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EXPLANATION FOR THE INSENSITIVITY TO TILTS OF THE
ELECTRON DIFFRACTION PATTERNS OF AMPHIBOLE ASBESTOS FIBERS

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ABSTRACT

The previously reported observation that the electron diffraction patterns of single amphibole UICC asbestos fibers are insensitive to tilts of $\pm 20^\circ$ along and perpendicular to the fiber axis (Skikne et al 1971) is experimentally confirmed. An explanation for this effect is proposed based on thin sample effects for small tilts and on the pseudo-hexagonal symmetry of these crystals for larger tilts. Because of this effect it is difficult to distinguish the three monoclinic forms of single amphibole asbestos fibers without previous study of standard (naturally occurring) single crystals.

INTRODUCTION

It is now well established that asbestos fibers are carcinogenic, and that they occur as air and water pollutants in the form of isolated fibers typically 0.5 μ m long and about a thousand angstroms in diameter (Wessolowski et al 1974). They are found in sizes too small and in concentrations too minute (less than 1 per cent) to preclude routine x-ray or scanning microscopic identification. However in this size and concentration range they are ideally suited for characterization using transmission electron microscopy.

Asbestiform minerals are found mainly in the serpentine (sheet silicate) and the amphibole (chain silicate) groups. These are shown in Table 1 with relevant crystallographic data. Chrysotile asbestos, a serpentine mineral, accounts for a majority of the world's production. It has also been extensively studied by electron microscopy by Timberell et al (1970), Pooley (1972), Langer and Pooley (1973), Langer et al (1974), Seshan (1974) etc. These studies all show that chrysotile asbestos can be recognized by its characteristic hollow channel. Since it is so well studied, its diffraction effects are not further considered here.

Recently interest has arisen in the possibility of identifying single fibers of the amphiboles in air and water pollution samples using data on lattice parameters obtained from the selected area electron diffraction facility of the electron microscope. This method involves tilting the unknown crystal to different orientations which then yield data on different characteristic interplanar spacings.

These may then be compared to x-ray data as has been suggested by several authors, (Hirsch et al 1965 etc.).

More recently Clarke and Rudd (1974) suggest that the diffraction patterns may be used to differentiate between the amphibole fibers. Here a contradiction is found in literature: Langer and Pooley (1973), categorically state: "the amphibole diffraction pattern is unique for the mineral group, but not for the individual mineral species. Instrumental variations, errors in pattern measurement, structural defects and twinning produce overlap patterns". Secondly, Skikne et al (1971) have reported that the diffraction patterns of single fibers of UICC amphiboles do not change with tilts of $\pm 20^\circ$ along and perpendicular to the fiber axis. Both these results imply that different d - spacings are difficult to obtain by the tilting of single fibers.

No careful study of the diffraction effects of amphibole fibers are found. In an attempt to index these diffraction patterns it was found that most workers have ignored the problems posed by pseudo-symmetry. This is examined in detail and shown how this can help explain the results of Skikne et al (1971).

In this paper the result of Skikne et al is also confirmed, an explanation for the effect is proposed and the implications of this result discussed.

In a later paper we (Seshan - Wenk 1977) shall present some indexed patterns of faulted and unfaulted naturally occurring asbestos minerals. The twinning law will be presented, from which the complicated diffraction patterns of the UICC single fibers may be understood.

We have not, but have proposed to study the complex diffraction patterns from single UICC asbestos fibers in detail.

EXPERIMENTAL

Fibers of the different UICC (Union International contre le Cancer) standard asbestos samples were prepared on carbon coated electron microscope grids half of which were coated with gold to provide an accurate calibration for the camera constant. They were then examined in a Philips 301 electron microscope fitted with a high angle tilt goniometer stage. And a Siemens 102 electron microscope with a high resolution stage.

RESULTS

Bright field images and selected area diffraction patterns from isolated crocidolite fibers tilted along the fiber axis and about an arbitrary axis are shown in Fig. 1 and 2 respectively. They were also tilted perpendicular to the fiber axis by $\pm 24^\circ$. The selected area apertures burned into the bright field images show the area contributing to the diffraction patterns. The rings in the diffraction patterns arise from the gold substrate and were used to calibrate the camera constant.

Measurements were made on the negatives using a simple light box and measuring eye piece. However the diffraction patterns from the UICC samples are not indexable straight away, because of the complexity of the diffraction patterns. We find however that indexable diffraction patterns are obtained in naturally occurring amphibole minerals where the fibrous nature is not well developed. Such crystals also have a

low density of microtwins.

The tilting experiments show that the selected area diffraction patterns of single amphibole fibers do not change noticeably for tilts of $\pm 20^\circ$ confirming the earlier observations of Skikne et al. These authors also observed that each asbestos type was associated with a specific periodicity of the closely spaced spots. Our continuing study (Seshan - Wenk 1976) of naturally occurring amphiboles suggest that this effect is related to the microtwinning observed in the natural as well as the UICC asbestos samples. This effect will be studied in detail. (Seshan - Wenk 1977).

A model to explain the insensitivity to tilts is given in the next section.

MODEL

Using the multiple dark field technique (Hirsch et al p. 298) it was found that the rows of closely spaced electron diffraction spots lie nearly perpendicular to the fiber axis. Further the spacing between the rows, corresponding to the c axis spacing, was calculated to be in the range 5.27 - 5.30 Å for the three clino-amphiboles studied. The bright field images in Fig. 1 are mounted to show this relationship to the diffraction pattern and the c axis direction and the (001) spacing is marked.

Then the widely spaced (100) and (010) planes, in the range 9.20 - 9.80 Å and 17.7 - 18.2 Å range respectively, Table 1, must run along the fiber axis. The 5.3 Å planes, lying at a characteristic distance which arises from the co-ordination of the silicate chains,

lie perpendicular to the c^* -axis. This is illustrated in Fig. 3a-b; the reciprocal lattice for the cell is shown in Fig. 3d. Such a crystal should give rise to the diffraction pattern shown in Fig. 3c and this is in fact observed experimentally (Fig. 1).

Figure 4c displays a high resolution micrograph of the area shown in Fig. 4a and Fig. 4b shows the corresponding beams which were recombined to image the lattice planes in Fig. 4c. As was assumed in the model the widely spaced 9.5 planes are seen to lie along the fiber axis.

From this model it follows that tilting about the fiber axis, should produce little change. Such tilts merely change the spot spacing along the closely spaced rows; these changes are difficult to detect. Further as is shown later extra reflections from other Laue layers and from twinning are expected.

To explain the insensitivity to small tilts perpendicular to the fiber axis, each reciprocal lattice point is to be considered extended in reciprocal space. A thin crystal, thin in the direction of the electron beam, should produce such an extension of the reciprocal lattice points (Hirsch et al p. 98). This is shown in Fig. 3d.

Since the reflecting sphere is relatively flat with respect to the c -axis spacing (radius of the reflecting sphere $27 \text{ \AA}^{-1}$ at 100keV; c -axis spacing $0.2 \text{ \AA}^{-1}$) and the extension of each reciprocal lattice point is $1/t$ (t is the thickness of the crystal in the beam direction) the tilt 2θ required to change or eliminate a certain reflection can be easily calculated.

The quantities used in the calculation are shown in Fig. 4. As in Fig. 3 the beam direction is parallel to the a^* -direction; the reciprocal

lattice spot and the Laue layer spacing are then $1/b$ and $1/a$ respectively. Assuming that the areas of the crystal which transmit the electron beam is about 100 Å thick,

$$1/t \cong 0.01 \text{ Å}^{-1}$$

and

$$\tan \theta = \frac{1/2(1/t)}{\text{spot spacing}}$$

$$= 0.005/0.05$$

$$= 0.1$$

therefore θ

$$= 6^\circ$$

This model predicts that tilts up to 12° may be required to eliminate a certain reflection.

The explanation for the apparent absence of change with tilts about the c-axis (fiber axis) lies in the pseudo-hexagonal symmetry exhibited by these crystals. This is seen in x-ray precession photographs taken along the c-axis (Fig. 6) and is replotted in Fig. 6b to show the pseudo-hexagonal symmetry. There then exists the main mirror planes m and two pseudo-mirror planes P_m thirty degrees from each other. This means that for tilts of a few degrees on either side of these mirror planes diffraction patterns of almost identical symmetry and spacing will be obtained.

Figure 6b also shows the reason why, often, electron diffraction spots from different zones will be superposed. The figure shows the Ewald sphere for electron diffraction passing through the $(\bar{4}, 12, 0)$ reflection. Symmetry requires that the orientation $(\bar{3}, 13, 0)$ has almost the same symmetry. Further, since all reciprocal lattice points are extended, reflections from the $(\bar{3}, 11, 0)$ layer will appear. It is highly likely that effects such as these give rise to the multiplicity of the spots seen in the diffraction patterns of Fig. 1 and 2. Therefore accurate

tilting experiments on standard naturally occurring single crystals are necessary to index and consequently distinguish the diffraction patterns unequivocally.

DISCUSSION AND CONCLUSIONS

The three clino amphibole asbestos minerals (amosite, crocidolite and tremolite) have almost identical lattice spacings. In fact the differences in lattice spacings between sodic (crocidolite) and calcic (tremolite) clino amphiboles are less than 0.5% (H.R. Wenk 1971). Even with accurate calibration, electron diffraction patterns only allow a determination on the range of 1 to 2% (Hirsch et al p. 128). Furthermore, as has been demonstrated here, the diffraction patterns of single fibers are complicated and tilting does not often distinguish the different crystal orientations. It is therefore difficult to distinguish between the clino amphiboles by lattice parameter measurements from selected area diffraction patterns contrary to the suggestions of Clarke and Rudd (1974). The same applies to the determination of lattice parameters from aggregates, which is a less sensitive method than using single crystals.

When the distinction between the clinoamphiboles is required, and only isolated fibers are available, the methods of x-ray microanalysis (Lorimer et al 1976), with resolutions of 1000 Å and which depend on the chemical species present, are possibly applicable.

We have also suggested that the complexity of the fiber diffraction patterns be understood by a study of standard, naturally occurring simple crystals. Such crystals give indexable diffraction patterns which can

then be used to index the fiber patterns (Seshan et al 1976).

Finally Skikne et al report several characteristic periodicities in the electron diffraction patterns of the clino amphiboles. Dark field and high resolution work in progress shows that these could arise from internal faulting; it is also hypothesised that these spots could arise from polytypism. These phenomena have been observed abundantly in other chain silicates such as wollostonite (Wenk et al 1976) and enstatite (Iijima et al 1976). However studies of large test crystals of known structure are necessary to investigate variations in the microstructure of these minerals which are important carcinogenic environmental pollutants. Such a study and an investigation to explain the geological conditions necessary to form a given asbestos texture is under way (Seshan et al 1977).

To summarize, it has been shown that the insensitivity to tilts of the amphibole UICC fibers can be explained on the basis of thin crystal effects and the pseudo-hexagonal symmetry of these minerals.

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TABLE 1

Mineralogical Data of Asbestos Minerals

<u>Name</u>	<u>Formula</u>	<u>Space Group</u>	<u>Mineral Group</u>	<u>Lattice Constants</u>	<u>Fiber Axis</u>
1. Chrysotile (serpentine)	$\text{Mg}_3 [\text{Si}_2\text{O}_5] (\text{OH})_4$	Cm	Sheet silicate	$a \approx 5.3, b \approx 9.2, c \approx 7.3$ $\beta \approx 93^\circ$	X or Y
2. Anthophyllite	$(\text{Mg}, \text{Fe}^{2+})_7 [\text{Si}_8\text{O}_{22}] (\text{OH}, \text{F})_2$	Pnma	Ortho amphibole	$a \approx 18.5-18.6, b \approx 17.7-18.1, c \approx 5.27-5.32$	Z
3. Amosite (grunerite)	$\text{Fe}_4^{2+} (\text{Fe}^{2+}, \text{Mg})_3 [\text{Si}_8\text{O}_{22}] (\text{OH})_2$	C2/m	Clino amphibole	$a \approx 9.6, b \approx 18.3, c \approx 5.3$ $\beta \approx 101.5^\circ$	Z
4. Crocidolite (riebeckite)	$\text{Na}_2 \text{Fe}_3^{2+} \text{Fe}_2^{3+} [\text{Si}_8\text{O}_{22}] (\text{OH}, \text{F})_2$	C2/m	Clino amphibole	$a \approx 9.75, b \approx 18.0, c \approx 5.3$ $\beta \approx 103^\circ$	Z
5. Tremolite	$\text{Ca}_2 \text{Mg}_5 [\text{Si}_8\text{O}_{22}] (\text{OH}, \text{F})_2$	C2/m	Clino amphibole	$a \approx 9.85, b \approx 18.1, c \approx 5.3$ $\beta \approx 104^\circ 50'$	Z
6. Actinolite	$\text{Ca}_2 \text{Fe}_5^{2+} [\text{Si}_8\text{O}_{22}] (\text{OH}, \text{F})_2$	C2/m	Clino amphibole	$a \approx 9.85, b \approx 18.1, c \approx 5.3$ $\beta \approx 104^\circ 50'$	Z

Table 1. Chart showing the division of asbestiform minerals into the serpentine and amphibole group, with their crystallographic data. Notice that the three monoclinic amphiboles have almost identical crystal parameters and that all of them have a characteristic c axis spacing of 5.3 Å.

FIGURE CAPTIONS

Fig. 1 The results of tilting an isolated fiber of UICC crocidolite along its axis through 48° is shown. The diffraction patterns are mounted corrected for image rotation and the c axis direction and spacing is marked. The rings are from the deposited gold film providing a reference. Notice that such tilting causes little change to the diffraction pattern.

Fig. 2 Here the fiber is tilted about an arbitrary axis by 48° . It is difficult to see any changes in the form of the diffraction pattern.

Fig. 3 (a) Shows a drawing of a typical fiber with the monoclinic cell dimensions of $a = 9.85 \text{ \AA}$, $b = 18.1 \text{ \AA}$, $c = 5.3 \text{ \AA}$ and $\beta = 104^\circ$.
(b) Shows the arrangements of lattice planes. The $9 \text{ \AA}$ planes (b planes) have been directly resolved in Fig. 4.
(c) Shows the diffraction pattern expected from a crystal such as in (b).
(d) Shows the reciprocal lattice with the reciprocal lattice points extended because of the small thickness of the crystal in the beam direction. The Ewald sphere, E.S, (which is not drawn to scale) is shown to illustrate how because of the extension of reciprocal lattice points reflections from other Laue layers appear. This is further discussed in Fig. 6b. From Fig. 3 it can be inferred (see text) that tilts parallel and perpendicular to the fiber axis does not cause the diffraction pattern to change.

Fig. 4 (a) Shows the area selected for examination in high resolution.
(b) Shows the electron diffraction pattern with the objective apperture over the beams which were recombined to obtain the lattice image.
(c) Shows the direct image of the $9 \text{ \AA}$ lattice planes as was assumed in the model (Fig. 3).

Fig. 5 Calculation of the tilt (2θ) required to eliminate a certain reflection. The crystal thickness (t) is about $100 \text{ \AA}$, the beam parallel to the a^* direction; the spot and layer spacings are $1/b$ and $1/c$ respectively.

Fig. 6a,6b X-ray precession photographs of actinolite (a clino amphibole isostructural with crocidolite and tremolite) taken along the c -axis. The pseudo hexagonal symmetry, the mirror planes m and the pseudo mirror planes Pm are shown for clarity in Fig. 6b. The a^* spacing is $0.102 \text{ \AA}$, $b^* = 0.558 \text{ \AA}^{-1}$ and the radius of the Ewald sphere for 100 keV electrons (E_w) is $27.02 \text{ \AA}^{-1}$. This is then a straight line on this scale and is shown here as passing through the $(\bar{4},12,0)$ zone. The pseudo mirror plane Pm_2 requires that the zone $(\bar{3},13,0)$ also has the same symmetry and lattice spacings. Further because of small crystal thickness all the reciprocal lattice points are extended. Consequently reflections of other zones $(\bar{3},11,0)$ for example will also appear. Considerations such as these make the different orientations difficult to distinguish and give rise to the complex diffraction patterns seen in Fig. 1 and 2.

XBB 7511-8240

Fig. 1

Fig. 2

XBB 7511-8239

XBL 755-6273

Fig. 3

XBB 755-3527

Fig. 4

XBL 7512-10,010

Fig. 5

Fig. 6a

XBL 763-6573

Fig. 6b

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