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MAGNETIC ORIENTATION OF AMPHIBOLE FIBRES

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ABSTRACT

Amphibole fibres have been exposed to a uniform magnetic field while suspended in a dilute solution of celloidin in amyl acetate. The solvent was allowed to evaporate while the field was maintained so as to obtain a coherent film of magnetically oriented fibres bonded together by celloidin. X-ray-diffraction patterns were then recorded in transmission geometry, and the orientation of the fibrils around their fibre axis was determined. The fibres are oriented in azimuth as well as lengthwise, though those that align normal to the field show a much more restricted range of azimuthal orientations than those that align parallel to the field. Crystallographic control of the principal magnetic axes is discussed; the orientation properties are not fully explained, but their attribution to magnetite present in bulk samples is rejected.

Keywords: amphibole asbestos, grunerite, X-ray diffraction, magnetic properties.

SOMMAIRE

On a placé des fibres d'amphibole, en suspension dans une faible solution de celloïdine dans l'acétate amylique, dans un champ magnétique uniforme. On a ensuite laissé évaporer le solvant, tout en conservant le champ, pour obtenir un film cohérent de fibres orientées selon leurs axes magnétiques et cimentées par la celloïdine. Les clichés de diffraction X par transmission ont permis de déterminer l'orientation des fibrilles autour de l'axe de la fibre. Ces fibres possèdent une orientation azimutale aussi bien que longitudinale, quoique celles qui sont perpendiculaires au champ magnétique montrent une gamme d'orientations azimutales beaucoup plus restreinte que celles qui sont parallèles au champ. On évalue l'origine cristallographique des principaux axes magnétiques; le mécanisme n'est pas encore bien compris, mais on exclut la possibilité que des plaquettes de magnétite soient à l'origine des propriétés d'orientation de l'amphibole.

(Traduit par la Rédaction)

Mots-clés: amphibole asbestiforme, grunerite, diffraction X, propriétés magnétiques.

INTRODUCTION

It has been known for some years (Timbrell 1972) that amphibole asbestos fibres are aligned by a magnetic field and may be divided into three types: P-fibres that align themselves parallel to the field, N-fibres that align themselves normal to the field, and those that align themselves at an angle to the field. Particularly interesting is the case of grunerite asbestos (amosite), which commonly contains both P- and N-fibres in the same specimen. Timbrell's observations, however, only reveal the orientation of the fibre length with respect to the field. In the present work we have investigated the orientation of the crystallographic axes of the oriented fibres by X-ray diffraction.

EXPERIMENTAL METHODS

Preparation of a satisfactory oriented specimen involves a number of compromises. The important features of the technique are those that permit a good degree of orientation in the plane of the film, a flat film to ensure planar orientation, an adequately amorphous support-film, and a satisfactory ratio of fibre to polymer so that the diffraction pattern of the fibre is visible against the rather dark background. We constructed glass cells from microscope cover slips; these cells, which measure 8 × 25 × 20 mm, fit between the pole pieces of a permanent magnet that gives a field of 1 T, and were made as large as possible to minimize surface-tension effects. Into such a cell we put 2 cm^3 of an ultrasonically dispersed suspension of 0.4 mg cm^{-3} of fibre in a solution of 0.6% celloidin in amyl acetate. The solution was then allowed to evaporate undisturbed in the magnetic field over several days, in the situation shown schematically in Figure 1. Thus orientation was effected in a suspension sufficiently dilute to give a good degree of orientation, but the resultant film contains a sufficient density of fibre to produce a good diffraction-pattern. After evaporation the sides of the cell were broken away, the edges of the film were scored and the film floated off the base on water. This film was held flat between a pair of brass washers. The film was approximately 40 μm thick, which is several times thicker than the thickest fibres.

X-ray-diffraction patterns were produced in transmission geometry using filtered Co$K\alpha$ radiation. Initially they were recorded with the specimen film and a flat photographic film both perpendicular to a 1-mm-diameter beam so that the diffraction patterns of grunerite (amosite) fibres in both orientations should be recorded under identical conditions. However, the measurement of spot positions on intersecting hyperbolic layer-lines poses some problems; in later investigations, we used a cylindrical camera and took alternate photographs with one

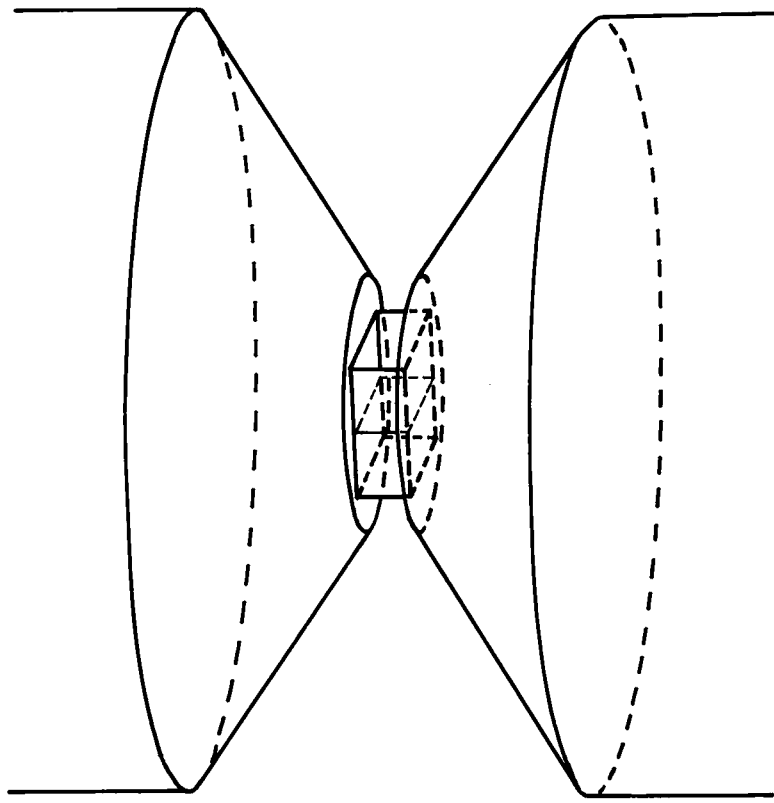

FIG. 1. Arrangement of cell, half filled with liquid, between the conical pole-pieces of the permanent magnet.

or other of the fibre populations parallel to the camera axis. We used both normal-beam and inclined-beam methods, the latter being arranged to give equi-inclination positions for particular layer-lines. The specimen was kept stationary throughout. Types and provenance of specimens studied are give in Table 1.

TABLE 1. MINERAL SPECIMENS STUDIED

Amosite	Penge, Transvaal
Amosite	India (locality unknown)
Crocidolite	Heuningvlei, South Africa
Crocidolite	Cochabamba, Bolivia
Anthophyllite	Paakila, Finland
Tremolite*	India; 2 specimens (localities unknown)
Tremolite*	Dorchester Co., Quebec
Tremolite*	Burcan, Turkey
Tremolite*	Thailand (locality unknown)

* Tremolite samples were kindly provided by Turner and Newall Ltd.

RESULTS

The X-ray-transmission photographs of amosite asbestos consist of two superimposed fibre-type patterns. Samples from both Penge, Transvaal and India (locality unknown) gave similar results. The patterns do not reproduce well because of the dark background from the celloidin relative to the weakness of the amosite pattern that is imposed by the need to use low concentrations of fibre in order to obtain good orientation. An indexed diagrammatic illustration of the zero- and first-layer lines of the normal beam pattern on a flat film has been produced from the observed patterns and is shown in Figure 2a. The set of reflections furthest from the centre, which are not indexed, are all that can be observed of a second-layer line. The pattern is confused by the two sets of crossing layer-lines, but it is clear that the zero-layer lines from the two types are quite different. Differences between the first-layer lines are less obvious. The measurements, on

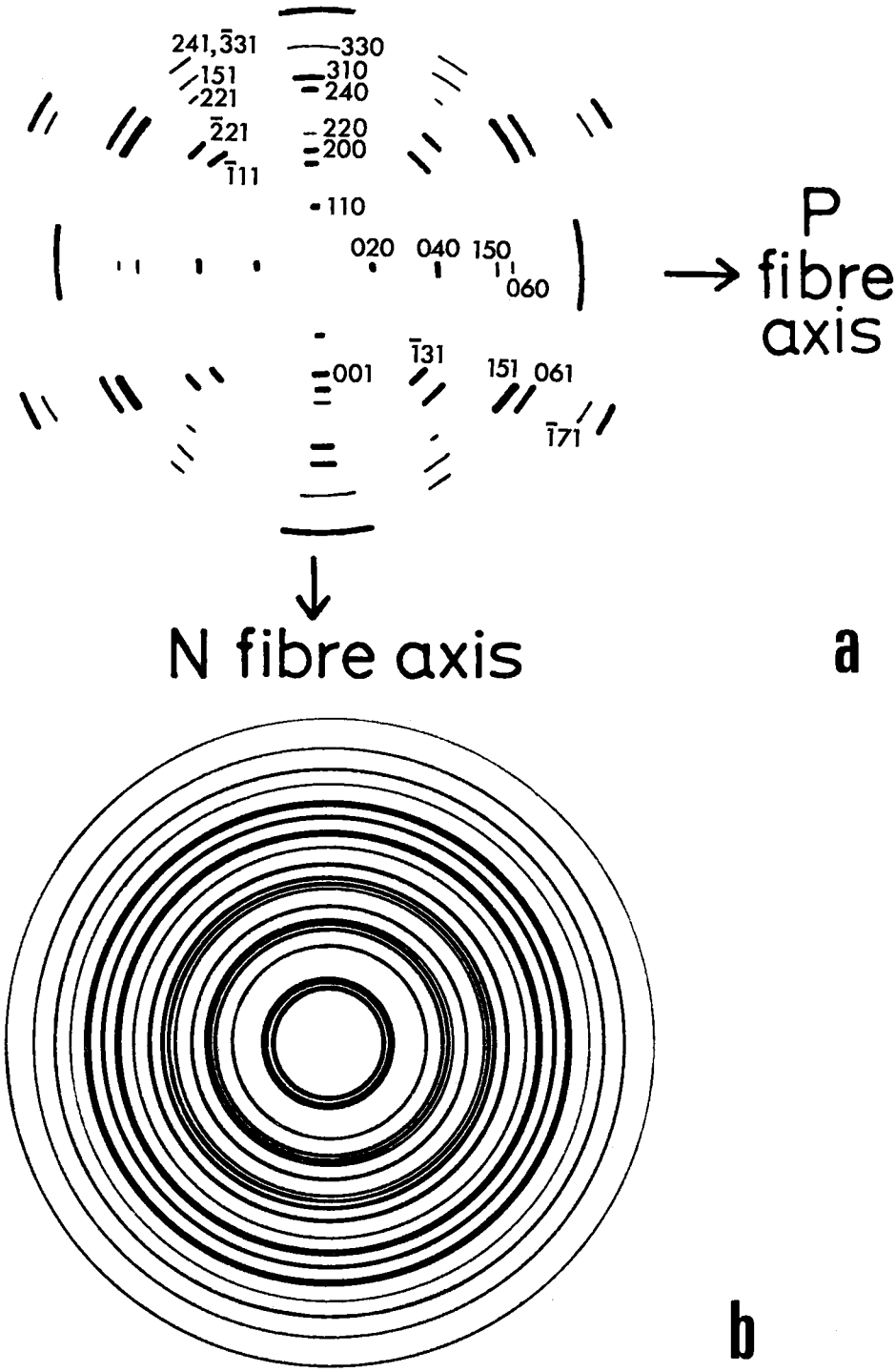

FIG. 2. Diagrammatic X-ray-diffraction pattern produced by crushed grunerite (amosite) fibres: (a) fibres aligned in a magnetic field; (b) fibres allowed to settle without the influence of a magnetic field. Arrows indicate directions of the fibre axes of P- and N-type fibres, respectively, parallel and normal to the field.

which the elucidation of these phenomena were made, relied on the simplification of straight layer-lines obtained for one type of fibre (at one time) by use of a cylindrical film, and in some cases improved resolution at the cross-over of layer lines from inclined-beam photographs. A blank experiment in which a specimen of the same material was prepared without a magnetic field produced the pattern shown diagrammatically in Figure 2b. The reflections present in the P- and N-type patterns, compared with reflections produced by the specimen prepared with no magnetic field, are summarized in Tables 2 and 3.

TABLE 2. ZERO-LAYER REFLECTIONS IN ORDER OF INCREASING d^* VALUE

NO MAGNETIC FIELD		MAGNETICALLY ORIENTED FIBRES			
		P		N	
$hk0$	I	$hk0$	I	$hk0$	I
020	M			020	S
110	S	110	S		
200	VW	200	M		
040	VW			040	S
220	W	220	W		
240	M	240	M		
-				150	W
060,310	VW	310	M	060	W
330(151)	M	330	W		

TABLE 3. FIRST-LAYER REFLECTIONS IN ORDER OF INCREASING d^* VALUE

NO MAGNETIC FIELD		MAGNETICALLY ORIENTED FIBRES			
		P		N	
$hk1$	I	$hk1$	I	$hk1$	I
001	VW			001	S
$\bar{1}11$	W	$\bar{1}11$	S		
$\bar{1}31$	VW			$\bar{1}31$	M
131	W				
$\bar{2}21$	M	$\bar{2}21$	M		
221	S	221	VW		
151(330)	M	151	W	151	S
061	S			061	M
-		241,$\bar{3}31$	W		
$\bar{2}61$	W				
-				$\bar{1}71$	W
$\bar{3}51$,331(080)	MW				
261($\bar{2}42$)	VW				

By a conventional consideration of the intersection of the sphere of reflection with the reciprocal lattice, we deduced the orientation of the crystallites required to produce the various observed reflections. These orientations were expressed in terms of the angle φ between y^* and the incident X-ray beam. For each reflection there are in general two values, φ_1 and φ_2, in a given quadrant, and each of these is repeated in other quadrants as $-\varphi$, $\pm(180-\varphi)$. This multiplicity allows for the fact that the positive direction of the z axis may be disposed in either sense. There is a reduction to a single value of φ in each quadrant for reflections of types $h0l$ (including $h00$) and type $0k0$ (but not $0kl$). By considering the values of φ for each reflection of the P-pattern and the N-pattern, one may deduce the range of φ required and prohibited by the reflections that are present and absent in each pattern. The P-pattern can be fully accounted for by a range of orientations either from 2 to 46° or from 11 to 63°, and values exceeding 77° are prohibited. The N-pattern can be fully accounted for by a range from 72 to 89° and values below 69° are prohibited. Thus the azimuthal orientations of the two populations are very different; that of the N population is much the more restricted in range and has the x^* axis within 20° of the normal to the plane of the specimen. The range of orientation of the P population has been less precisely defined but avoids the whole of that occupied by the N population, and must extend over at least a half and quite possibly two-thirds of the whole range 0 to 90°, but at the lower end. These orientations are summarized on stereographic pole figures in Figure 3.

In addition to the normal-beam photographs, other photographs were taken with the beam inclined to the z axis to give equi-inclination geometry for one of the first-layer lines. This changes the azimuth required to produce each reflection; we had hoped that changes in spot intensity between normal- and inclined-beam settings would indicate changes of multiplicity within the range of azimuths present, and so help to define the ranges of φ more precisely. No such correlation was observed; we must conclude that the frequency distribution of φ within its range is by no means flat, and perhaps not even unimodal, at any rate for the P population.

Subsequent experiments were carried out on tremolite, crocidolite and anthophyllite. Crocidolite exhibits a very poor degree of orientation, but produces a P-type pattern only. In this pattern, the same zero-layer reflections are present as in the amosite P-pattern, but the first-layer reflections are too diffuse to index. Anthophyllite produces a P-type pattern only; from the reflections indexed in this pattern, it was not possible to deduce any definite restrictions on the range of azimuths. Tremolite from different sources gave different degrees of orientation, the best being one from India, though with all samples only N-type patterns were produced. As in the amosite N-type pattern, the beam was perpendicular or nearly perpendicular to y^*, and the ranges of φ deduced for the different samples varied from (80 to 90°) to (70 to 90°).

Discussion

Both types of fibril, N-type and P-type, lie with their z axes in the plane of the celloidin film (Fig. 3). In the case of P-type fibrils, this is a direct result of the orienting effect of the magnetic field, which is parallel to this plane. N-type fibrils, on the other hand, must exist in the liquid suspension with their z axes at all angles to the base of the cell, and these axes are only constrained into the plane of the cel-

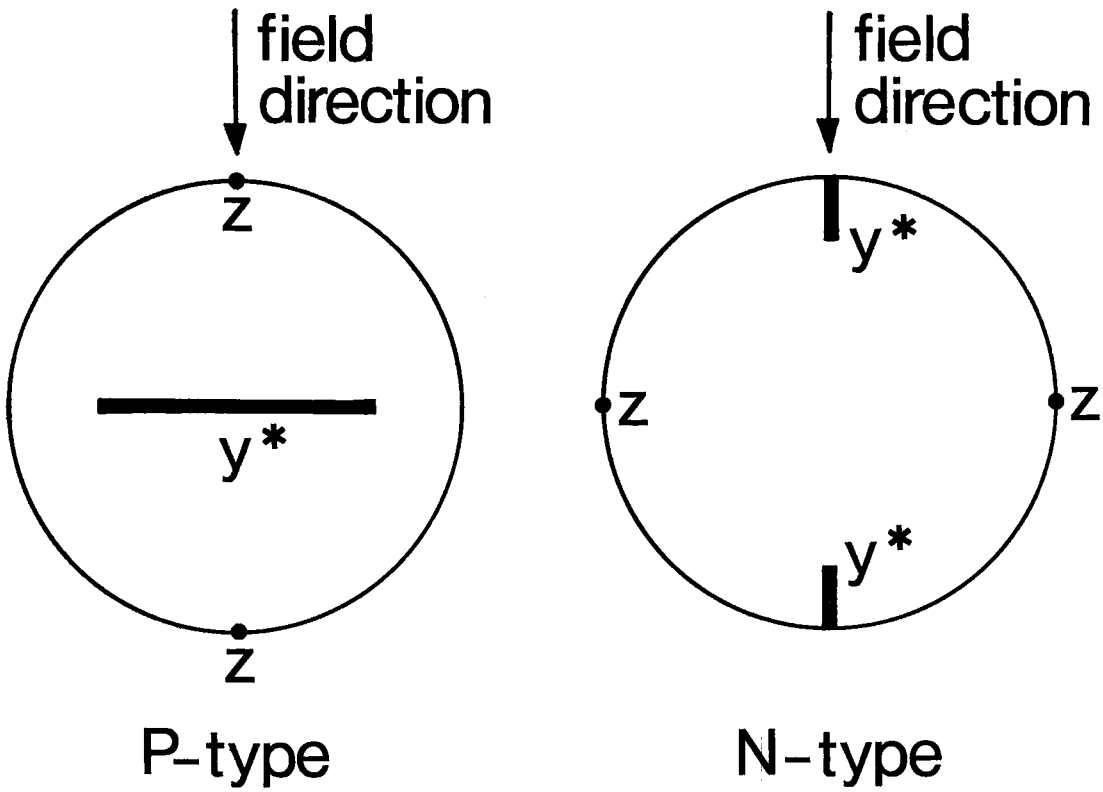

FIG. 3. Stereographic projection of the approximate directions of the z and y^* axes of magnetically oriented fibrous grunerite, projected onto the plane of the celloidin film, which was horizontal during the evaporation of the solvent.

loidin film as the solvent evaporates. The good definition of the first-layer line of the N-type pattern on the X-ray photograph shows that this constraint into the plane of the film is substantially complete, despite the fact that many of the fibres are shorter than the thickness of the celloidin film.

It is clear that N-type fibrils are more precisely oriented in azimuth than those of P-type (Fig. 3). This is understandable since the magnetic field is presumably operating to orient the fibres in azimuth when they lie perpendicular to the field. It is evident then that if the N-type fibres are paramagnetic or ferromagnetic, as reported (Timbrell 1979), their greatest magnetic susceptibility is along [010].

The much less perfect, but nevertheless marked, azimuthal orientation of the P fibres is less easily understood. It is certainly not due to mechanical settling onto (110) faces of amosite or crocidolite, which would give orientations outside the ranges observed. Electron micrographs of sections perpendicular to fibrils (Franco *et al.* 1977, Cressey *et al.* 1982) also suggest that the shapes of the sections are not strongly anisotropic. It is possible that the orientation is affected by magnetic-field gradients perpendicular to the field, which could be neither measured nor eliminated. The blank experiment in which a specimen of the same sample of grunerite was prepared by the same method but away from a magnet indicated that there is no restriction of azimuths during settling without the influence of a magnetic field.

Timbrell (1979) has suggested on the basis of susceptibility measurements that the magnetic properties of the iron-containing amphiboles are due to magnetite inclusions. The presence of magnetite was certainly indicated by the curves of magnetic susceptibility of bulk specimens, but whether this is relevant to the orientation properties of individual fibrils depends on a proof that the magnetite is contained within the fibrils. Fleet (pers. comm.) has observed that amphiboles commonly contain magnetite in two orientations, similar to the inclusions described in pyroxenes (Fleet *et al.* 1980). However, specimens that we prepared in a magnetic field on electron-microscope grids show that the amosite continues to show P- and N-type behavior in very fine fibrils at least down to about 0.2 μm in diameter,

so that if such inclusions are responsible for the behavior, they must be extremely fine, and at least two orders of magnitude smaller than those reported by Fleet *et al.* (1980). We have examined amosite fibres in the electron microscope at resolutions that would reveal such inclusions down to unit-cell dimensions, and have not observed any, although fine-scale talc-like material, serpentine and chlorite, all alteration products of the amphibole, are present on fibre surfaces and within cracks (Cressey *et al.* 1982). Moreover, both the orientations of magnetite inclusions observed by Fleet *et al.* (1980) would give rise to orientation of the fibrils with y^* perpendicular to the magnetic field, contrary to our observation of the behavior of N-type fibrils. We therefore believe that an explanation of the properties must be sought within the structure itself or as modified by the impurities that we observe.

The orientation of the N-types fibres, both longitudinally and in azimuth, is explained if the axis of greatest magnetic susceptibility, χ_{max}, is parallel to the y axis, which must in any case be one of the principal magnetic axes. If χ_{max} is not parallel to the y axis, then it must be in the xz plane, and an inclined orientation would be expected. We have observed this in a synthetic cobalt fluor-richterite. However, the monoclinic fibres of crocidolite and amosite are highly twinned on (100), so that if the angle between z and χ_{max} of a single crystal is small, the fibres would behave as P-type fibres. In anthophyllite (orthorhombic), the direction of χ_{max} could be along the z axis.

No explanation has been found for the difference between the P and N fibres that are both present in amosite. Their chemical compositions, determined by their X-ray spectra in the analytical electron-microscope, are not significantly different. Magnetically oriented specimens of amosite were also examined by TEM to check for any morphological differences between P and N fibres. P fibres tend to be larger than N fibres, but there is considerable overlap in the size ranges. For the amosite fibres observed in the TEM experiments, P fibres were found to range from 5 to 50 μm in length and 0.5 to 1.5 μm in width; N fibres were found to be 1 to 40 μm long and 0.2 to 0.8 μm wide.

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