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The Structure of Chrysotile. III. Ortho-Chrysotile

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Ortho-chrysotile, like clino-chrysotile, is based on a cylindrical lattice of type c_2. The specimen studied in most detail is orthorhombic of the 1st kind with lattice parameters $a = 14{\cdot}63$, $b \simeq 9{\cdot}2$, $c = 5{\cdot}34$ Å. The structure has been determined by trial-and-error and by Fourier methods. It is shown that the structure of the individual layers is almost identical with that of the layers in clino-chrysotile, but alternate layers are inverted end to end. This leads to a different stacking arrangement, which is still consistent with a cylindrical structure.

1. Introduction and experimental

Ortho-chrysotile (Whittaker, 1951) occurs in intimate admixture with the better known clino-chrysotile in specimens from many sources, but specimens rich in ortho-chrysotile are very rare. The variety is almost absent from the much-studied Quebec deposits. Methods for the analysis of mixed specimens by X-ray diffraction, and a survey of the distribution of ortho-chrysotile, have been published elsewhere (Whittaker & Zussman, 1956).

Ortho-chrysotile exhibits the same diffraction peculiarities which have led to difficulties in the determination of the structure of clino-chrysotile and which have been described in Part II (Whittaker, 1956). The close relationship of the two varieties is shown by the fact that the positions and intensities of their *h*00 reflexions are identical within the experimental error, and their diffuse 0*kl* reflexions show no greater differences than do those from specimens of clino-chrysotile from different sources. These differences are probably due to differences of texture rather than of atomic arrangement.

The specimen used in the present work was from Cuddapah, Madras, India. It was in the form of a fibre pencil measuring 11 mm. in length and 0·15 × 0·10 mm. in cross-section. The experimental methods and corrections were as described in Part II. Comparison of the intensities of the *h*00 reflexions and the *h*0*l* clino-chrysotile reflexions from this specimen with those from the specimen studied in Part II showed the specimen to contain 22% of clino-chrysotile. The intensities of the *h*0*l* ortho-chrysotile reflexions were therefore multipled by a factor 100/78 to put them on to the same scale as the *h*00 intensities.

2. Lattice parameters and symmetry

The specimen studied has an orthorhombic cylindrical lattice with parameters

$$a = 14{\cdot}63 \pm 0{\cdot}01,\ b \simeq 9{\cdot}2,\ c = 5{\cdot}34 \pm 0{\cdot}01\ \text{Å}\,.$$

The values of *a* for ortho- and clino-chrysotile are such that the perpendicular spacing of the layers is identical.

An equi-inclination photograph of the central region of the 6th layer line with Cu $K\alpha$ radiation shows a strong meridional reflexion bracketed by very weak and rather diffuse helical reflexions. The specimen therefore consists predominantly of material with an orthorhombic cylindrical lattice of the 1st kind. Since the specimen of clino-chrysotile studied in Part II had a helical lattice it is tempting to associate the weak helical reflexions with the clino-chrysotile present. However, extensive surveys of many specimens from different sources will be necessary before a correlation can be established between ortho- and clino-structure on the one hand and regular and helical cylindrical lattices on the other.

Determination of the value of *b* is subject to the same difficulty as in the case of clino-chrysotile.

Absent reflexions are the same as for clino-chrysotile, so that the lattice is of type c_2, and the radial projection on (100) is centred. The possible two-dimensional space groups associated with the structure are *p*11*m* or *p*11*g* for the projection down [010] and *a*1*m*1, *a*11*m*, or *a*2*mm* for the projection on (100).

3. Trial-and-error analysis of the structure

Since the intensities of the *h*00 reflexions of ortho- and clino-chrysotile are identical within the experimental error (the residue $\Sigma|I_{\text{cl.}}-I_{\text{or.}}|\div\Sigma I_{\text{cl.}}$ is only 6%) it follows that the x co-ordinates of the atoms must be virtually identical in the two structures and that ortho-chrysotile must also have a kaolin-like layer structure. The space group *p*11*m* is not compatible with such a structure and is therefore not considered further. However, as the evidence from the reflexion positions does not eliminate the possibility that the structure is monoclinic with $\beta = 90°$, but without orthorhombic symmetry, it is necessary to consider *p*111 as a possible space group as well as *p*11*g*.

It has been shown in Part II that two possibilities exist for the structure of a chrysotile layer, depending on which of two alternative sets of close-packed positions is chosen for the magnesium atoms. But in terms of orthogonal co-ordinates the difference between the atomic parameters of the two structures is merely equivalent to an opposite choice of the positive direction of the z axis. It follows that there is no distinction between the hypothetical ortho-chrysotile structures in which the magnesium occupies position A or position B (see Part II for nomenclature) provided that it occupies the same position in every layer. Such a structure would have the space group *p*111. On the other hand the space group *p*11*g* would correspond to the occupation of alternate positions in alternate layers.

The intensities of the *h*0*l* reflexions from the pseudo-orthorhombic structure were calculated from the assumed atomic co-ordinates given in Table 1. These are orthogonal co-ordinates corresponding to the same atomic arrangement as Table 1 of Part II. As has been explained in Part II, it is possible to compare the calculated and observed intensities without a knowledge of the relative displacement of the two layers in the structure provided that different scaling factors are admitted for h even and odd. Since the structure is only pseudo-orthorhombic it is necessary to compare $|F_c|^2_{h0l}+|F_c|^2_{\bar{h}0l}$ with $|F_o|^2_{h0l}$. The results of this comparison are completely unsatisfactory and eliminate the possibility of this structure.

Table 1. *Co-ordinates*

The origin is taken on one of the glide lines in the projection.

	Assumed		Found	
	x	z	x	z
O_1	0	0·220	−0·02 to 0	?
O_2	0	0·470	+0·017	0·460
Si	0·038	0·220	0·033	0·216
O_3 and OH_1	0·150	0·220	0·150	0·223
Mg	0·225	0·387	0·225	0·390
OH_2 and OH_3	0·292	0·054	0·292	0·050

The intensities of reflexions from the structure with space group *p*11*g* cannot be calculated in the absence of information as to the relative shift, Z, between the layers. However, they can be calculated as functions of the type

$$|F_c|^2 = A+B\sin 2\pi lZ+C\cos 2\pi lZ\ .$$

These functions can then be plotted graphically, and a number of pairs of *h*0*l* reflexions can be chosen whose intensity ratios are sensitive to Z. The best value of Z can then be chosen to satisfy simultaneously the observed values of the ratios. The value found in this way from nine pairs of reflexions was $Z = 0{\cdot}441$, and a comparison of the corresponding values of $|F_c|^2$ and $|F_o|^2$ is shown in Table 2. These values lead to a residue $\Sigma||F_o|^2-|F_c|^2|\div\Sigma|F_o|^2$ of 0·21, provided that different scaling factors are accepted for the different layer lines. This shows the correctness of a structure based on the space group *p*11*g*. The structure is therefore truly orthorhombic and not pseudo-orthorhombic.

Table 2. *Comparison of* $|F_o|^2$ *and* $|F_c|^2$

Values for *h*00 reflexions are omitted as they do not differ significantly from those given in Part II

hkl	$\|F_o\|^2$	$\|F_c\|^2$	*hkl*	$\|F_o\|^2$	$\|F_c\|^2$
002	?	3	004	?	3
102	9	6	104	72?	41
202	178	123	204	81	74
302	64	79	304	12	8
402	26	24	404	29	24
502	66	72	504	38	32
602	35	30	604	44	37
702	84	98	704	5	3
802	29	30	804	53	65
902	55	69	904	21	21

4. Fourier refinement

The phases of the *h*00, *h*02, and *h*04 reflexions were calculated from the co-ordinates assumed for a single layer and from the value of Z derived above. An electron-density synthesis was then computed with the observed amplitudes of all but three of the observable reflexions, the calculated amplitudes of these three which could not be observed satisfactorily, and the calculated phases. The electron-density map obtained is shown in Part I (Whittaker, 1953), and the atomic co-ordinates derived from it are shown in the last two columns of Table 1.

The electron-density map obtained for ortho-chrysotile is less satisfactory than that for clino-chrysotile. Spurious detail, concentrated in bands parallel to the c axis, is more marked, and the O_1 atom is not resolved at all from Si. The former circumstance is probably associated with the fact that the ratio of $|F_o|^2\div|F_c|^2$ for the non-zero layer lines is only 62% of that for the zero layer line. This may be due to under-estimation of the intensities of the *h*0*l* reflexions on account of (*a*) poor resolution from the clino-chrysotile reflexions and (*b*) a positive error in the estimated proportion of ortho-chrysotile in the specimen as a result of no allowance having been made for the possible presence of fibres with a disordered structure, i.e. 'mistakes' in the layer sequence corresponding to transitions within one fibre from the ortho- to the clino-chrysotile structure, and vice versa.

A further cause of error in the Fourier summation is the limited range of *h*0*l* reflexions that were used. Weak higher-order *h*02 and *h*04 reflexions certainly occur on the photographs but are so obscured by the heavy background on the layer lines that their intensities cannot be estimated satisfactorily. In view of the difficulty encountered in the refinement of the clino-chrysotile structure and the still greater uncertainty of the data in this case no attempt has been made to obtain a further degree of refinement. Nevertheless, some conclusions can be drawn from the present results which are probably significant, and these are discussed in the next section.

5. Discussion

The atomic x co-ordinates derived from the electron-density maps of ortho- and clino-chrysotile are not entirely independent results, since the same intensity data for the *h*00 reflexions were used in both the syntheses. The identity of the x co-ordinates of silicon and magnesium in the two structures therefore does little to establish any closer similarity of structure than can be deduced from the virtual identity of the *h*00 reflexions of the two chrysotile varieties. Consideration of the $Si–O_3$ bond length and of the asymmetric position of the magnesium atoms between the sheets of O_3+OH_1 and OH_2+OH_3 therefore follow exactly the same lines as in Part II. On the other hand, relative differences in the x co-ordinates of O_1 and O_2 could occur without any appreciable effect on the *h*00 reflexions, and could therefore be derived independently in the two structures from the effects of the *h*0*l* reflexions.

In fact the x co-ordinates of O_1 and O_2 can be determined only very approximately, especially in the case of the unresolved O_1. Nevertheless, the shape of the combined $Si+O_1$ peak suggests that $x(O_1) < x(O_2)$, and that the difference between the two values is similar to that in clino-chrysotile, although the actual values of both the co-ordinates are slightly different from the values in clino-chrysotile. The latter fact confirms the independence of the results for the two varieties in this case.

The z co-ordinates obtained from the Fourier syntheses for the two varieties are of course mutually independent. In both structures O_2 is found to be almost vertically over the projected position of the OH groups in the layer below, and in both structures the departure from exactitude in this relationship is 0·10 Å. The identity of this result in the two structures provides converging evidence on the following points which have been discussed in Part II:

(*a*) That the layers are completely disordered relative to one another in the direction of the b axis, and that they pack together as though the atoms were smeared into sets of parallel corrugations in this direction.

(*b*) That the mutual register of the layers is determined by the O_1 atoms which fit into the grooves between the hydroxyl groups of the layer below. Hence we have *a priori* evidence in favour of the just detectable difference between $x(O_1)$ and $x(O_2)$.

(*c*) That $z(O_1)$ (which cannot be determined from the electron-density map) differs from $z(\mathrm{Si})$ by 0·10 Å. In ortho-chrysotile the space group requires that this difference should be in opposite directions in alternate layers. But since the whole layer structure is also inverted in alternate layers the difference is in the same sense in every layer with respect to the internal structure of the layer, whereas in clino-chrysotile it alternates in this respect as well.

It is therefore concluded that the stacking arrangement of the layers in ortho-chrysotile is based on the same principles as in clino-chrysotile and is affected in the same way by the cylindrical structure. The difference in the two arrangements arises from the application of the same principles when the alternative Mg and OH positions are occupied in alternate layers.

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