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The Structure of Chrysotile. IV. Para-Chrysotile

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The name para-chrysotile has been proposed for the minor constituent of many chrysotile specimens which has a 9·2 Å axis parallel to the fibre axis. It is shown that this material has an orthorhombic cylindrical lattice of the 2nd kind with lattice parameters $a = 14{\cdot}7 \pm 0{\cdot}1$, $b = 9{\cdot}24 \pm 0{\cdot}02$, $c \simeq 5{\cdot}3$ Å. The structural principles established for ortho- and clino-chrysotile are shown to apply to para-chrysotile also, and to explain the peculiarities of the diffraction pattern, especially the large number of absent reflexions.

1. Introduction

It is well known that diffraction photographs of some specimens of chrysotile show weak extra layer lines in positions indicative of a fibre axis repeat of 9·2 Å. On normal-beam photographs taken with Cu $K\alpha$ radiation the first three such layer lines are observable, and they exhibit only diffuse intensity maxima. Aruja (1943) showed that these reflexions are approximately in the positions to be expected for the strongest diffuse reflexions from a material with the same structure as chrysotile but with the [010] or [031] axis oriented along the fibre axis. On this basis he concluded that this material constitutes not more than about 3% of typical chrysotile specimens from Thetford, Quebec. Hargreaves & Taylor (1945), on the other hand, found that the proportion of the material varied in specimens from different African sources, and showed that the extra layer lines disappear after prolonged extraction of the specimens with water. They therefore suggested that the material might consist of layers stacked in a less orderly manner than in chrysotile. It has also been stated (Whittaker, 1951) that the material is probably absent from a specimen of chrysotile from Cuddapah, India, which contains a high proportion of ortho-chrysotile. It is now known that specimens from this source are uniformly free from the material in detectable amounts, independently of their ortho-chrysotile content, which is very variable.

More recently (Whittaker & Zussman, 1956) it has been found that some specimens from South Africa give subsidiary layer lines of the order of three times as intense as those from Thetford chrysotile. The availability of these specimens and the use of equi-inclination rotation photographs (Whittaker, 1953) have revealed considerably more reflexions than were available to the earlier workers, and make possible the structural deductions described below. The name para-chrysotile has been proposed for the material responsible for the subsidiary reflexions (Whittaker & Zussman, 1956).

2. Experimental data

The positions of the 18 observed reflexions of para-chrysotile are listed in Table 1. These have been collected from photographs taken with Cu $K\alpha$ radiation in the normal-beam position and in the equi-inclination positions for the 2nd, 3rd, 4th and 6th layer lines. The 5th and 7th layer lines are within the range of observation, but owing to their respective proximity to the 3rd and 4th layer lines of ortho- and clino-chrysotile, they are very unfavourably placed for observation and have not been detected.

It is found, in accordance with Aruja's results, that more or less diffuse reflexions occur on the 1st, 3rd, 4th and 6th layer lines in positions corresponding approximately to 0*kl* reflexions from independently scattering layers with the same structure as chrysotile. The positions of these reflexions from ortho- or clino-chrysotile are not exactly the same as from para-chrysotile, however, since in the former case the reflexions occur at integral multiples of c^* but with various displacements from the integral multiples of b^*.

Table 1. *Positions of para-chrysotile reflexions on photographs taken with* Cu $K\alpha$ *radiation*

Layer line	ξ	Proposed indices	$c^*_{app.}$	$a^*_{app.}$
Zero	0·614	002	0·307	—
1st	0·307	011	0·307	—
	0·889	013	0·296	—
	1·482	015	0·296	—
2nd	0	020	—	—
3rd	0·28–0·37	031	?	—
	0·873	033	0·291	—
	1·472	035	0·294	—
4th	~0	040	—	—
	0·600	042	0·300	—
6th	0·017	060	—	—
	0·106	160	—	0·106
	0·211	260	—	0·106
	0·311	360	—	0·104
	0·413	460	—	0·103
	0·530	560	—	0·106
	0·606	062	0·303	—
	1·168	064	0·292	—

The $0kl$ reflexions from para-chrysotile, on the other hand, occur at integral multiples of b^* but suffer displacements from the integral multiples of c^*. This is shown by the values of $c^*_{app.}$ in column 4 of Table 1. These values correspond to 'apparent' values of c ranging from 5·02 Å to 5·30 Å. This variation is comparable in extent to that obtained for $b_{app.}$ from ortho- and clino-chrysotile. The positions of the layer lines indicate a value of $b = 9{\cdot}24 \pm 0{\cdot}02$ Å.

On even layer lines only, there occur reflexions at or near $\xi = 0$ which are indexed as $0k0$. On the 6th layer line the meridional reflexion is resolved into a pair, showing that the reflexion is not exactly at $\xi = 0$. Such resolution is not to be expected on the 2nd layer line if the displacement is proportional to k. On the 4th layer line there is a faint indication of it, but it is scarcely measurable.

On the 6th layer line only, there appears a set of reflexions indexed as $hk0$ whose positions are in arithmetic progression to within the experimental error (which is as much as ±0·010 on account of the extreme weakness of some of the reflexions). These reflexions suggest an orthorhombic lattice with an a parameter of about $14{\cdot}7 \pm 0{\cdot}1$ Å, i.e. not significantly different from that of ortho-chrysotile. The discrepancy between this conclusion and the displacement of the 060 reflexion is discussed below.

Only one reflexion is detectable on the zero layer line, and this may be indexed as 002 and regarded as a special case of the $0kl$ reflexions discussed above. If any $h00$ reflexions occur they must be superimposed on those of the major components of the specimen.

3. Discussion

The following classes of reflexions are absent:

(i) all hkl and $h0l$;
(ii) $0kl$ with $k+l \neq 2n$ (including $0k0$ with $k \neq 2n$ and $00l$ with $l \neq 2n$);
(iii) $hk0$ with $k \neq 6n$;
(iv) $h00$ with $h \neq 2n$ (this may be asserted although its converse is not proved).

The observed facts show directly that para-chrysotile must have a layer structure in which the layers are arranged with uniform inter-layer spacings and are ordered to some extent in the b direction but are mutually disordered in the c direction. Such an arrangement is most readily explained in terms of a cylindrical lattice, especially in view of the analogy with the other varieties of chrysotile. This conclusion is confirmed by the displacement of the 060 reflexion. The positions of the other $h60$ reflexions preclude the explanation of this displacement by the assumption that the a and b axes are oblique, but the anomaly can be explained if para-chrysotile is based on a helical cylindrical lattice (orthorhombic of the 2nd kind). By use of the same arguments as in Part II (Whittaker, 1956*a*) it may be shown that, if the helix is of unit order, the mean radius of the fibrils must be about 97 Å. This is so close to the value of 84 Å obtained in the same way for clino-chrysotile, and in accordance with other evidence on the size of chrysotile fibres which will be discussed in a subsequent paper, that the assumptions appear very probable.

Since reflexions with h odd occur on the 6th layer line but not on the zero layer line it is concluded that para-chrysotile, like the other chrysotile varieties, has a cylindrical lattice of the type c_2.† That is, alternate layers in the structure are differently disposed in the direction of the fibre axis with respect to their neighbours.

It has been shown in the preceding papers of this series (Whittaker, 1956*a*, *b*) that, owing to the complete inter-layer disorder in the azimuthal direction, the layers of ortho- and clino-chrysotile pack together as though the atoms were smeared out into corrugations. The atoms O_1 and O_2 (see Fig. 3 of Part II) cannot both lie in the troughs of the corrugations presented by the hydroxyl groups of the layer below, and as O_1 has the lower x co-ordinate of the two atoms it is O_1, which lies in the troughs, while O_2 lies over the crests of the corrugations. We may expect that similar considerations will govern the lattice geometry of para-chrysotile, but it must not be assumed *a priori* that the x co-ordinates of O_1 and O_2 will differ in the same way in para-chrysotile as in the other varieties. This difference is a second-order one and might easily be affected by the different distortions of the layers attendant on their being curved about a different axis.

Reference to Fig. 3 of Part II shows that in para-chrysotile the hydroxyl groups will behave as corrugations having troughs at $y = (2n+1)/12$, i.e. at intervals of $b/6$. Whatever be the relationship of the oxygen atoms of the next layer to this series of corrugations, it is reasonable to assume that it will be insensitive to displacements of $nb/6$, and that such displacements will occur at random. This at once explains the absence of $hk0$ reflexions except when $k = 6n$. This disorder would be expected to lead to diffuse scattering on the even layer lines (the $hk0$ reflexions would be extinguished on the odd layer lines in any case owing to the centring). Such diffuse scattering is observable on the 2nd layer line, and is in fact responsible for the meridional intensity on this layer line on normal-beam photographs. It may be noted that in the other varieties of chrysotile similar random displacements are to be expected in steps of $c/2$, but this cannot be distinguished (either structurally or by its diffraction effects) from the effect of the centring of the layers.

Purely geometrical considerations enable us to conclude further that in para-chrysotile, as well as in the other varieties, the atoms O_1 must have a lower x co-ordinate than O_2 and must lie over the troughs between the rows of hydroxyl groups of the layer

* The lattice is of the type c_2 in the nomenclature introduced by the author (Whittaker, 1955), but in the case of para-chrysotile the transposition of axes means that it is strictly b_2.

below, for the atom O_2 is at $y = \frac{1}{4}$, and it would therefore lie over a trough if the second layer were undisplaced with respect to the first. In these circumstances the $h06$ reflexions would indicate a spacing of 7·3 Å instead of twice this. If O_1 lies over the troughs, however, alternate layers must suffer a relative displacement of $b/12$ so that a c_2 type of lattice will be produced, in accordance with the observations. The further alternative, that the O_1 and O_2 atoms might both lie at the same level and at positions midway between the crests and troughs of the layer below, can also be ruled out. This would introduce the possibility of equivalent relative shifts of $\pm b/24$ in each layer, and would therefore lead to extinction of the $hk0$ reflexions except for $k = 12n$.

Since the chrysotile layers may be expected to have a plane of symmetry perpendicular to the b axis, there is no possibility of a further polymorph related to para-chrysotile in the same way as clino-chrysotile is related to ortho-chrysotile.

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Isomorphous Replacement and Phase Determination in Non-centrosymmetric Space Groups

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This paper deals with problems arising from the method of isomorphous replacement with heavy atoms in crystalline proteins. It is assumed that a series of isomorphous compounds is available, with the heavy atoms occupying different positions in each compound. The problems which arise are twofold. The first is the determination of the position of the heavy atoms in each compound separately, and the second consists in finding their relative positions in different compounds. If centrosymmetric projections are available, both problems can be solved with the help of Fourier series using $(|F_H|-|F|)^2$ as coefficients, F_H and F being the structure factors of the protein–heavy-atom compound and of the protein respectively. In the absence of centrosymmetric projections the positions of the heavy atoms can be found in each compound separately by means of Fourier series using $(|F_H|^2-|F|^2)$ as coefficients and employing a special device to remove the ambiguities inherent in such syntheses. When this has been done, the relative positions of the heavy atoms in different compounds can be found with the help of one of two possible correlation functions. One is a Fourier series using the products A_1A_2 as coefficients, A_1 and A_2 being the real parts of the structure factors of the heavy-atom-free compound, referred to the different heavy-atom positions, or the centres between them, as origins. The other function is a Fourier series using the products

$$[(|F_{H_1}|^2-|F|^2)(|F_{H_2}|^2-|F|^2)]$$

as coefficients, F_{H_1}, F_{H_2} and F referring respectively to two different heavy-atom compounds and to the pure protein. The correlation functions are tested on a hypothetical case and are shown to give satisfactory results.

1. Introduction

Isomorphous replacement with heavy atoms is a method of phase determination commonly used in the structure analysis of organic compounds. In proteins this method was first applied by Green, Ingram & Perutz (1954), but was confined to the determination of the signs of reflexions with real structure amplitudes. On account of their optically active nature all proteins crystallize in non-centrosymmetric space groups, so