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THE STRUCTURE OF POVLEN-TYPE CHRYSOTILE

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ABSTRACT

New observations on the X-ray and electron diffraction patterns of Povlen–type chrysotile are described, and it is shown that a "Povlen-type orthochrysotile" exists in addition to the clinochrysotile. Various models of the structure are evaluated, and the only one that is found to accord with the observations is a polygonal tubular structure, possibly with a more normal cylindrical core.

SOMMAIRE

De nouvelles observations sur diagrammes de diffraction des rayons-X et de diffraction électronique du chrysotile de type Povlen montrent qu'outre le clinochrysotile existe aussi un orthochrysotile de type Povlen. Différents modèles de structure sont évalués, et le seul qui corresponde aux observations est celui d'une structure enroulée en tube polygonal dont la partie centrale aurait la forme cylindrique habituelle.

(Traduit par le journal)

INTRODUCTION

This paper is an attempt to interpret the characteristic features of diffraction patterns given by so-called Povlen-type chrysotiles. These diffraction effects were reported as early as 1956 by Eckhardt in a discussion of the nature of "schweizerite". Some electron diffraction patterns published by Zussman *et al.* (1957, Fig. ld) and by Zvyagin (1967, Fig. 53) show similar features. The term "Povlen-type clinochrysotile" was, however, introduced by Krstanović & Pavlović (1964) and applied to a group of clinochrysotile specimens (identified from their powder patterns), which shared unusual fibre diffraction patterns: viz. "sharp reflections on all layer lines up to the sixth", as distinct from normal chrysotiles which give sharp reflections only on even–order layer lines. Neither in that paper, nor in a subsequent one (1967) did Krstanović & Pavlović define in any detail the special features in these diffraction patterns, although it seems from their discussion that the extra reflections on the first layer line were superimposed upon or replaced the tail of the 130 reflection. Unfortunately, nothing can be deduced concerning the extra sharp reflections observed on higher order layer lines.

Eckhardt and Zussman *et al.* assigned indices of type 13*l* to the extra reflections of the first layer line, but such indices are meaningless in the context of a cylindrical structure (Whittaker 1954, 1955a,b, 1957) with its inevitable azimuthal disorder between layers. Both Zussman *et al.* and Krstanović & Pavlović sought to justify their adoption of indices of this kind by suggesting that Povlen-type chrysotiles are fundamentally lath-like. This is, however, difficult to reconcile with the rotational symmetry exhibited by electron diffraction patterns obtained by Zussman *et al.* from fibres <2000Å in diameter. We have observed a Povlen-type orthochrysotile electron diffraction pattern from a fibre only 700Å across (Fig. 2b), and it is inconceivable that this fibre is not based upon a structure with at least approximate rotational symmetry.

Further features which suggest that the texture of Povlen-type chrysotile is more akin to cylindrical chrysotile than to platy lizardite are the paucity of *hkl*-type reflections and the presence of diffuse reflections particularly on odd-order layer lines.

PRESENT OBSERVATIONS

We have observed X-ray and electron diffraction effects from a number of more or less splintery chrysotile fibre specimens, including several from the Oxford University Museum labelled "schweizerite" (Figs. 1 and 2, and Table 1). Some of the X-ray photographs were kindly supplied by Dr. F. J. Wicks of the Royal Ontario Museum. These samples have provided examples of Povlen-type clinochrysotile diffraction patterns similar to those reported by the previous workers mentioned above, and also of the analogous pattern related to orthochrysotile (Fig. lb) not reported previously. The coordinates of the extra reflections on the first layer line, observed in X-ray diffraction, are given in Table 2.

A notable feature of the X-ray fibre diffraction photograph of Povlen-type orthochrysotile

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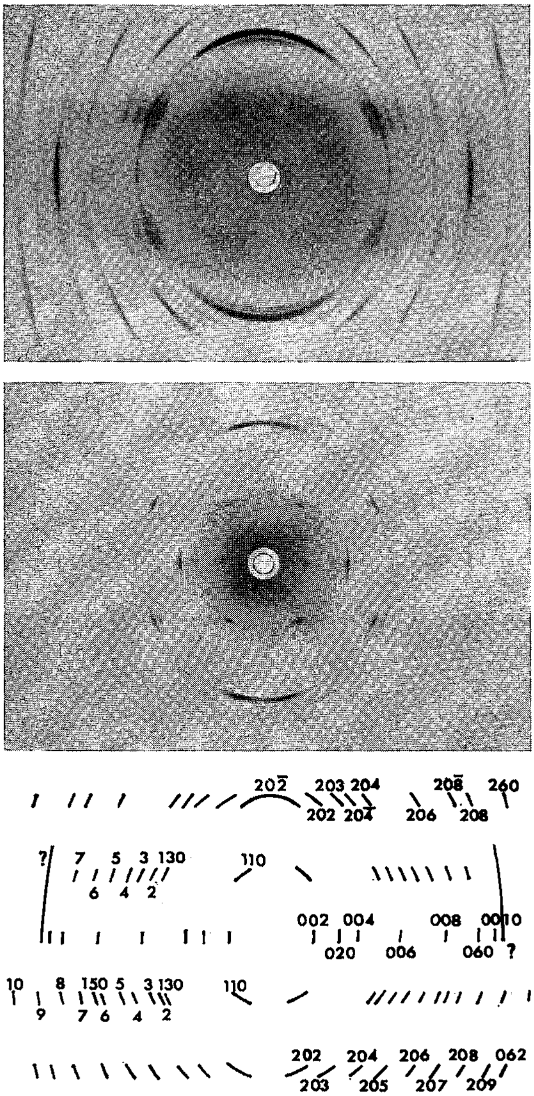


FIG. 1. X-ray diffraction patterns of fibres of Povlen-type chrysotile taken with Cu$K\alpha$ radiation on a camera of 30mm radius: (a) clino-type (specimen 9652); (b) ortho-type (specimen 8/20F); (c) indexed key to (a) and (b). The zero layer line is common to the two photographs; the upper part corresponds to (a) and the lower part to (b). Extensions of the arcs have been made uniform for the sake of clarity, except for one extraneous powder ring (marked ?). Only the l index of $13l$ reflections is given; other indices are in full.

(Fig. 1b) is the existence of weak arcs linking reflections on the first and second layer lines. The latter are in the positions of the $20l$ reflections to be expected from a two-layer orthochrysotile. Similar stronger arcs appearing on fibre photographs of Povlen-type clinochrysotile (Fig. 1a) appear to link reflections on the first and second layer lines similarly, but these reflections are not at identical Bragg angles.

The extra reflections given by the ortho-specimens are straight-forwardly indexable as an extensive series of $13l$ reflections. In the case of the clino-specimens a problem arises in that $13l$ and $13\bar{l}$ should have distinct coordinates. However the resolution is such that they would probably not be separated even if both series were present, and the indices are given in terms of $|l|$.

The electron diffraction patterns (Fig. 2a, c) display similar features to the X-ray fibre photographs, but without the extended arcs that can be attributed to the effects of misorientation of fibrils within a fibre bundle. Observations with the electron microscope suggest that the fibrils of Povlen-type chrysotiles are somewhat coarser than those from normal chrysotile.

The electron diffraction pattern of the ortho-

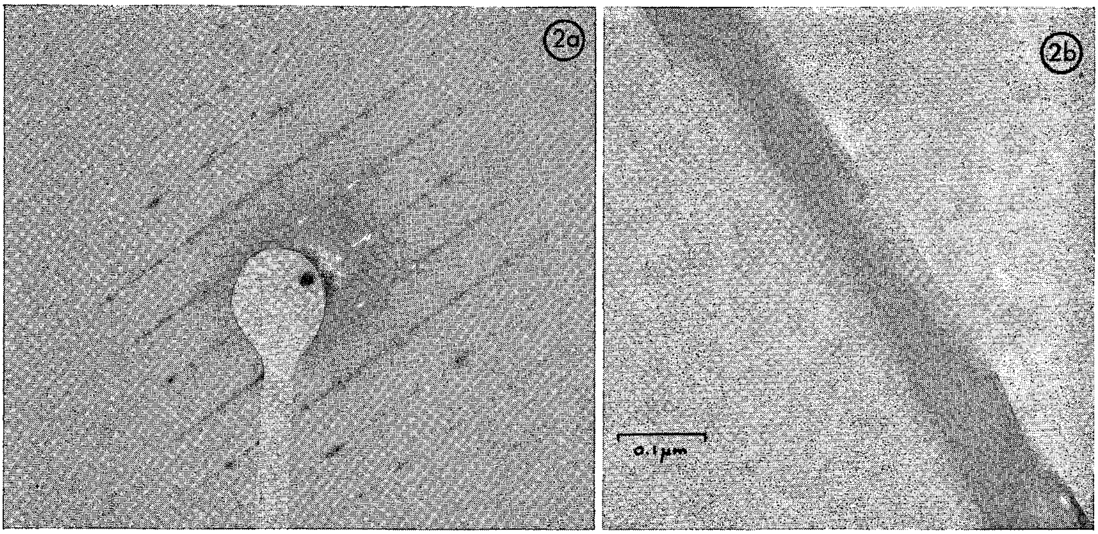
TABLE 1. LIST OF SPECIMENS AND PHOTOGRAPHS STUDIED

Specimen Number	Institution	Description	Locality
8/20F	1	Apple-green splintery fibres (labelled orthochrysotile)	Unknown
3950, 3953, & 9652	2	Greenish-yellow splintery fibres (labelled schweizerite)	Findeten Glacier near Zermatt.
X-ray fibre photographs (courtesy of Dr. F.J. Wicks) of			
M31388	3	Splintery pale apple-green vein serpentine, originally labelled picrolite. Found to be mainly Povlen-type clinochrysotile.	East Broughton, Quebec, Canada.
M28002	3	Splintery, verging on fibrous, very pale green vein serpentine associated with carbonates. Found to be mainly Povlen-type orthochrysotile.	Havelock Mine, Swaziland.
M8507	3	Splintery apple-green vein serpentine originally labelled picrolite. Found to be Povlen-type clinochrysotile.	Montreal Pit, (near Black Lake Village) East Broughton, Quebec, Canada.

Key to Institutions: (1) Department of Geology and Mineralogy, Oxford; (2) Oxford University Museum; (3) Royal Ontario Museum.

TABLE 2. REFLECTIONS ON THE FIRST LAYER LINE OF X-RAY DIFFRACTION PATTERNS OF POVLEN-TYPE CHRYSOTILE

Ortho-type			Clino-type		
ξ (Å^{-1})	*I*	*hkl*	ξ (Å^{-1})	*I*	*hk*|*l*|
0.09	s	110	0.10	vs	11 0
0.32	s	130	0.33	s	13 0
0.35	vs	132	0.36	vs	13 2
0.38	s	133	0.40	mw	13 3
0.42	ms	134	0.44	m	13 4
0.47	vs	135	0.49	w	13 5
0.52	ms	136	0.55	m	13 6 + 150
0.54	w	150	0.61	vw	13 7
0.58	s	137	0.68	w	13 8
0.63	s	138	0.99	mw	19 0
0.70	ms	139			
0.76	m	1,3,10			
0.78	vw	170			
0.82	w	1,3,11			
0.88	vw	1,3,12			
0.98	mw	190			



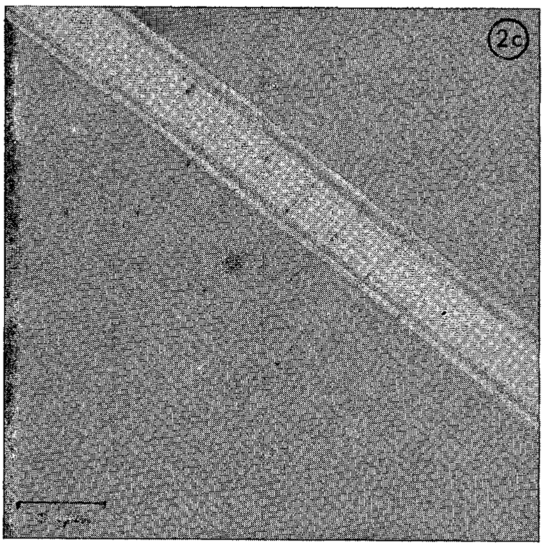


FIG. 2. Selected-area electron diffraction patterns and micrographs of Povlen-type chrysotile: (a) clino-type (specimen 9652), diffraction; (b) E.M. image of (a); (c) E.M. image superimposed on diffraction pattern of ortho-type (specimen 8/20F) in arbitrary relative orientation.

specimen 8/20F confirmed the presence of the series of extra reflections on the first layer line (Table 2), and revealed a corresponding series of reflections 332, 334, 338 and 3,3,12 following the 330 reflections on the third layer line, together with the usual 310 tailed reflection. The only reflection of detectable intensity on the fifth layer line was the tailed 510. Electron diffraction by the clino-specimen 9652 also confirmed the X-ray results on the first layer line, but the third and fifth layer lines are more difficult to interpret. The expected tailed reflections 310 and 510 are anomalously absent, and a continuous streak of approximately uniform intensity occupies these layer lines at $\xi < 3b^*$. On these layer lines the $h3l$ and $h3\bar{l}$ reflections would be in distinct positions (though $33l$ and $33\bar{l}+1$ would coincide), but although a series of spots follows 330 and 530 it is not possible to index them unambiguously. A probable $39l$ spot with $|l|=2$ follows 390.

INTERPRETATION

Because of the requirement for a model possessing at least some measure of rotational symmetry about the fibre axis, an effort was made initially to interpret the diffraction phenomena from Povlen-type chrysotile within the context of a cylindrical model.

It seemed possible that the unusual diffraction effects might be due to an abundance of (perhaps thin-walled) fibres of abnormally large diameter. Intensity profiles for some of the diffuse reflections of chrysotile were therefore computed, as an extension of the treatment by Whittaker (1957), to explore the effects arising from a variation in fibre parameters—in particular the diameter and wall thickness. Computer programs were developed to calculate the contributions of layers of increasing radius to the intensity profiles of selected reflections, based upon the expressions given by Whittaker (1957). The statistical weighting scheme described by Whittaker was applied in such a way as to investigate the diffraction effects to be expected from fibre bundles containing high proportions

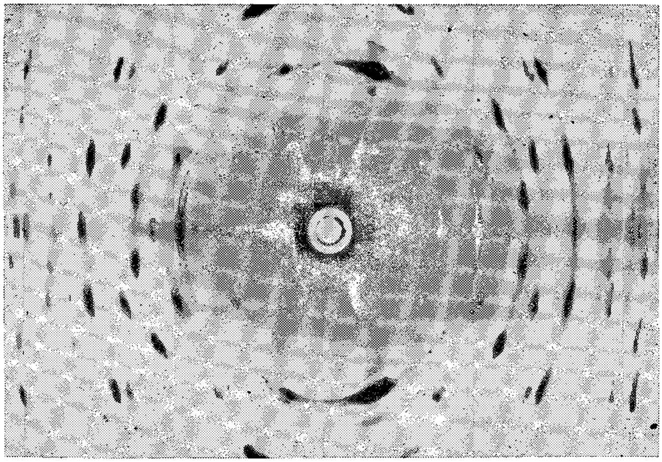


FIG. 3. X-ray rotation photograph of magnesite crystal from intergrowth with chrysotile, Birthday mine, Shabani, Rhodesia.

of either thick-walled or thin-walled, large diameter fibres, up to a maximum outer diameter of 580Å. This limit was imposed by the excessive computation time required to evaluate the Bessel functions of the very high orders that were involved.

The intensity profiles of the diffuse reflections calculated for these fibre diameter distributions showed in some instances the development of sharp maxima following the initial maximum, but they did not correspond well with the features observed in the fibre diffraction patterns. It seems unlikely that the diffraction effects from Povlen-type chrysotile can be interpreted in terms of a cylindrical model which is broadly similar to normal chrysotile.

Another possible model was suggested by the fact that one can obtain diffraction patterns resembling Figure 1b, from specimens containing (imperfect) fibre orientations of crystals about a crystallographic axis that is inclined to a symmetry axis, as in the magnesite photograph of Figure 3. An analogous effect could be given by chrysotile if the axis of curvature of the layers were [110] and the direction of azimuthal disorder due to the curvature made an angle of 60° with the fibre axis. Such a fibre would be a very extreme case of the helical cylindrical structures discussed by Whittaker (1955b). Such helical structures are normally characterised by a splitting of the diffuse *hk*0 reflections above and below their respective layer lines, but in this extreme case of a helix angle of 60° it can be shown that these reflections would notionally belong to layer lines at $h\lambda/2a$ but that their splitting would amount to $\pm k\lambda/2a$, so that the two parts of the split reflections would lie on normal layer lines at positions coincident with those of *hk*0 reflections of normal chrysotile (e.g. 020 would split to the normal positions of 110 and $\bar{1}10$, and 110 would split to the normal positions of 110 and 020). At the same time the sharp 20*l* reflections would appear at a ζ-value corresponding to the position of the normal first layer line. Thus a mixture of normal chrysotile with helical material of this kind would account for Figure 1b. Equally, a composite fibre containing both types of material would account for the zero, 1st, and 2nd layer lines of Figure 2, but unfortunately the hypothesis fails to account for the higher layer lines. The "meridional gap" characteristic of helical structures (Cochran *et al.* 1952) should lead to a suppression at $\xi < 9b^*$ of the sharp 60*l* reflections predicted by the model to lie on the 3rd layer line, whereas in fact these anomolous reflections occur down to $\xi = 3b^*$, just as they do on the 1st layer line. Similar reflections on the 3rd, 5th and 7th layer lines of X-ray photographs taken with Mo$K\alpha$ radiation present the same problem.

It seems then that these reflections must be assigned indices of the type *hkl*, and we therefore have to accept a measure of ordering in the *b*-axis direction which must involve a departure from the normal cylindrical structure of chrysotile. The hypothesis of polygonal tubes seems to be the only way of reconciling the flat layers required to explain the indexing with the approximate rotational symmetry indicated by the patterns as a whole. The absence of *hkl* reflections other than those for which $k = 3n$

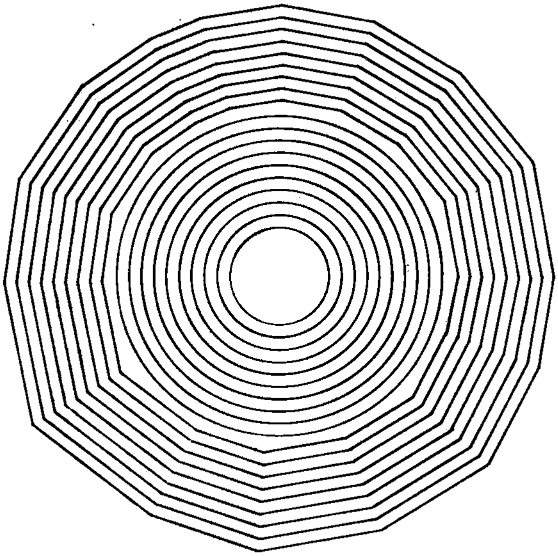


FIG. 4. Schematic drawing of proposed cross-sectional structure of a Povlen-type chrysotile fibre.

(and $h+k=2n$, imposed by centering) is not surprising as the relationship between successive serpentine layers is unlikely to be sensitive to random displacements of

$$\pm \frac{nb}{3}.$$

In some of the electron diffraction patterns the tails of the 110 reflections (and to a lesser degree the tails of other $h10$ reflections) present a more uneven profile than is usual. These subsidiary maxima cannot be indexed as $11l$-type reflections and it is thought that they may be a result of imperfect rotational symmetry, such as would arise from a fibre with polygonally arranged layers. In X-ray diffraction the presence of many fibres in random orientation about the x-axis would result in this spottiness of $h10$ reflections being smoothed out.

From some of the electron diffraction patterns it seems that part of the Povlen-type chrysotile fibres consists of normal cylindrical chrysotile. We suggest that this cylindrical material is likely to form the central core of the fibre, whereas the polygonally-arranged flat layers occur as an outer shell. This model is illustrated schematically in Figure 4, and the indices assigned on the basis of this model to the observed reflections are given in Table 2. The alternative hypothesis of a polygonal core surrounded by cylindrical material seems less likely.

The relative intensities among the $20l$ reflections of chrysotile are sensitive to the stacking arrangement of the layers in the radial direction in the fibrils, and it was from a consideration of the $20l$ and $40l$ reflections that the stacking was determined (Whittaker 1956a,b). The stacking arrangements that occur in both the normal polytypes of chrysotile ($2M_{c1}$ and $2Or_{c1}$) appear to result from the curvature of the layers (Wicks & Whittaker 1975), and the stacking arrangement in lizardite with its flat layers is quite different. Since our hypothesis is that Povlen-type chrysotile contains substantial regions built up from flat layers, it is surprising that the $20l$ reflections from Povlen-type clinochrysotile have (at least to a first approximation) the same relative intensities as those from normal chrysotile $2M_{c1}$, as this implies that the two forms have the same stacking arrangement. On the other hand, Povlen-type orthochrysotile gives $20l$ reflections with quite different intensities from those of normal chrysotile $2Or_{c1}$. In fact, these intensities give a good match (Middleton 1974) to those calculated for Bailey's polytype $2H_1$ (Bailey 1969), which is consistent with the suggestion of a flat-layer structure.

These results, therefore, continue to pose a structural problem with regard to Povlen-type clinochrysotile, and also raise doubts as to the propriety of regarding "Povlen-type orthochrysotile" as chrysotile at all, if it is structurally more closely related to lizardite.

CONCLUDING REMARKS

The possibility of explaining the unusual diffraction effects from Povlen-type chrysotile in terms of a model based upon curved layers has been shown to be unlikely. We therefore suggest that in Povlen-type chrysotiles the serpentine layers are essentially flat and that the stacking sequence is partly ordered. In view of the requirement for a considerable measure of rotational symmetry, we further suggest that these flat layers are arranged polygonally, possibly around a core of cylindrical chrysotile. The model proposed accounts for the observed diffraction effects and is compatible with our morphological observations with the electron microscope.

Since the completion of our work the model has been rendered more credible by some electron microscope observations by Cressey & Zussman (1976) who have observed polygonal cross-sections in serpentine mesh textures, and in material from specimen 9652 of Table 1. These observations clearly suggest that structures of the type that we have postulated can exist. We also understand that Yada (private comm. 1975) has observed polygonal structure in a synthetic serpentine preparation.

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