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THE NATURE OF PARACHRYSOTILE

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ABSTRACT

The structural and textural features of parachrysotile have been re-examined on the basis of electron-diffraction patterns of single fibrils found in a specimen of nemalite from Jeffrey mine, Asbestos, Québec. Some of the diffuse reflections, hitherto regarded as cross-grating reflections from layers in a cylindrical structure, show humps of intensity similar to those produced by Povlen-type chrysotile. Intensity profiles calculated for a cylindrical structure do not reproduce these humps of intensity. However, contrary to earlier suggestions, the fibrils are not lathlike, for the symmetry of a single-fibril diffraction pattern approximates that of a single-crystal rotation photograph. Parachrysotile probably resembles Povlen-type chrysotile in containing a variable amount of a polygonal tubular component.

SOMMAIRE

On réexamine les caractéristiques structurales et texturales du parachrysotile à la lumière de clichés de diffraction électronique de fibrilles uniques provenant d'un échantillon de némalite de la mine Jeffrey d'Asbestos (Québec). Certaines des réflexions floues, attribuées aux couches d'une structure cylindrique, montrent des maxima d'intensité semblables à ceux que produit le chrysotile de type Povlen. Des profils d'intensité calculés pour une structure cylindrique ne reproduisent pas ces maxima. Cependant, contrairement à certaines idées précédemment avancées, ces fibrilles ne sont pas en forme de latte, car la symétrie du cliché de diffraction que donne une fibrille unique ressemble à celle d'un diagramme de cristal tournant. Le parachrysotile ressemble probablement au chrysotile de type Povlen par la quantité variable d'un composant tubulaire à section polygonale.

(Traduit par la Rédaction)

INTRODUCTION

It was first observed by Aruja (1943) that X-ray fibre photographs of chrysotile commonly show weak subsidiary layer-lines indicating a fibre repeat of 9.2 Å, as well as the main layer lines corresponding to 5.3 Å. Three such subsidiary layer lines occur on normal-beam photographs taken with Cu $K\alpha$ radiation, and they contain only diffuse reflections. Aruja showed that these reflections occur approximately in the positions to be expected for the strongest reflections from a material with the chrysotile structure but with the axis [010] or [130] as the fibre axis. He concluded that his specimens from Thetford (Qué.) contained about 3% of this material. Hargreaves & Taylor (1945) showed that the content varied; they found a specimen from Shabani, Rhodesia to contain a significantly smaller amount. Whittaker & Zussman (1956) found even greater ranges, from 0 to 10% in material from different sources.

Hargreaves & Taylor (1945) also showed that the subsidiary layer-lines disappear after prolonged extraction of the chrysotile with water, and that the dried extracted material gives a powder photograph containing only broad bands corresponding in position to the diffuse reflections on the subsidiary layer-lines. This led them to suggest that the subsidiary layer-lines arose "not from a small proportion of chrysotile fibre structure (complete as such, with the degree of perfection proper to chrysotile) in an abnormal orientation, but rather from the presence of a small proportion of the material with an imperfection in stacking of successive sheets."

Using specimens showing contents of the material responsible for the subsidiary layer-lines of about 10%, and by taking equi-inclination fibre photographs, Whittaker & Zussman (1956), extended the diffraction data to the 6th subsidiary layer-line. This contains sharp reflections indicating a cell dimension of 14.6Å perpendicular to the layers, contrary to the suggestion of Hargreaves & Taylor. Whittaker & Zussman named the constituent responsible for these layer lines *parachrysotile*. Whittaker (1956) showed that the reflections could all be explained on the basis of a cylindrical fibril structure entirely analogous to that of chrysotile. A splitting of the meridional 060 reflection

indicated that the material possessed a helical cylindrical lattice.

Prior to this work, Honjo & Mihama (1954) reported that one fibril of chrysotile (out of 50 fibrils studied) gave a selected-area electron-diffraction pattern indicating a 9.2 Å fibre repeat, and they assumed it to have a cylindrical structure. Since then Shitov & Zvyagin (1966) have also found parachrysotile by electron diffraction, but "in combination with clino and ortho forms of chrysotile in individual tubular crystals selected for diffraction." Yada (1967) published a high-resolution electron micrograph of parachrysotile with 4.5 Å ($\frac{1}{2}b$) fringes transverse to the length, but this fibril seemed to be of a lathlike nature. However, Yada & Iishi (1974) observed more recently the first-formed fibrils in the experimental serpentinization of forsterite to be rather crudely cylindrical and to have the parachrysotile orientation.

Thus, with the possible exception of the photograph obtained by Honjo & Mihama, details of which were not published, there has been no direct electron-diffraction confirmation of the X-ray work of Whittaker (1956), and there have been some contrary indications. Whittaker's X-ray work was based on a small number of reflections on the 6th layer line, and involved the assumption that parachrysotile gives a set of 00*l* reflections on the zero-layer line coincident with those of the major component of the specimen (chrysotile–$2M_{c1}$), which are therefore not separately observed.

Present Observations

During an examination of a dispersed sample of nemalite (Whittaker & Middleton 1979) from a slip-fibre vein from the Jeffrey mine, Asbestos, Québec, several chrysotile fibrils that gave diffraction patterns of parachrysotile were observed in the electron microscope. Some of these fibrils were composite and gave combined diffraction patterns of parachrysotile and chrysotile–$2M_{c1}$ or chrysotile–D_c or brucite, but some were pure parachrysotile. It is possible, but not certain, that some of the combined patterns came from intergrowths like those observed by Shitov & Zvyagin (1966). These fibrils were somewhat coarser than normal chrysotile, ranging from 600 to 1000 Å in diameter. They gave diffraction patterns showing the full symmetry of a rotation photograph (*i.e.*, reflections from both the zones *hk*0 and 0*kl*), indicating that they are not laths but approximately cylindrical fibrils, similar to normal chrysotile except for the different crystallographic orientation. As pointed out above, the 00*l* reflections from parachrysotile coincide with similar reflections from normal chrysotile, and their existence has hitherto been only inferential. In the present work, however, 00*l* reflections have been observed from pure parachrysotile. The electron-diffraction patterns also confirm the existence of sharp reflections of type 0*kl* on layer lines for which $k = 6n$, since the 12th layer line as well as the 6th could be observed (Table 1). In addition to these sharp reflections, the diffuse cross-grating *hk*0-type reflections which had been observed in the X-ray photographs were also observed in the electron-diffraction patterns. These *hk*0 reflections are similar in character to

TABLE 1. POSITIONS AND INDICES OF PARACHRYSOTILE REFLECTIONS

ξ(Å^{-1})	Indices	ξ(Å^{-1})	Indices
Zero layer line		Sixth layer line	
0.14	002	0	060
0.28	004	0.07	061
0.39	200;201	0.15	062
0.41	006;202	0.28	064
0.43	203	0.40	260
0.47	204	0.48	067
0.56	008;206	0.57	068
0.77	400	0.62	069
0.84	0,0,12	0.68	0,6,10
		0.69	460;0,6,10
First layer line			
		Eighth layer line	
0.20	110		
0.59	310	0	080
Second layer line		Ninth layer line	
0	020	0.20	190
		0.23	192
Third layer line		0.34	194
		0.58	390
0.19	130		
0.24	132	Tenth layer line	
0.27	133		
0.33	134	0	0,10,0
0.38	135		
0.46	136	Twelfth layer line	
0.57	330;138		
0.72	1,3,10	0	0,12,0
		0.07	0,12,1
Fourth layer line		0.14	0,12,2
		0.28	0,12,4
0	040	0.39	2,12,0
0.39	240	0.80	4,12,0

the diffuse *hk*0 reflections of normal chrysotile. This is especially true of the 110 reflection, but quite strong, relatively sharp humps were observed in the tails of the 200, 130 and 190 relections (Fig. 1). If indexed (Table 1), these humps would have to be three-dimensional reflections of type *hkl*, which are forbidden for a structure with a truly cylindrical lattice.

Interpretation

Earlier work (Whittaker 1957, Middleton & Whittaker 1976) on the intensity profiles of the diffuse reflections from cylindrical chrysotile layers has shown that intensity humps on their tails can arise in some instances without invoking three-dimensional order. Such humps can be regarded as analogous to the modulation in an intensity profile that arises from multiplying together the Fourier transforms of a lattice and the contents of a unit cell, but complications arise in cylindrical structures which make the results sensitive to the values of the inner and outer radii of the cylinder. The effect of the different axis of curvature of the layers means that the earlier work could not be applied directly to parachrysotile. Computations were therefore undertaken to see whether the observed humps on the reflections could be simulated on the basis of reasonable assumptions regarding the radii.

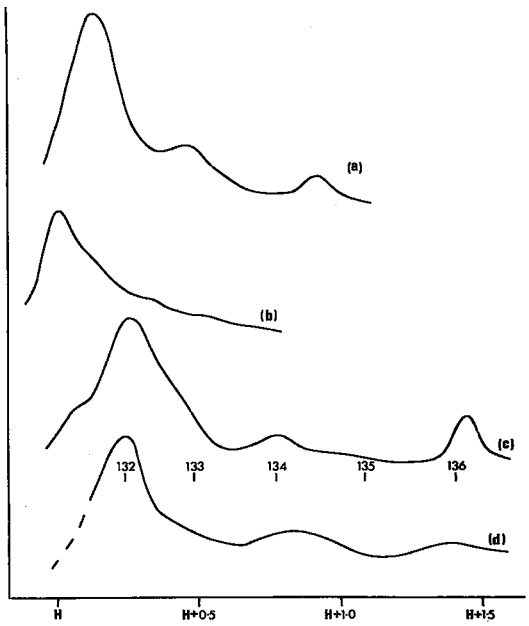

FIG. 1. (a) – (c) Observed intensity of profiles of reflections 200, 110 and 130 (respectively) in the electron-diffraction patterns of parachrysotile from the Jeffrey mine, Québec. (d) Corresponding profile of 130 from an X-ray diffraction pattern of parachrysotile from New Amianthus mine, Transvaal. The horizontal scale is calibrated in $h = \xi/a^*$. H is an integral value of h. The calculated positions of 13l reflections are indicated on (c).

For this purpose the formula given by Whittaker (1957) was modified:

$$I(\xi, k) = \sum_m \sum_H p_m^2 \{ | \sum_j f_j \exp(2\pi i\, k y_j/b) \cos(2\pi H x_j/a)\, J_{Hp_m}(p_m h a_{m,j}/a) |^2 + | \sum_j f_j \exp(2\pi i\, k y_j/b) \sin(2\pi H x_j/a)\, J_{Hp_m}(p_m\, h a_{m,j}/a) |^2 \}$$

where $I(\xi, k)$ is proportional to the intensity at ξ on the kth layer line, m is the ordinal number of a cylindrical layer of radius $mc/2$, $a_{m,j}$ is the circumferential repeat-distance at the radius of the jth atom in the mth layer, p_m is the number of repeating units in the mth layer, f_j is the scattering factor of the jth atom, H is the integral index of the *Hk*0 reflection, h is the same index regarded as a continuous variable, *i.e.*, $h = \xi a/\lambda$, J_{Hp_m} is the Bessel function of order Hp_m. Intensity profiles were calculated for the 200, 110 and 130 reflections, with inner radii down to $m = 3$ and outer radii up to $m = 40$. Except for the smooth profile of 110, no sign of reasonable agreement or even of a trend towards agreement could be obtained with the humps on the profiles. It is therefore concluded that these features of the diffraction pattern cannot be accounted for on the basis of a cylindrical structure.

Similar difficulties were encountered in explaining the humps on the tails of certain diffuse reflections of Povlen-type chrysotile, and we suggested (Middleton & Whittaker 1976) that this material contains flat serpentine layers arranged polygonally, possibly surrounding a cylindrical core. The existence of such polygonal fibres was subsequently confirmed by their direct observation in thin cross-sections in the electron microscope by Cressey & Zussman (1976). There are strong resemblances between the reflection profiles reported here for parachrysotile and those given by Povlen-type chrysotile, and both materials form fibrils of greater diameter than ordinary chrysotile – a circumstance that may be expected to accompany polygonalization. We therefore propose that the humps are to be regarded as *hkl* reflections from polygonal material. The significant departures of the

humps from the calculated *hkl* positions have not been investigated, but are not unreasonable for such broad reflections. The Fourier transform of the structure will vary markedly across the breadth of the ideal profile, when it is so broad, thereby shifting the peak. Absence of *hkl* reflections for which $k \neq 3n$ (which is also usual for Povlen-type chrysotile) is probably due to the presence of random displacements by $nb/3$.

We therefore interpret our observations on the parachrysotile in nemalite from the Jeffrey mine as indicative of a polygonal tubular structure. This does not imply, however, that all parachrysotile is of this nature. The present specimen did not give a split 060 reflection (characteristic of a helical cylindrical lattice) like the specimen from Transvaal investigated by X rays. Comparison of the 130 profiles (Fig. 1) shows that the Transvaal specimen has much less distinct humps than the one from the Jeffrey mine, and therefore probably consists predominantly of truly cylindrical fibrils. Thus it seems likely that parachrysotile may have a whole range of structures from truly cylindrical to predominantly polygonal. This is the situation in ordinary chrysotile, as shown by the series of 130 profiles in Figure 2. Yada's (1967) observation of lathlike parachrysotile can also be simply explained either as a sector broken from a polygonal fibril during specimen preparation, or even as an occasional truly lathlike overgrowth broken off from the outside of a polygonal fibril.

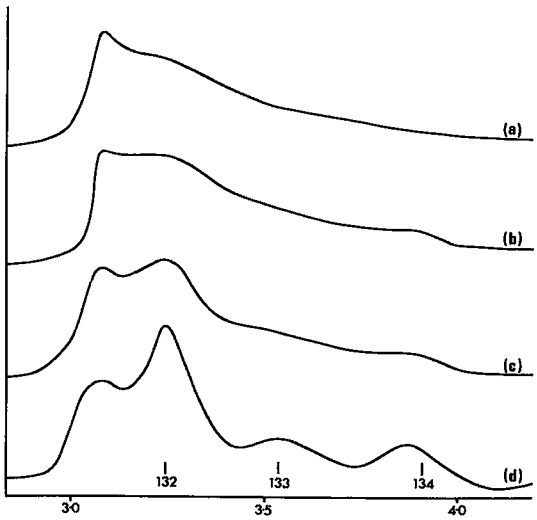

FIG. 2. Comparative development of 13*l* "humps" on the 130 profiles given by specimens of ordinary chrysotile from various sources. (a) Cuddapah, India; (b) Gath's mine, Shabani, Rhodesia; (c) Shabani, Rhodesia; (d) Povlen-type, Zermatt, Switzerland. The horizontal scale is calibrated in $k = \xi/b^*$.

CONCLUDING REMARKS

As in the case of Povlen-type chrysotile, the interpretation of our observations in terms of a polygonal arrangement of flat serpentine layers raises a question as to whether such material should be regarded as lizardite rather than parachrysotile. In the case of Povlen-type clinochrysotile we showed (Middleton & Whittaker 1976) that the layer stacking is essentially identical to that in chrysotile–$2M_{cl}$, so that there is a discrepancy between the layer stacking and the morphology, whereas in Povlen-type orthochrysotile the layer stacking is unlike that in chrysotile-$2Or_{cl}$ and like that in lizardite–$2H_1$. Detailed calculations of the 0*kl* intensities for parachrysotile as a function of layer stacking have not been attempted. The fact that they only occur for $k=6n$ can be interpreted in one of two ways: (i) as indicative of chrysotile-like stacking; such stacking would be compatible with total disorder parallel to x (although clearly this disorder would not actually be present in the polygonal regions that give *hkl* reflections) and random displacement by $nb/6$ in the y direction. The consequences of this hypothesis have already been worked out (Whittaker 1956) and shown to be compatible with the 2-layer cell suggested by the 0*kl* reflections. (ii) As indicative of some kind of hitherto unknown disordered lizardite-like stacking with random displacement of $ma/2 + nb/3$. However, alternative (ii) would be difficult to reconcile with the 2-layer cell; the general similarity of the reflections on the electron-diffraction patterns of predominantly polygonal material with the X-ray reflections of predominantly cylindrical material also argues in favor of a chrysotile-like stacking. Thus the balance of evidence favors the classification of polygonal parachrysotile with chrysotile rather than with lizardite.

Another point of interest is that parachrysotile shares with antigorite the distinction of curvature about the y axis, whereas the polytypes of chrysotile have layers curved about the x axis. From the aqueous-extraction experiments of Hargreaves & Taylor (1945), it seems that parachrysotile is less stable than chrysotile. On the other hand, there is much evidence of many kinds (relevant references given by Wicks & Whittaker 1977) to suggest that antigorite is

more stable than chrysotile. The stability of antigorite has usually been attributed to the fact that every layer in the structure is able to adopt an optimum radius of curvature, whereas this is not so in a tubular structure. However, as curvature about the *y* axis is apparently the less advantageous one on the evidence of parachrysotile, one must assume that it is adopted in antigorite because there would be greater difficulties at the lines of inflection in building a corrugated structure with curvature about the *x* axis.

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