when there is no reflection hkl observed in the row with the index h between the values $8H-4$, and $8H+4$. To indicate the fact that the first index refers to a cluster of spots (and not to a single reflection in terms of the large unit cell) a subscript $_H$ is added, where necessary.

The following are the reflections (clusters) observed in terms of the sub-unit cell:

$00l_H$ all orders in l (observed for l up to 8)

$0k0_H$ only if k even (observed for $k = 2, 4, 6$)

$H00$ only if H even (observed for $H = 2, 4, 6$)

$H0l$ all orders in l, only if H even (observed for l up to 8, $H = 2, 4, 6$)

$Hk0$ only if $H+k$ even (observed for k up to 9, H up to 6)

Hkl all orders in l, only if $H+k$ even (observed on 229 occasions, for 113 different numerical combinations of the indices).

The probable space-groups for the sub-unit cell, consistent with the observed reflections, would be $C_{2h}^3 = C2/m$, $C_2^3 = C2$, or $C_s^3 = Cm$. These are the same space-groups as found for chrysotile.

4. Comparison of antigorite with chrysotile.

Comparing the a-axis rotation photograph of antigorite with the fibre diagram of chrysotile, the differences are: (i) in antigorite the a-axis is approximately eight times longer (in chrysotile it is 5.32kX). (ii) The 'tail' of certain reflections is shorter in antigorite, being one-half of that of the corresponding reflections of chrysotile. (iii) The reflections $hk0$ and hkl, which are very smeared-out in chrysotile, are reasonably sharp in antigorite. (iv) The $00l$'s and $h0l$'s fail to resolve into Cu-Kα doublets in chrysotile, but are resolved in antigorite.

There is a strong analogy between the intensities of the reflections of the minerals, particularly the $00l$'s and $0k0$'s. These comparisons induce one to suggest that antigorite has the same sequence of atomic planes parallel to (001) as chrysotile, which is built of kaolinite-like sheets with magnesium substitution, viz., $O_6-Si_4-O_4(OH)_2-Mg_6-(OH)_6$, and repeat.[1] One such layer measures approximately 7.3kX in thickness. In chrysotile the c-axis was taken 14.6kX, because of a few very weak $20l$ reflections, which may be absent in antigorite, or may be lost in the background.

Out of similar layers the structures of chrysotile and antigorite have to be built

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[1] Unpublished work, but an abstract, together with a photograph of the X-ray pattern of chrysotile, has appeared in an article entitled 'Summarized proceedings of conference on X-ray analysis, Oxford, 1944', in Journ. Sci. Instr., 1944, vol. 21, p. 15. [M.A. 9–39.] Chrysotile from Thetford, Quebec, is monoclinic, with a 5.32, b 9.2, c 14.62kX, β $93.2°$. The notation of the a and c axes has been interchanged, as compared with earlier publications, to bring the proposed structure into conformity with other sheet structures of silicates. Cf. also B. E. Warren, Amer. Min., 1942, vol. 27, p. 235 (abstract).

up so as to explain the peculiarities of their respective X-ray patterns. It seems that the problem can be divided into two parts: the explanation of the streaks parallel to the c^* direction, and the 'fine structure' of the clusters.

The streaks in the X-ray pattern of antigorite can be adequately explained by assuming that from sheet to sheet (or, possibly, every second sheet) an error occurs in the packing, viz. at random, in steps of $nb/3$, or owing to the base centering of the sub-unit cell, $ma'/2+nb/6$, where m and n are any integers whose

Si$_4$O$_{10}$ LAYER   BRUCITE LAYER   SEQUENCE

OF LINKED Si$_4$O$_4$ TETRAHEDRA
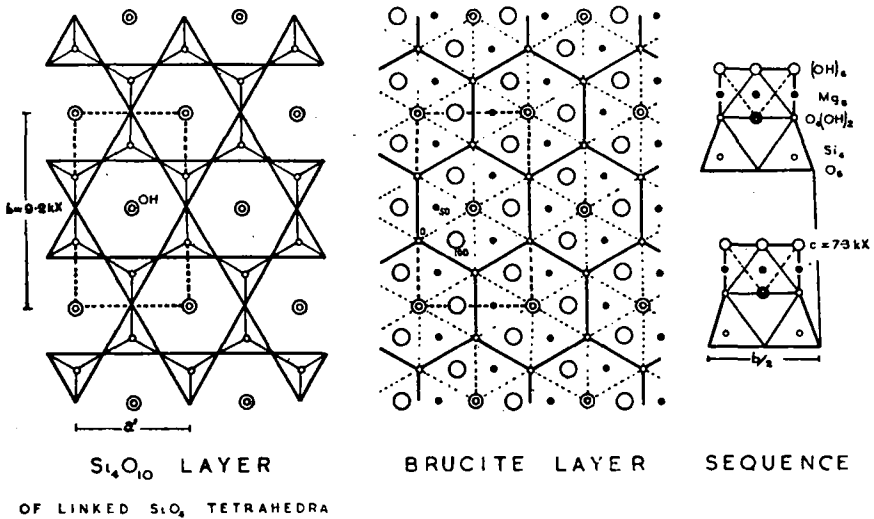
FIG. 4. Kaolinite-like sheet structure of chrysotile. LEFT: Si$_4$O$_{10}$ layer obtained by hexagonal linkage of SiO$_4$ tetrahedra. Silicon ions in the middle of the tetrahedra are not indicated. Double circles indicate the positions of hydroxyl in the plane of oxygen ions, at the top of the tetrahedra. MIDDLE: a projection of a brucite-like layer. Magnesium ions are situated in the octahedral cavities (black dots) between two close-packed hexagonal layers of (OH)$_6$ (open large circles), and O$_4$(OH)$_2$ respectively. RIGHT: a schematic representation of the sequence of atomic layers.

sum is even. Such a limited randomness ensures that the lamellae (7·3kX or possibly 14·6kX thick) scatter incoherently, except when the index k is a multiple of three (or $3H+k$ is a multiple of six). In the latter case, conventional crystalline reflections should appear, as they actually do in antigorite. When $k \neq n \times 3$ (or $3H+k \neq n \times 6$), streaks perpendicular to the lamellae should, and do, appear in the X-ray pattern. Such a limited randomness would predict that only the reflections with $k \neq n \times 3$ are streaky, and also it determines correctly the length of the streaks.[1] The proneness to a slip between the sheets of antigorite is easily understood by reference to text-fig. 4. Though the top of the 'brucite layer', and the base of SiO$_4$ tetrahedra contain the same number of ions per unit cell, their pattern is somewhat different, hence the instability of the fitting on top of each other of the sheets.

Unlike in chrysotile, no other distortion of the lattice (such as bending, or finite size) is required in antigorite to explain the length of the streaks or line

[1] Cf. P. P. Ewald, Proc. Physical Soc., 1940, vol. 52, pp. 167–174. [M.A. 8–133.]

broadening. However, as the streaks observed in case of antigorite are not symmetrical about the integer lattice point, as the theory of two-dimensional lattice reflections requires (cf. Ewald, loc. cit.), such a limited randomness in the packing of layers is not a full explanation.

Another mathematical treatment of the appearance of the streaks is given by A. J. C. Wilson,[1] in the case of cobalt, for powder photographs. In the type of defects of the crystals of antigorite, as described above, an error occurred in the piling up of sheets of identical structure factors. In cobalt, however, the structure factor may vary from one unit cell to the next. Such a variation in the structure factor is liable to happen in every structure where the unit cell has more than one structurally equivalent set of positions. This kind of 'mistake' may also occur in kaolinite-like sheets, in the choice of filling in the octahedral cavities with magnesium atoms. The octahedral cavities are formed between the close-packed layers of $O_4(OH)_2$ ions at the top of the sheet of SiO_4 tetrahedra, and $(OH)_6$ ions, text-fig. 4. There are two equivalent positions for the $(OH)_6$ layer, with a relative displacement of $a'/3$, consequently there are also two sets of octahedral cavities. The reflections with the index H a multiple of three would be independent of such variations in the structure factor—a fact notably manifested in the relative sharpness of the reflections of the third layer-line (a 5·3kX) of chrysotile. Although these reflections have not been observed on the Cu-Kα photographs of antigorite, it is likely that such a variation in the structure factor has some contributory effect to the appearance of the streaks. As a basis for a further study, the streaks shown on the c-axis oscillation photographs (pl. V, fig. 1) are particularly suitable.

A diffuseness of reflections parallel to one or another of the crystallographic directions has been observed on several occasions before. Hendricks[2] reproduces a number of Weissenberg photographs of micas on which streaks appear. He observes that amongst silicates such random layer structures which cause the streaks are more likely to appear when all the octahedral cavities are filled, that is, when the sheet is of higher symmetry. This is the case with magnesium silicates, of which antigorite and chrysotile are examples. In these silicates, however, according to Pauling[3] the sheets should be curved, because of the difference in the fundamental periodicity of Si_2O_5 and brucite $Mg(OH)_2$ sheets respectively.[4] In chrysotile the sheets seem to be curved to such an extent that the mineral is fibrous, and its X-ray pattern shows extensive line broadening. In antigorite no deformation of this kind is required to explain the X-ray pattern, except, perhaps, the slight asymmetry of the streaks. The expected stresses in the crystals of antigorite may have been avoided by crystallizing in a slightly different structure, owing to different geological conditions on its formation, as compared with chrysotile. For instance, although it seems that chrysotile and antigorite have the same sequence of atomic planes parallel to the (001) plane, antigorite may have a chain structure, as compared with a sheet structure proposed for chrysotile.

[1] A. J. C. Wilson, Proc. Roy. Soc., Ser. A, 1942, vol. 180, pp. 277–285. [M.A. 8–362.]

[2] S. B. Hendricks, Amer. Min., 1939, vol. 24, pp. 729–771. [M.A. 7–496.]

[3] L. Pauling, Proc. Nat. Acad. Sci., 1930, vol. 16, pp. 578–582. [M.A. 4–465.]

[4] The corresponding identity periods in the sheets of Si_2O_5 and $Mg(OH)_2$ are in the ratio of 16 to 17, a fact which seems to be of some importance in view of the observed distances between the centres of gravity of the clusters, and between the strongest spots in certain a^* row-lines, which were also 16 and 17 units in the index h respectively (cf. section 2 (ii)).

This assumption is supported by two considerations. Firstly, though the identity periods in silicates vary between 8·9 and 9·5kX, or twice this, for one axis, and between 5·1 and 5·5kX for the other, the axial ratio remains fairly constant for the same type of linking of the SiO_4 tetrahedra. This ratio is between 1·694 and 1·703 for the chain structures (tremolite, anthophyllite, diopside, hypersthene), and between 1·732 and 1·738 for the sheet structures (muscovite, phlogopite, pyrophyllite, talc, kaolinite, nacrite, dickite, cronstedtite). For ideal hexagonal structures the ratio of orthohexagonal axes is 1·732. For antigorite this ratio is 1·703 (in terms of the sub-unit cell), which places it amongst the chain structures, whereas chrysotile with its axial ratio of 1·729 comes near to the group of sheet structures.

Secondly, as Hendricks (loc. cit.) has shown, there exists a certain polymorphism in the sheet structures when the sheets are highly symmetrical and undistorted. This leads to a large unit cell in the direction perpendicular to the sheet. In antigorite, however, the lengthened a-axis lies in the plane of the sheet; thus, such a polymorphism could be pictured more easily on a model of chain structure, the chains running parallel to the a-axis. [If this is the case, the apparent fibrousness parallel to b(9·2kX) (cf. section 1) would be only a 'false fibre effect', produced by the cutting of microfolded true fibres approximately parallel to the true fibres (cf. Selfridge, loc. cit.).]

Although it is possible that the cause of the observed lengthening of the a-axis of antigorite is a distortion of a different kind, the possibility of a chain structure cannot be overlooked. (Cf. also a description of chrysotile as an amphibole, by Warren and Bragg.[1]) It is hoped to discuss this question of distortions in the structure of antigorite at a later date.

5. Heat-treated antigorite.

The reports of previous workers on the decomposition of antigorite on heating are somewhat at variance. Based on X-ray evidence, some authors report that antigorite decomposes into forsterite Mg_2SiO_4 and enstatite $MgSiO_3$ (cf. Caillère, loc. cit.); others have found only forsterite (cf. Gruner).[2] In the present study, only the reflections corresponding to forsterite, and no trace of enstatite, have been found on powder photographs of antigorite from Mikonui, heated for 20 hours at 750° C. [Chrysotile from Thetford, Quebec, however, heated for 25 hours at 1000° C. shows a very weak line corresponding to the strongest Debye line of enstatite.]

Some oscillation and Laue photographs of antigorite were also taken, after heating the specimen in air up to 1300° C. A complete indexing of the spots has not yet been attempted in the case of antigorite, but the pattern seems to be similar to that of heated chrysotile. The main features are that the X-ray pattern of antigorite changes into that of forsterite gradually, without becoming diffuse at any stage of the process. Those reflections which are streaky in the pattern of unheated antigorite do not become more distinct after heat-treatment, but are the last of all the spots of the old pattern to disappear. This proves that the cause of the streaks is a distortion not of the kind which can be relieved by

[1] B. E. Warren and W. L. Bragg, Zeits. Krist., 1930, vol. 76, pp. 201–210. [M.A. 4-466.]
[2] J. W. Gruner, Amer. Min., 1939, vol. 24, p. 186.

annealing, e.g., not a mechanical strain. The persistence of the reflections with the index l zero shows that the linkage of the atoms is strongest in the ab plane. The reflections of the new pattern (forsterite), which are elongated along the Debye lines, indicate that the crystallites of the decomposition product are alined with more than one of their crystallographic directions parallel to a given axis.

No new Debye lines appear on photographs of antigorite heated at 1300° C. for 17 hours, as compared with the same length of heating at 760° C. At higher temperatures, however, the last remnants of the pattern of antigorite have disappeared, and a small change in the relative intensities of the spots on the existing Debye lines takes place. This, presumably, indicates that no structural change, but rather a re-orientation of the existing crystallites, takes place at higher temperatures. It is possible that the same stage of decomposition, and orientation, could be obtained at somewhat lower temperatures by prolonged heat-treatment.

A Laue photograph of antigorite heated for 17 hours at 760° C. shows radial streaks only, which are more numerous, and without any spots on them, as compared with a photograph taken of the same flake in the same orientation before the heating. This was to be expected, considering the increased randomness in the orientation of crystallites in the specimen, as already shown on the oscillation photographs of the same specimen.

In conclusion, it seems, on the X-ray evidence, that serpentine minerals of composition $H_4Mg_3Si_2O_9$ decompose on heating either into a mixture of forsterite and enstatite (Caillère, loc. cit.), or forsterite alone. For the latter case, Prof. C. E. Tilley suggested the following reaction: $2H_4Mg_3Si_2O_9 \rightarrow 3Mg_2SiO_4 + SiO_2 + 4H_2O$. The presence of fused silica is in a good agreement with the observed refractive index 1·610 of the decomposition product of chrysotile, at least. [A note on the heat-treatment of chrysotile will be published elsewhere.] The question whether the experimental conditions during the heat-treatment of serpentine minerals have any influence on the results of decomposition has not yet been examined.

6. A comparison of powder photographs of antigorites from different localities.

Antigorite from Antigorio valley had the finest grain of the three specimens, and splinters of it gave fairly uniformly blackened powder lines. Antigorite from Hokitika was coarser, but splinters of it were still not good enough for single-crystal work. It seemed, though, that in the specimens investigated the a- and c-axes were orientated entirely at random, while the b-axis seemed to lie within a cone of semi-angle less than 15°.

Powder photographs of the three minerals (including antigorite from Mikonui) are comparable in their general features, though discrepancies exist. Antigorite from Antigorio valley exhibits resolved Debye lines in some places, where the other antigorites show broad bands only. Those bands may be due either to the deformation produced in powdering the specimens, or else the a-axis in the antigorite from Antigorio valley is a submultiple of that found in the material from Mikonui.

Conclusions.

Antigorite from Cropp river, Mikonui, New Zealand, has been examined by the turning crystal, powder, and Laue methods. The unit cell is monoclinic with

a 43·4, b 9·24, and c 7·26kX, and β 91·4°. There are two notable features on the oscillation photograph of antigorite: (1) The appearance of streaks, which bridge the layer-lines on the c-axis photographs whenever the index k is not a multiple of three. (2) In the a^* row-lines the spots of any intensity cluster about certain values of the index h. Regarding the clusters of spots in the a^* row-lines as single reflections in terms of a sub-unit cell, with the constants b, c, and β as above, but the a-axis eight times shorter, the X-ray pattern of antigorite can be compared with that of chrysotile. This sub-unit cell has a space-group $C^3_{2h} = C2/m$, and it is tentatively suggested that antigorite has the same structure as chrysotile, namely, a polar arrangement of kaolinite-like sheets of atomic layers of the following sequence: O_6–Si_4–$O_4(OH)_2$–Mg_6–$(OH)_6$ parallel to the (001) plane. A restricted randomness in the packing of these sheets (7·3kX thick), such as in steps of $ma'/2 + nb/6$ where $a' = a/8$, and m and n are any pair of integers (including zero) whose sum is even, would explain the appearance, and the length, of the observed streaks. A better explanation for the intensity distribution in the streaks is, however, required to account for the asymmetry with respect to the integer lattice points. A distortion of a different kind would be responsible for the observed lengthening of the a-axis.

The density calculated from X-ray data is 2·51 g./cm.³, as compared with 2·60 g./cm.³ obtained by flotation. Powder photographs prove that on heating antigorite decomposes into forsterite (and, perhaps, fused silica); no trace of enstatite was found.

Acknowledgements.

EXPLANATION OF PLATE V.

X-ray photographs of antigorite from Mikonui, New Zealand, taken in a cylindrical camera of 60·0 mm. diameter, using filtered Cu-Kα radiation.

FIG. 1. c(7·3kX) axis oscillation photograph, X-ray beam oscillating in a sector 15–30° from the b(9·2kX) axis.

FIG. 2. b(9·2kX) axis oscillation photograph, X-ray beam oscillating in a sector –2·5° to +2·5° from the a(43·4kX) axis. A negative of the central part of the film (slightly reduced) is also reproduced, to bring out the h10 spots at small h values, on the first layer-line.

FIG. 3. a(43·4kX) axis rotation photograph. A maladjustment of the specimen by 0·7° in the ac plane causes the distortion of the layer-lines, observed at some distance from the centre of the film.
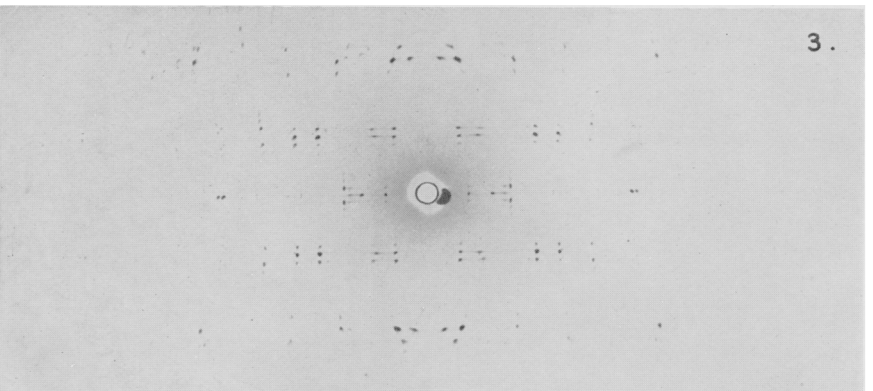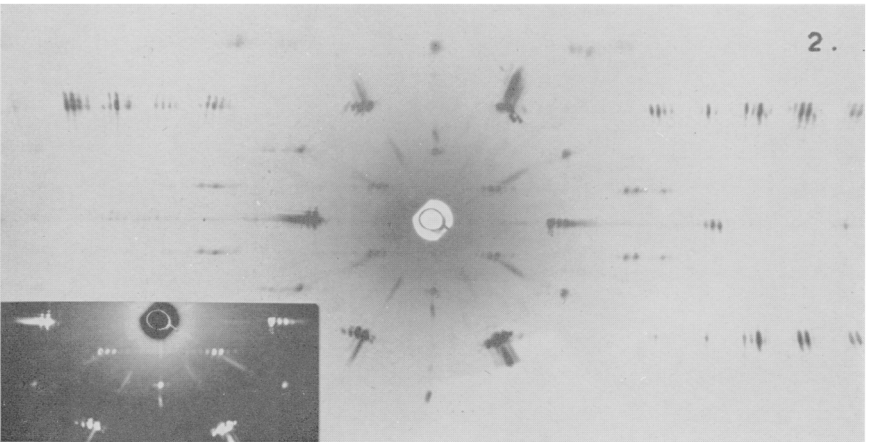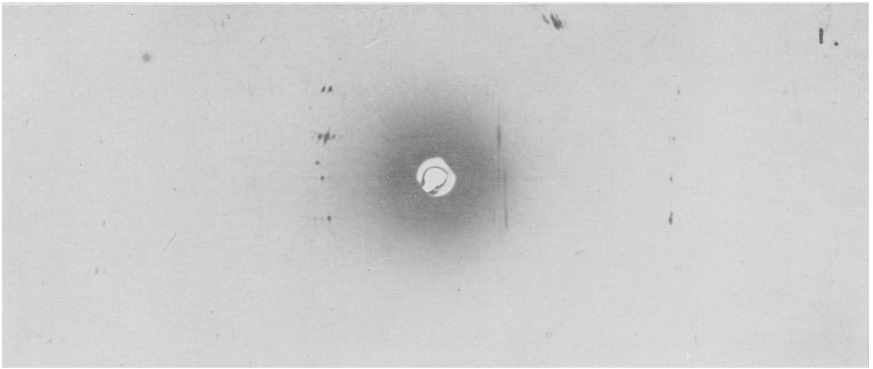
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