# Investigation of the crystal structure of antigorite.

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SUMMARY OF PREVIOUS X-RAY WORK.

SELFRIDGE (1936) examined by chemical, optical, and X-ray powder methods a large number of specimens of serpentine minerals (ideal formula  $H_4Mg_3Si_2O_9$ ), many of which were known as antigorite. He found that nearly all gave similar powder photographs, indicating a close structural relationship, but that there were noticeable differences on the basis of which the specimens could be separated into two groups, one giving a photograph similar to that of chrysotile asbestos, and the other containing the varieties called antigorite. Gruner (1937) came to similar conclusions, and in addition he indexed most of the reflections using the cell dimensions a 5.33, b 18.5,  $c 2 \times 7.33$  Å.,  $\beta 93^\circ$ , remarking in particular on the correspondence between 00*l* reflections in the two groups.

Aruja (1944) reported investigation of an antigorite from Mikonui, New Zealand, this being the first X-ray 'single-crystal' study of a serpentine mineral. He determined the cell dimensions and space group, and noted the close relationship between these data and those of chrysotile (table I). In this case both 00l and 0k0 reflections were seen to be similar to those from chrysotile. The most outstanding feature of the X-ray photographs obtained is that of the large 'a'-axis (table I). Aruja's conclusions were mainly as follows.

That there is in the antigorite structure a sequence of atomic planes parallel to (001) similar to that in chrysotile. Taking the sub-cell 'a'dimension as one-eighth of the large cell value, i.e. 5.44 Å., it was suggested that the resulting axial ratio b:a = 1:1.703 may indicate a chain structure parallel to 'a' rather than a sheet structure, and that the coarsely fibrous nature parallel to the 'b'-axis observed in many antigorites was due to what Selfridge (1936) had described as a 'false fibre' effect. The large 'a'-axis was interpreted as a superlattice dimension, perhaps due to a regularly occurring distortion, or else a polymorphism of the sort exhibited by sheet structures but here involving atomic chains. Streaks occurring through certain diffraction spots were partly accounted for by assuming some randomness in the sequence of successive cells.

TABLE I. Comparison between cell dimensions of chrysotile and antigorite.

		a.	ь.	c.	β.
Chrysotile (Whittaker, 1952)	 	5.33	$9 \cdot 2$	$2 \times 7.33$ Å.	$93^{\circ} 7'$
Antigorite (Aruja, 1944)	 	43.5	9.26	7.28	91.24

### MORPHOLOGY AND OPTICS.

The rock specimen<sup>1</sup> from Cross river, Mikonui, New Zealand, and its constituents were described by Bonney (1908), and a description of the antigorite crystals was given by Aruja (1944). Some further observations have now been made.

Two different kinds of antigorite grain occur in the rock. The crystal used for the X-ray analysis was a small rectangular plate with morphology and optics as follows. Length of plate parallel to b. 'c'-axis nearly perpendicular to plate. Cleavage, probably (100), parallel to the 'b-'axis; occasional (010) and perfect (001) cleavage. Extinction well defined and straight.  $\alpha 1.560, \beta 1.563, \gamma 1.564 \pm 0.001$  (Na-light); 2V negative  $55 \pm 2^{\circ}$ ; dispersion weak, r > v;  $\gamma = b$ ,  $\alpha$  and  $\beta$  nearly parallel to c and a respectively.

There are also present, in roughly equal quantity, grains which have a mottled appearance between crossed nicols, and have small inclusions of a magnetic iron-ore. The mean refractive index of such grains is  $1.563\pm0.002$ . The two types of grain were separated magnetically and the X-ray powder photographs of the two fractions were seen to be almost identical. It is assumed, therefore, that the difference between them is one of texture only. (The iron-ore mineral is present in such small quantity that it does not give observable lines on a moderately exposed powder photograph.)

The optical properties listed above are similar to those reported by Selfridge (1936) for several varieties of antigorite, but in the latter cases where 2V was observed it was found to be small. Similar values are given also by Hess, Smith, and Dengo (1952),  $\alpha 1.5615$ ,  $\beta 1.5660$ ,  $\gamma 1.5670\pm0.0005$ ,  $2V 47\frac{1}{2}\pm\frac{1}{2}^{\circ}$ , but the crystallographic axes were not explicitly determined. If what is there described as a (100) parting is in fact (010) then the optical scheme is the same as that described

<sup>1</sup> The specimen (no. 11566) was kindly supplied from the Department of Mineralogy and Petrology, Cambridge University. above. If it is truly (100) then the  $\beta$  and  $\gamma$  directions are reversed with respect to the 'a'- and 'b'-axes.

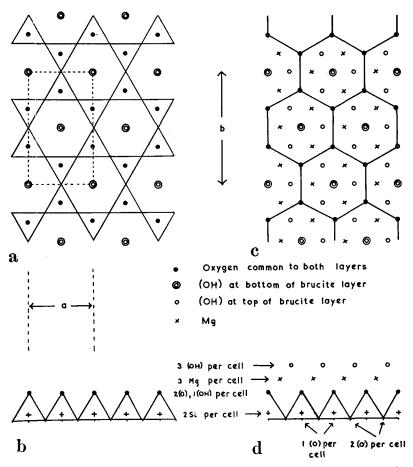


FIG. 1. (a) Tetrahedral  $Si_2O_5$  network in plan. (b) Tetrahedral network as viewed along 'b'-axis. (c) Tri-octahedral layer. (d) Chrysotile layer.

## CURVED SHEETS.

It has been shown conclusively (Aruja 1943, Whittaker 1953) that the structure of chrysotile asbestos is essentially of the layered type illustrated in fig. 1. As with kaolinite, each layer consists of a tetrahedral  $\text{Si}_2\text{O}_5$  network (shown *a* in plan, and *b*, as viewed along the *'b'*-axis), above which lies *c*, an octahedral layer, the two parts sharing

a plane of O and (OH) ions. The 'b'-axis projection of the composite layer is shown in fig. 1d.

Pauling (1930) predicted that such a composite sheet could exist only if curved, since the natural repeat distance in the brucite layer (5.4 Å.) is greater than that in the tetrahedral layer below it. The X-ray work of Aruja and of Whittaker, and electron micrographs by Bates, Sand, and Mink (1950), and by Noll and Kircher (1951), have shown that this curving does in fact occur in chrysotile asbestos, forming cylindrical tubes by bending of the sheet about the 'a'-axis. But there appears to be no convincing reason why bending about some other crystallographic direction should not occur. If about the 9.2 Å. axis the effect would be to make this the fibre axis repeat distance instead of 5.3 Å.

An X-ray examination of several varieties of coarsely fibrous serpentine minerals showed that this fibre axis does frequently occur (Zussman, 1953). Fibre photographs have been taken of specimens belonging to either of the two Selfridge groups. Those classified as 'serpentine' were found to have a fibre axis repeat distance of approximately 5.3 Å., while the antigorites have 9.2 Å. The specimens exhibit differences of colour and/or texture and are listed in table II, using the names by which they were described in the museum collections from which they were obtained.

Reference no.*	Specimen.	Repeat distance along fibre axis (in Å.).
O. 19376	Serpentine asbestos (Shabani mine, Southern Rhodesia)	$5\cdot 3$
O. 16328	Serpentine (New York)	5.4
O. 1899	Serpentine (Montville, N.J.)	$5 \cdot 3$
O. 9652	Schweizerite (Zermatt)	5.3
O. 3930	Schweizerite (Zermatt)	5.3
B.M. 47963	Marmolite (Hoboken, N.J.)	5.3
B.M. 1908.97	Metaxite (Saxony)	$5 \cdot 3$
M. N.2522	Serpentine (Montville, N.J.)	$5 \cdot 3$
O. 16336	Picrosmine (Tyrol)	$9 \cdot 2$
C. T.W.2915	Picrolite (Taberg, Sweden)	9.3
C. T.W.2914	Antigorite (Shipham Range?)	$9 \cdot 2$
C. 19343	Antigorite (Hokitika, N.Z.)	9.2
C. 19544	Picrolite (locality ?)	$9{\cdot}2$

TABLE II. Fibre axis repeats in serpentine specimens.

\* The prefixed letters O, B.M., C, and M indicate that the samples were obtained from mineral collections of the Oxford University Museum, the British Museum, the Cambridge University Department of Mineralogy and Petrology, and the Manchester Museum, respectively. The work of Hess, Smith, and Dengo (1952), Nagy (1953), Roy and Roy (1953), and others, has suggested, and in some cases demonstrated, that the occurrence of a platy rather than a fibrous habit in a serpentine mineral is associated with certain features of its chemical composition, e.g. replacement of Mg or Si by Al, or a high (Si,Al): (Mg,Al) ratio. Either of these would serve to produce a better fit between components of a layer and hence reduce its tendency to curve. It would seem now that two minerals with identical composition involving a certain degree of curvature may yet appear dissimilar through having a different axis of curving (fibre axis). The occurrence of one fibre axis rather than the other in such a case may be a consequence of physical conditions at the time of crystal growth.

## PLAUSIBLE STRUCTURES.

The possibility of curvature about the 'b'-axis suggests an explanation of the large 'a'-axis of antigorite (Mikonui) in terms of a corrugated sheet. A model of this sort was described by L. Onsager.<sup>1</sup> It has an alternating wave nature of periodicity 43.5 Å., the polar sheet inverting at each line of inflexion. Both this and another similar model, to be described later, would be consistent with other observed features such as:

- 1. Some similarity between the structures of antigorite and chrysotile, particularly in the c-direction.
- 2. The (100) cleavage noted in the single crystal. (Lines of inflexion will probably involve some discontinuity and therefore weakness.)
- 3. Streaky diffraction spots when  $k \neq 3n$ , where n is an integer. (Randomness of stacking can easily occur by displacements of layers in the 'b'-axis direction.)

But it is clearly desirable that more direct evidence be obtained, ideally the complete matching of the diffraction intensities with those derived from a trial structure. The remainder of this paper is concerned with an attempt to approach this goal.

## THE X-RAY DATA.

One prerequisite for a more complete analysis was the production of clearer X-ray photographs. Complicating features of those obtained by Aruja are the extra spots given by misoriented fragments, and the

<sup>&</sup>lt;sup>1</sup> Reported in summarized proceedings of a conference on the structures of silicate minerals (Robinson and Shaw (1952)), and described by Prof. Onsager in private communication.



FIG. 2. Antigorite (Mikonui). Weissenberg (h0l) photograph. Ni filtered Cu- $K\alpha$  radiation.

fuzziness of Weissenberg photograph reflections tending to merge them where they are closely spaced. A small crystal  $(0.25 \times 0.1 \times 0.07 \text{ mm.})$ has been found which gives photographs almost free from these defects. *hol* reflections only were recorded with a Weissenberg camera using Ni filtered Cu-K $\alpha$  radiation, exposure times varying from 10 minutes to 24 hours (fig. 2). Intensities were measured visually and corrections applied for Lorentz and polarization factors but none for absorption effects.

From fig. 2 it can be seen that all reflections with the exception of some at high angle are clearly resolved and sharp. The reflections from a small misoriented fragment do not interfere with the main array. Low-angle reflections, not shown here, were recorded on other photographs taken with the beam-trap off-set.

The nature of this diffraction pattern can be better evaluated by reference to fig. 6, which contains a diagrammatic representation of the weighted reciprocal lattice. In this diagram vertical black strokes are drawn at points of the reciprocal lattice, the length of a stroke being made roughly proportional to the observed intensity of the corresponding X-ray reflection.

Clusters of reflections tend to occur around points with h = 16n or 17n (n = integer), i.e. on the sub-cell reciprocal lattice, but, as Aruja pointed out, maxima do not always occur at the centre of a group, and neither maxima nor geometrical centres of groups occur at strictly constant h values. The number of reflections in a group varies in an apparently irregular manner.

## TRIAL STRUCTURES.

A type of corrugated sheet which departs as little as possible from planarity is that illustrated in fig. 3a (compare fig. 1d) and is referred to henceforth as the 'rectified wave' model. This shows one cell of the proposed structure as viewed along the 'b'-axis. In order that the cell shall have a = 43.5 Å. it must contain  $8\frac{1}{2}$  repeats of the sub-cell (5.3 Å.) along the curve (9 repeats would require an unduly small radius of curvature). A way in which this might reasonably occur was suggested by Onsager for his 'alternating wave' model in which, at an inversion, a system of 8- and 4-membered rings occurs instead of the usual hexagonal network of the tetrahedral layer (fig. 4). This introduces an additional 5.3/2. On building a 'ball and spoke' model it was seen that this 8:4 ring system is possible even where no inversion of the layer occurs, provided that small departures from normal bond angles

are allowed. If such a mechanism is employed at each discontinuity of the rectified wave, a model consistent with the cell dimensions results. In the 'alternating wave' model the 8:4 ring system can be assumed only at every other inversion if an  $8\frac{1}{2}$ -fold axis is to be explained.

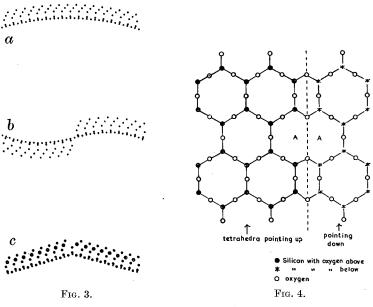


FIG. 3. (a) One cell content of 'rectified wave' structure.
(b) ,, ,, ,, ,, 'alternating wave' structure.
(c) ,, ,, ,, 'zig-zag' structure.
FIG. 4. System of 8- and 4-membered rings in tetrahedral silicate layer.

#### THE DIFFRACTION SPECTROSCOPE.

A method for rapidly testing trial structures has been developed at the Physics Department of the Manchester College of Technology. A full description is given in various papers, Hughes and Taylor (1952), Hanson, Lipson, and Taylor (1953), Hanson (1953), and an abstracted version is presented in the following paragraphs.

Use is made of the similarity between two phenomena: the diffraction of light by a set of holes, and the diffraction of X-rays by a set of atoms. The optical apparatus is illustrated in fig. 5. Monochromatic light from a source A is focused at a pinhole B. The divergent beam is rendered parallel by lens C and brought to focus by D in the plane F after reflection at mirror E. If a card containing a set of holes is placed at O the diffraction pattern produced is focused in the plane F, where it may be viewed through a microscope or photographed.

The X-ray diffraction pattern is a 3-dimensional one, but that part of

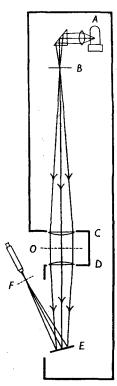


FIG. 5. Schematic representation of diffraction spectroscope. (Taylor, Hinde, and Lipson, 1951.)

it in the equatorial plane (the kOl reflections in the present case) depends only upon the x and z atomic co-ordinates, i.e. upon a projection of the atomic positions on to the xz plane.

The projection is drawn on a large scale and rapidly transformed into a punched mask by means of a specially constructed reducing pantograph. The optical diffraction pattern produced, called the 'optical transform', is photographed and can then be compared with the X-ray data of the weighted reciprocal lattice drawn to the correct scale and superimposed.

The first model tested by this method was one of a single cell of the rectified wave type, using a radius of curvature of approximately 60 Å. and the z co-ordinates given by Aruja (1943) for chrysotile. The centres of different scattering power corresponding to single, double, and triple oxygen, double silicon, and triple magnesium ions were simulated by holes made with punches of different sizes. Fig. 6 shows the optical transform of this model with weighted reciprocal lattice superimposed. The two patterns should be compared at reciprocal lattice points, since it is only there that X-ray intensities are observed. (Adding a large number of cells to the model would not affect the relative intensities at lattice points, but would give an optical transform with lower intensity between them.)

A qualitative similarity between the two transforms can at once be recognized, but they differ in two important respects. The fan-shaped regions of high intensity in the optical transform have a wider angular spread than those of the X-ray pattern, and the maxima of the former are more closely spaced along the  $a^*$ -axis. Both of these features were taken to indicate that a larger radius of curvature was required, and the effect of making this change to R = 100 Å. is shown in fig. 6b. The value of R, which was judged to give the best correspondence, was  $85 \pm 5$  Å.

## CRYSTAL STRUCTURE OF ANTIGORITE 507

An attempt was next made to discover how successive sheets of the structure are stacked, since there are two ways in which the  $\beta$  angle can be produced. Masks were punched containing 5 unit cells in the 'c'-axis

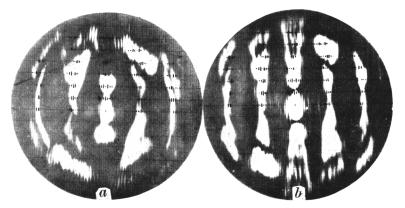


FIG. 6a. Optical transform of single cell of 'rectified wave' structure with radius of curvature R = 65 Å. Superimposed is a weighted reciprocal lattice corresponding to the X-ray data.

FIG. 6b. The same, with R = 100 Å.

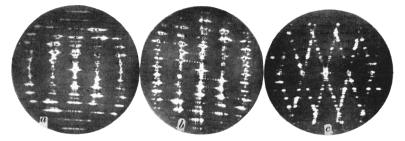


FIG. 7a. Optical transform of 5 cells of 'rectified' structure.
FIG. 7b. ,, ,, ,, ,, ,, 'alternating' structure.
FIG. 7c. ,, ,, ,, ,, ,, 'zig-zag' structure.
Each has the weighted reciprocal lattice superimposed.

direction, arranged to represent the two possibilities and at the same time enabling a more accurate representation of the scattering powers of the different ions (see Hanson 1953).

The 'optical transform' (fig. 7*a*) which fitted the X-ray data was that from the structure with  $\beta$  angle as illustrated in fig. 8 (similar to that of clino-chrysotile, Whittaker 1953). Trial was then made of the 'alternating wave' structure (fig. 3b) using a radius of curvature of 40 Å. so that the 'peak-to-valley' distance was

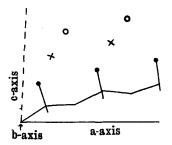


FIG. 8. Mode of stacking of suc-

cessive layers. Symbols as in fig. 1

approximately 3.5 Å. Its optical transform did not appear to fit the X-ray data at all closely, but considerable improvement was obtained by using instead a radius of 65 Å. The transform obtained using this value is shown in fig. 7b.

A further possible though unlikely corrugated structure which does not involve curving of the sheets is the zig-zag arrangement of fig. 3c, and its optical transform is shown in fig. 7c.

It should be noted that the large cell-size of antigorite imposes a severe test on the optical system of the instrument, whose imperfections are shown by the extent to which the transforms lack centro-symmetry.

## POWDER PHOTOGRAPH AND CHEMICAL ANALYSIS.

Powder photographs were taken using a 9-cm. camera and Ni filtered Cu- $K_{\alpha}$  radiation. The derived interplanar spacings and visually estimated intensities are compared in table III with data given by Hess, Smith, and Dengo (1952), for antigorite from Caracas, Venezuela. The similarity of the two sets shows that the varieties have similar crystal structures, and the presence of the large cell in the Caracas variety is additionally indicated by the low-angle lines of spacing 5.78 to 6.95 Å. which were observed using a counter spectrometer.

Dr. R. A. Howie was able to separate a small amount of pure antigorite from the rock, and carried out a chemical analysis in this department the results of which are compared in table IV with that published by Hess, Smith, and Dengo for antigorite from Caracas, Venezuela. The latter workers first derived the formula  $(Si,Al)_{4\cdot16}(Mg, \&c.)_{5\cdot88}O_{10\cdot43}(OH)_{7\cdot57}$ , which was based upon 18(O,OH) ions. Observing that this departed considerably from the ideal serpentine formula  $Si_4Mg_6O_{10}(OH)_8$ , and that Mg:Si ratio was close to 7:5, they recalculated assuming this ratio, and derived the formula  $(Si,Al)_{4\cdot97}(Mg, \&c.)_{7\cdot03}O_{12\cdot95}(OH)_{8\cdot05} \cdot 1\cdot 4H_2O$ , which approximated to the general formula  $Si_5Mg_7O_{13}(OH)_8 \cdot nH_2O$ .

Brindley (1954) has criticized this procedure, pointing out that the analysis may be recalculated on the basis of 2Si ions, resulting in the formula  $Si_2(Mg, \&c.)_{2.927}O_{5.105}(OH)_{3.720}$  which departs little from the

(p. 500).

CRYSTAL STRUCTURE OF ANTIGORITE

ideal for serpentines by having small deficiencies in Mg and (OH) ions. It was suggested also that the excess of O above 5 may be due to a process of dehydration.

1, Caracas, Vent		2. 2.		and Dengoj, 2				
$d(\text{\AA.}).$		$d(\text{\AA.}).$	Int.	d(Å.).	Int.	2.	Int.	
		<i>u</i> (A.).	mu,			$d(\mathbf{A}.).$	Int.	
8.05	10			1.781	14	1.780	_	
7.30	400	7.28	9	1.755	4	—	3	
6.95	<b>24</b>			1.736	10	1.740	1	
6.51	16	6.46	$\frac{1}{2}$	1.688	<b>2</b>			
6.10	6		—	1.640	2	·	<u> </u>	
5.78	8	5.82	$\frac{1}{2}$	1.584	3			
4.67	6)	4.64	3	1.560	$12^{\circ}$	1.554	$\mathbf{\tilde{5}}$	
4.62	7 j	4.04	э	1.540	9			
4.27	4	4.26	<b>2</b>	1.535	9	1.533	4	
4.01	6	3.91	1	1.524	13	1.517	<b>2</b>	
3.63	300	3.60	8	1.509	8	1.500	<b>2</b>	
3.51	<b>24</b>	<u> </u>		1.497	10	1.492	1	
2.88	<b>2</b>			1.479	7	1.477	1	
2.59	4)	0.50	0	1.466	6	1.461	1	
2.57	8)	2.58	<b>2</b>	1.462	6			
2.52	70	2.51	10	1.451	10	1.447	1	
2.46	9)	0.45		1.448	9			
2.42	38 (	2.45	3	1.443	5			
2.39	9	2.39	$^{2}$	1.438	3			
2.35	5	2.31	$\frac{1}{2}$	·		1.415	$\frac{1}{2}$	
2.237	6	2.24	$\frac{1}{2}$	1.339p		1.339	12 12	
2.208	7	$2 \cdot 209$	ĩ	1.328				
2.167	22	2.169	<b>5</b>	1.314p		1.315	4	
2.150	20	2.153	3			1.300	1	
2.126	4	2.121	14			1.289		
2.035	4			1.279p		1.280	$\frac{1}{2}$	
1.886	3			1.261p	_	1.264	1	
1.830	12	1.831	<b>2</b>	1.209p	_			
1.815	23	1.811	1	The second P			·	

TABLE III. X-ray powder patterns of antigorite. 1, Caracas, Venezuela (Hess, Smith, and Dengo). 2. Mikonui, New Zealand.

All lines in column 1 except those marked p were recorded by Geiger counter spectrometer. Intensity estimates are on different arbitrary scales.

TABLE IV. Chemical analyses of antigorite.

1, Caracas, Venezuela (Analyst, L. C. Peck in Hess, Smith, and Dengo, 1952). 2, Mikonui, New Zealand (Analyst, R. A. Howie).

	······································						
		1.	2.		1.	2.	
$SiO_2$		43.60	43.45	MgO	41.00	<b>41</b> ·90	
$TiO_2$	••••	0.01	0.02	CaO	0.05	0.04	
$Al_2O_3$		1.03	0.81	Na2O	0.01	0.02	
$Cr_2O_3$		0.02	n.d.	K <sub>2</sub> O	0.03	0.02	
$Fe_2O_3$		0.90	0.88	$H_2O +$	$12 \cdot 18$	12.29	
FeO		0.81	0.69	$H_2O-$	0.08	0.04	
NiO		0.16	n.d.		$\overline{99.92}$	$\overline{100.19}$	
MnO	•••	0.04	$\mathbf{nil}$	Sp. gr	2.607	2·60 (Aruja, 1944)	

In the present investigation, knowledge of the cell dimensions and density of the crystalline material allows the derivation from the analysis of absolute values for the atomic proportions, which are independent of structural assumptions. The cell content is seen to be:

$$\underbrace{(\mathrm{Si}_{33\cdot 2},\mathrm{Al}_{0\cdot 7})}_{33\cdot 9}(\underbrace{\mathrm{Fe}_{0\cdot 5}^{''},\mathrm{Fe}_{0\cdot 4}^{''},\mathrm{Mg}_{47\cdot 7},\mathrm{Ca}_{0\cdot 3})}_{48\cdot 9}\mathrm{H}_{62\cdot 6}\mathrm{O}_{148}$$

which is consistent with the following sequence of atoms in successive curved planes: 51(O), 33.9(Si,Al), 34.4(O) and 15(OH), 48.9(Mg, &c.), 47.6(OH).

The crystal structure proposed involves  $8\frac{1}{2}$  repeats of the sub-cell in the tetrahedral layer, i.e. 34 Si atoms per cell. It may also be noted that the 'rectified wave' model clearly implies a deficiency of Mg and (OH) ions, since at the junction of neighbouring 'arches' there is insufficient room for an extra half sub-cell in the octahedral layer. Moreover, the two (OH) ions at the top of the tetrahedral layer in positions marked A (fig. 4) would be unduly close to one another and would probably also be omitted. Allowing for these deficiences, the numbers of atoms in successive planes would be as follows: 51(O), 34Si, 34(O) and 15(OH), 48Mg, 48(OH). The structural model is thus in accord with the chemical data and with the observed density, within the limits of experimental error.

Assuming that the Caracas variety has cell dimensions very close to those of the Mikonui antigorite, and using the observed density value 2.607, its cell content may be derived from the analysis as:

$$\underbrace{(\underbrace{Si_{33\cdot 1},Al_{1\cdot 0}}_{34\cdot 1})(\underbrace{Fe_{0\cdot 6}^{''},Fe_{0\cdot 5}^{'''},Mg_{46\cdot 9},Ni_{0\cdot 1}}_{48\cdot 1})H_{62\cdot 4}O_{147\cdot 3},}_{48\cdot 1}$$

corresponding to the sequence 51(O), 34(Si,Al), 33.9(O) and 15(OH), 48.2Mg, &c., 47.4(OH), which compares favourably with that calculated from the Mikonui analysis, and with that of the structural model.

It would seem that the correct way to treat the Caracas data would be by an extension of Brindley's method, whereby some of the Al is grouped together with Si, and then the formula calculated to make (Si+Al) equal 2. This could perhaps not have been justified in the absence of other data, but it is interesting to note that this allocation shares the trivalent ions equally among 'octahedral' and 'tetrahedral' sites.

#### SUMMARY AND CONCLUSIONS.

The 'optical transform' method has been used to support the theory that a curved and corrugated-sheet structure exists in the crystals of antigorite studied. It is not possible to decide at present which of two types of corrugation is correct, an 'alternating wave' with radius approximately 65 Å. or a 'rectified wave' with  $R \sim 85$  Å., although the latter seems to be structurally more plausible. The manner in which successive layers are stacked has been determined.

The present investigation indicates only the broad lines on which the structure is based and little can yet be said about the detail of structure at the junction of neighbouring 'arches', particularly with regard to the octahedral layer. Using one of the proposed structures, however, it may be possible to initiate, in the case of the correct one, a series of 'Fourier refinements' leading to an electron density map.

Chemical formula, and the measured density, are consistent with the proposed structure; furthermore, analysis, density, optics, and powder photograph indicate that the antigorite from Caracas studied by Hess, Smith, and Dengo is essentially the same as that from Mikonui, possessing the large cell and, it is here suggested, the corrugated-sheet structure. It would appear, then, that small deficiencies in Mg (as compared with the ideal serpentine), and small replacements by Al, may result in a tabular rather than fibrous morphology by means of the super-cell described, and not necessarily through reducing the sheet curvature.

Brindley (private communication, Nov. 1953) has described another variety of antigorite from Unst, Shetlands, which has a 43.8, b 9.22, c 14.53 Å. and is orthorhombic. Thus the 'large cell' variety, which has hitherto been regarded as anomalous and non-representative of the antigorite group, may in fact be typical. The evidence for the existence of curved sheets in the platy crystals makes it seem most likely that the coarsely fibrous varieties of antigorite also have the sheet structure, curved about the 9.2 Å. axis. These and other varieties, including that from the type locality Val Antigorio, Piedmont, may all embody the Mikonui structure but with varying degrees of perfection.

Finally, it is hoped that this investigation has demonstrated the usefulness of the diffraction spectroscope for rapidly testing complex variants of a basic structure in an attempt to explain unusual diffraction effects.

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