Canadian Mineralogist
Vol. 31, pp. 447-458 (1993)

ELECTRON AND X-RAY PETROGRAPHY OF AN UNUSUAL SERPENTINE FROM THE TILLY FOSTER MINE, BREWSTER, NEW YORK

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ABSTRACT

The pseudocubic cleavage of an unusual serpentine from the Tilly Foster mine, Brewster, New York, was first investigated by J.D. Dana in 1874, who concluded this serpentine to be a pseudomorph. Investigators since have suggested that this pseudocubic serpentine does not fit into the standard classification of serpentine (chrysotile, lizardite, antigorite) and have variously argued that the pseudocubic structure belongs to the serpentine itself, is partly crystalline and partly amorphous, or is a new type of serpentine. We have investigated the microfabric of Tilly Foster serpentine using SEM, TEM and XRD methods. High-resolution SEM imaging has proved to be essential in the elucidation of the true nature of this material. The Tilly Foster serpentine is composed of large (but very thin) single-crystal plates of antigorite interleaved with composite matted-fiber layers of chrysotile. Antigorite–chrysotile layered units occur in mutually perpendicular array in different blocks throughout the "crystal", giving rise to the morphological pseudocubic cleavage. We believe that interpretation of the growth process of this serpentine composite involves the pseudomorphic replacement of a precursor with orthogonal cleavages. The replacement may have taken place in three stages: (1) nucleation and oriented growth of plates of antigorite on an orthogonal array of cleavage surfaces of the precursor, (2) nucleation and oriented growth of chrysotile fibers on the antigorite, (3) wholesale replacement of the precursor by chrysotile. Chrysotile fibers intergrown with antigorite are observed to be oriented with their *X* fiber axes either parallel to *Y* of antigorite or rotated approximately ±60° from *X* of antigorite, but rarely with *X* fiber axes parallel to *X* of antigorite.

Keywords: serpentine, Tilly Foster mine, pseudocubic cleavage, pseudomorph, antigorite, chrysotile, Brewster, New York.

SOMMAIRE

Le clivage "pseudo-cubique" d'une serpentine étrange provenant de la mine Tilly Foster, à Brewster, New York, a d'abord attiré l'attention de J.D. Dana en 1874. Il a conclu que cette serpentine s'est formée par pseudomorphose. Ceux qui ont travaillé sur ce matériau par la suite ont trouvé que cette serpentine pseudo-cubique ne concorde pas avec le schéma de classification courant (chrysotile, lizardite, antigorite), et ont proposé soit que la structure pseudo-cubique appartient à la serpentine même, que les échantillons sont en partie cristallins, en partie amorphes, ou qu'il s'agit d'une nouvelle sorte de serpentine. Nous avons étudié ce matériau en utilisant la miscroscopie électronique à balayage et par transmission, ainsi que la diffraction X. Les images à haute résolution obtenues par microscopie électronique à balayage se sont avérées essentielles dans la caractérisation complète de ce matériau. La serpentine de Tilly Foster est faite de plaquettes relativement grandes mais très minces d'antigorite monocristalline, interfoliée avec des couches faites d'un amas de fibres de chrysotile. Les unités stratifiées à antigorite + chrysotile sont agencées de façon perpendiculaire en divers blocs dans le "cristal", ce qui explique le clivage morphologiquement pseudo-cubique. Nous croyons que cet échantillon composite de serpentine est le résultat du remplacement d'un précurseur ayant des clivages orthogonaux. Le remplacement aurait procédé en trois étapes: 1) nucléation et croissance orientée de plaquettes d'antigorite sur les clivages orthogonaux du précurseur, 2) nucléation et croissance orientée de fibres de chrysotile sur l'antigorite, et 3) remplacement complet des restes du précurseur par le chrysotile. Les fibres de chrysotile en intercroissance avec l'antigorite sont orientées avec leur axe principal (*X*) soit parallèle à *Y* de l'antigorite ou déplacé d'environ ±60° par rapport à l'axe *X* de l'antigorite, et, plus rarement, avec l'axe *X* des fibres parallèle à l'axe *X* de l'antigorite.

(Traduit par la Rédaction)

Mots-clés: serpentine, mine de Tilley Foster, clivage pseudo-cubique, pseudomorphe, antigorite, chrysotile, Brewster, New York.

Introduction

Almost all serpentines described in recent years seem to fit into the classification scheme used by Whittaker & Zussman (1956) and modified by Wicks & Whittaker (1975), although studies by transmission electron microscopy (*e.g.*, Cressey & Zussman 1976, Cressey 1979) indicate that, on a fine scale, the different serpentines commonly occur as intimate mixtures. With the availability of high-resolution transmission electron microscopes, it has been possible to image the layer structures of serpentine directly, and such studies have shown that it is not at all uncommon for serpentine sheets to pass along their length from one form to another. For example, Veblen & Buseck (1979) illustrated sheets passing from a flat structure (lizardite) to a cylindrical one (chrysotile), and Cressey & Hutchison (1983, in prep.) reported corrugated (antigorite) sheets passing into a rolled-up (parachrysotile) form.

It has been difficult, however, to classify a serpentine with an unusual morphology from the Tilly Foster iron mine, Brewster, Putnam County, New York. What are almost certainly specimens of this type of serpentine have been studied and reported by J.D. Dana (1874), Friedel (1891), E.S. Dana (1892, 1915), Mügge (1903), Hamberg (1904), Koeberlin (1909), Manchester (1931), Frondel (1935), Caillère (1936), Trainer (1938, 1939, 1940, 1941, 1942), Faust & Fahey (1962) and Aumento (1967). It is generally described as serpentine in cubic pseudomorphs or pseudocubic serpentine. It seems to have a variable chemical composition. Aumento's work in particular, together with that of some of the earlier investigators, has been reviewed by Wicks (1969).

Dana (1874) described hand specimens from all over the mine in detail; some cubic pseudomorphs consist of just serpentine, whereas others are serpentine and dolomite intergrown in blades or layers. Both serpentine and dolomite appear to have nearly perfect cubic cleavage, but closer inspection shows that this is not a true cleavage, as fragments are not infinitely divisible into smaller cubes. Subdivision of the serpentine eventually produces small blocks with no cleavage property, but rather a wax-like, massive material, whereas small fragments of dolomite display the usual rhombohedral cleavage. Dana concluded that serpentine (and dolomite) have pseudomorphically replaced an unknown cubic mineral, of which no traces remain. Around this locality, serpentine also occurs in other pseudomorphic forms, probably after calcite, apatite, chlorite, chondrodite, enstatite, hornblende, biotite, dolomite, brucite, and an unknown tabular or platy mineral. Other minerals at this locality also form pseudomorphs. The magnetite ore itself is considered to have formed by the metasomatic replacement of metamorphosed dolomitic limestones that occur interbedded with granitic and syenitic gneisses (Koeberlin 1909).

Investigators of the Tilly Foster serpentine since J.D. Dana have variously argued that the pseudocubic structure belongs to the serpentine itself, is partly crystalline and partly amorphous, or is a new type of serpentine. In the most detailed study using modern methods, Aumento (1967) used optical microscopy, thermal analysis (DTA and TGA), X-ray powder diffraction (Debye–Scherrer camera, counter diffractometer and Guinier focussing camera), single-crystal X-ray diffraction (precession and Weissenberg cameras), and transmission electron microscopy (using dispersed crushed grains). He noted that one of the three cleavages is more perfect than the other two. Both the cleavage and the large size of the crystals (5 mm described by Aumento) seem to be unique among the serpentines. He also observed what appeared to him to be polysynthetic twinning; antigorite is the only other serpentine that develops twinning, and this occurs uncommonly. The Tilly Foster serpentine has a noticeably lower specific gravity (2.45) than the other serpentines (2.55 – 2.60). Optically it differs from the other serpentines in having lower indices of refraction and an inclined extinction (7° – 10° to crystal edges; other serpentines have parallel extinction).

Aumento's diffraction studies indicate a superlattice structure along the X axis similar to antigorite, and possibly along the Z axis also. However, the evidence for a superlattice along the Z axis is weak and has been questioned by Wicks (1969). Displacements of $\pm a/3$ and $\pm b/3$ in the stacking of layers are evident from Aumento's precession photographs. He also published electron micrographs from dispersed particles that show two morphologies: fibers 150 – 250 Å in diameter giving an electron-diffraction pattern similar to that of chrysotile, and large irregular plates, giving an electron-diffraction pattern similar to that of antigorite. The plates are crossed by regular parallel lines approximately 160 Å apart which, as Aumento pointed out, is approximately four times the superlattice parameter along the X axis. The plates seem to break along these lines, and commonly have crinkled edges which, Aumento suggested, were curling because of the strain caused by the mismatch between the sheets of octahedra and tetrahedra. However, Wicks (1969) has pointed out that the relationship 160 Å $\approx$ 41.5 $\times$ 4 is not valid on either geometrical or crystallographic grounds, because (1) the antigorite plates give normal single-crystal antigorite-type electron-diffraction patterns, although the 160 Å parallel lines are rotated from layer to layer, and (2) the curling of such layers would produce parachrysotile (fiber axis = Y) and not clinochrysotile (fiber axis = X), yet clinochrysotile is the form observed. The significance we place on the 160 Å spacing is discussed later.

Aumento suggested that this mineral could either be an intimate mixture of serpentine polymorphs, or it could be a new serpentine polymorph. His preferred interpretation was that the Tilly Foster serpentine is a new unstable serpentine polymorph. "Its unit cell is made up of six superimposed fundamental serpentine layers, with each successive layer displaced relative to its neighbors by $\pm a/3$ and $\pm b/3$, and, or by a rotation of ±60°. Individual layers are further modulated periodically in the *a* crystal direction. The stacking errors and layer modulations result in a crystal with superlattice-controlled *a* and *c* parameters" (Aumento 1967). He also suggested that this polymorph is only stable in the macroscopic state, and changes into simpler (chrysotile-like) units when ground mechanically. However, the evidence is weak, and his interpretation has been disputed on several grounds by Wicks (1969).

In order to elucidate the nature of Tilly Foster serpentine, we have investigated the undisturbed texture of this unusual mineral by transmission X-ray diffraction, by transmission electron microscopy (TEM) on samples prepared by ion-thinning, and by high-resolution scanning electron microscopy. The specimens studied by Aumento using TEM were prepared by crushing and dispersion, which destroyed original structures and orientations. Crushed grains also adopt preferred orientations on the electron microscope grid. Ion-thinning permits the study of mineral grains in the orientations and spatial relationships in which they were formed in the rock. In order to obtain three-dimensional images at magnifications between and largely overlapping the ranges of magnification obtainable by optical microscopy and by TEM, scanning electron microscopy is required. High-resolution SEM imaging has proved to be essential in the elucidation of the true nature of Tilly Foster serpentine. All our observations have been made on samples from the Tilly Foster mine (specimen BM47236), held in the mineral collection of The Natural History Museum. Although this is not the identical specimen studied by Aumento, the unique morphological characteristics of this mineral identify it as the same type of pseudocubic serpentine investigated by Aumento (1967) and earlier investigators.

Our studies, combining electron-optical and X-ray texture photographs, lead us to believe that Tilly Foster serpentine is composed of large (but very thin) plates of single-crystal antigorite interleaved with composite matted-fiber layers of chrysotile. These antigorite–chrysotile layered units occur in a mutually perpendicular array in different blocks throughout the "crystal", giving rise to the morphological pseudocubic cleavage.

Results and Discussion

SEM observations

Some of our early attempts to study Tilly Foster serpentine, using a simple SEM operating at 15 or 20 kV accelerating voltage, provided no detailed information, as only low-resolution images could be obtained because of the high penetration of the beam under these conditions. No further progress was possible until high-resolution SEM became available. In the present study, images of cleavage fragments of Tilly Foster serpentine were recorded using a Hitachi S–800 field emission SEM operating at 8 kV. Imaging at a low accelerating voltage is possible with this instrument because of the high-brightness source (field emission gun). Operation at a low kV results in minimal electron penetration in the specimen, which allows ultrathin surface layers to be imaged clearly with a resolution approaching 20 Å at high magnification. This low penetration of the beam and high-resolution capability have proved to be essential in the imaging of the antigorite. This is because the antigorite occurs only as ultrathin (< 500 Å) plates between layers of chrysotile in Tilly Foster serpentine. These plates are almost invisible when viewed in the SEM using a high accelerating voltage, because the beam passes right through them. The antigorite and chrysotile components in the sample were identified by TEM, electron diffraction and XRD. These observations will be described and discussed later.

Figure 1 is a secondary-electron SEM image of one surface of a rectangular block of Tilly Foster serpentine. This image shows the near-planar surface immediately below a plate of antigorite (now removed), and is composed of matted coplanar fibers of chrysotile. Within the layer, the majority of the chrysotile fibers clearly lie with their long dimension in two main orientations at about 60° to each other. These directions are indicated by the pale-colored lineations visible at the surface, and also by fibers (brighter in appearance owing to electron build-up and edge effects) that have been partly plucked from the surface. This distinct orientation of fibers appears only to apply to fibers close to, or in contact with, the plates of antigorite. From our electron-diffraction observations in the TEM, these two predominant directions of chrysotile fibers are always observed to be ±30° from the *Y* crystallographic axis of the associated antigorite. (Alternatively, this orientation can be described as ±60° from the *X* crystallographic axis of the antigorite). This observed crystallographic relationship allows us, with some confidence, to ascertain the direction of the *Y* axis of the antigorite plate that was in contact with the chrysotile layer shown in Figure 1. Thus determined, the *Y* axis of antigorite was aligned almost parallel to the straight edge produced by the distinct cleavage break that appears in Figure 1. In fact, careful measurement of the main directions of chrysotile shows that the *Y* axis of the antigorite was aligned at about 7° to the cleavage break for the block on the right of the cleavage. For the main block (to the left of the cleavage), the *Y* axis of the antigorite appears to have been aligned at about 0° to the cleavage break, and for a surface layer slightly lower down in this block (shown exposed on the far left of the image), the antigorite appears to have been oriented with *Y* at about 10° to the cleavage. These angular relationships are consistent with our X-ray results (reported here) and with optical observations (also reported by Aumento 1967) that extinction angles

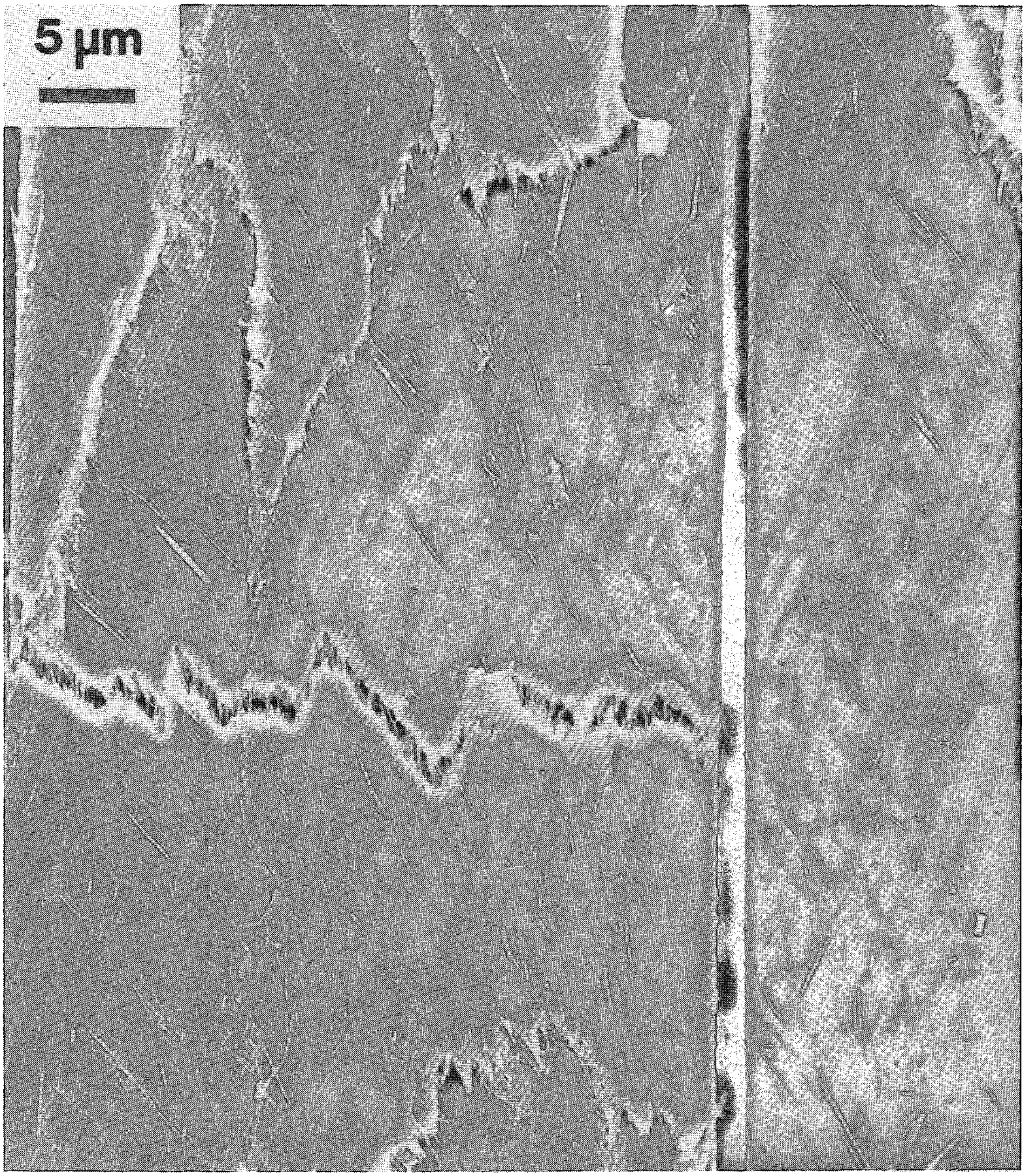

FIG. 1. Cleavage surface of Tilly Foster serpentine, imaged in the SEM, showing the near-planar surface immediately below a plate of antigorite (now removed). This surface consists of coplanar fibers of chrysotile that lie predominantly in two directions at 60° to one another.

between vibration directions and cleavage edges are in the range 0–10° for cleavage fragments of the Tilly Foster material viewed in crossed polars in the optical microscope. The image shown in Figure 1 also clearly demonstrates that the morphological macrocleavage is not a true cleavage, as planar fracture will only occur within antigorite plates or at the junction between antigorite and matted layers of chrysotile. The straight fracture seen in the figure indicates the presence of a thin plate of antigorite (just visible) normal to the image

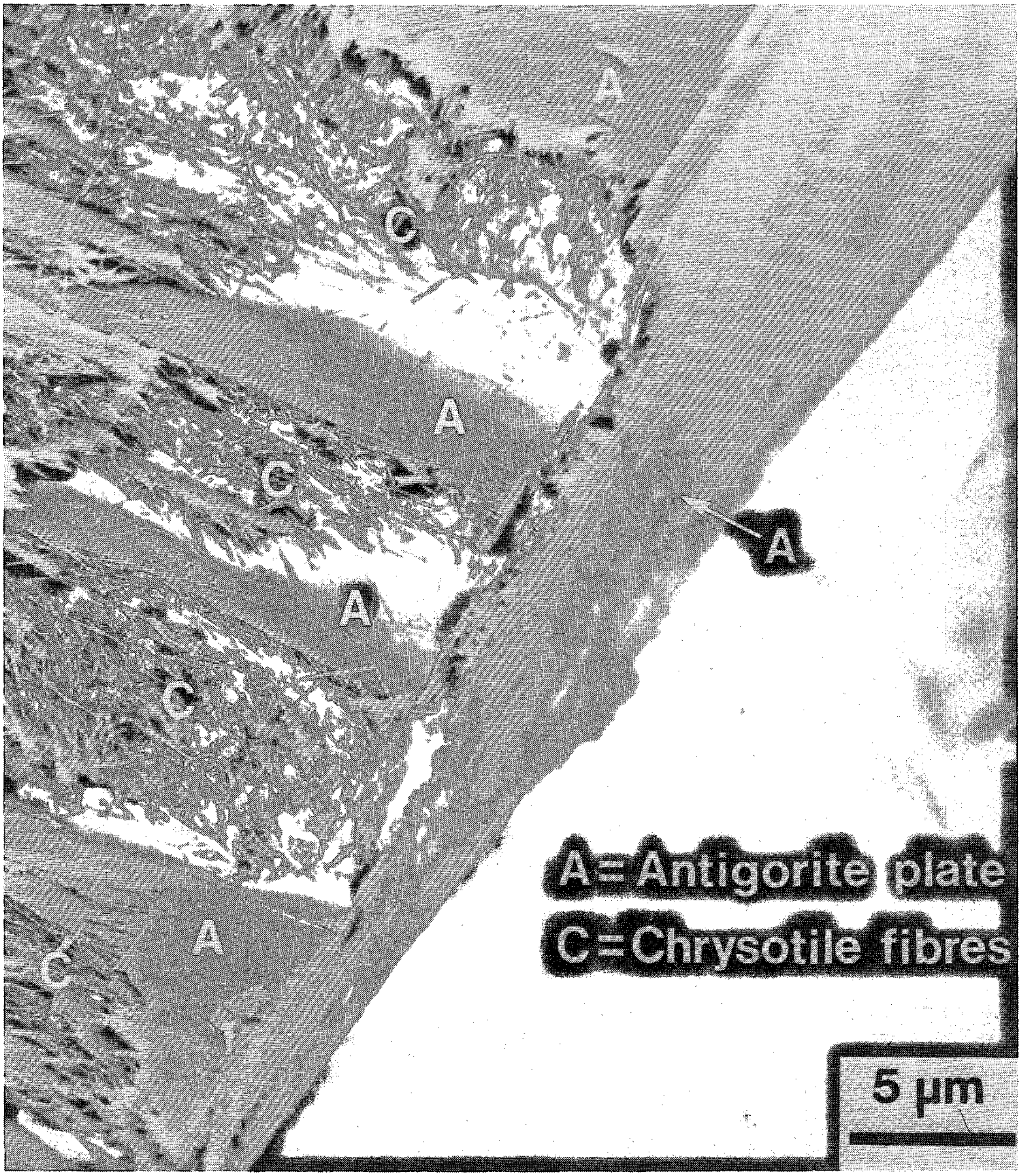

FIG. 2. SEM image of a stepped fragment of Tilly Foster serpentine, showing that planar fracture occurs along the thin plates of antigorite. Layered units in between antigorite plates consist of chrysotile fibers.

surface. As clearly illustrated in this image, any other fracture of this composite will be nonplanar.

The SEM image shown in Figure 2 is typical of fractured Tilly Foster serpentine. Clearly, this serpentine is a composite, being made up of a multiple sandwich of asbestiform fibers separated by thin plates. From our TEM and XRD investigations, we have established that the fibers are clinochrysotile and that the thin plates are single crystals of antigorite. Distinct blocks of these multiple-layered units occur throughout Tilly Foster serpentine "crystals". The orientation of the layers within any one block is constant, but may be in any one of three mutually perpendicular directions relative to layers in adjacent blocks. The edge dimensions of such blocks vary greatly from micrometers to millimeters. Figure 2 shows a very thin block, along the right-hand edge of the sample. It is bounded by two large plates of antigorite, in near-vertical orientation, with a single unit layer of chrysotile fibers between them. The remnant of a third plate of antigorite across the thin width of this block is visible in the upper part of the micrograph. The total width of this block is only about 1.5 μm. The thin block occurs adjacent to a much larger, multilayered, block. The layering in this larger block is perpendicular to the layering in the adjacent thin block. Planar fractures occur only along the antigorite layers. As the antigorite layers are arranged in a mutually perpendicular array and are commonly very extensive in area, this planar geometry of the fractures gives rise to the observed cubic macrocleavage property, typically yielding orthogonal cleavage fragments with edges up to 5 mm in length. Aumento (1967) reported that one of the three "cleavages" was more perfect than the other two for the material he studied. Our observations are similar, in that fragments of the material we studied commonly have the shape of rectangular blocks rather than perfect cubes. These blocks, on further breaking, yield rectangular platelets, several millimeters long, which are almost micaceous in habit. Such micaceous flakes can be produced by parting from any one of the three perpendicular surfaces of a parent "cleavage" block. The micaceous habit is indicative of the morphology of the antigorite sheets, each of which is a single crystal, very thin and extremely extensive in area. Clearly, the distribution of antigorite sheets controls the pattern and spacing of the planar fractures.

Also visible in Figure 2 is evidence for the relative orientations of the *Y* axes of the four antigorite crystals that form the main steps of the block. As already discussed, the orientations of chrysotile fibers immediately adjacent to a crystal of antigorite allow the *Y*-axis direction of antigorite to be established. In this figure, the acute angle between the two orientations of chrysotile fibers can be easily seen where they protrude from beneath the antigorite layers, and by the lineation of fibers on antigorite surfaces. From these observations, it is clear that two orientations of antigorite are present: the antigorite forming the top step of the block has its *Y* axis aligned almost parallel to the (vertical) boundary cleavage of the block; the other layers of antigorite are each aligned with their *Y* axis almost normal to this boundary cleavage. Thus, in any one multiple-layer block, layers of antigorite may have crystallographic orientations that are rotated relatively through 90° (±10°) in the *X–Y* plane. This rotation orientation is probably the origin of the apparent polysynthetic twinning on (001) described by Aumento (1967).

A higher-magnification view of fractured Tilly Foster serpentine is shown in Figure 3. Two plates of antigorite, one about 500 Å thick and another even thinner, can be recognized by their platy habit and irregular edge-fracture. Each of these plates is a single crystal. Chrysotile fibers are seen to form matted layers parallel to the antigorite layers. Individual single-crystal fibers of chrysotile can be distinguished, and their cylindrical morphology is just discernible.

TEM observations

Cleavage fragments of Tilly Foster serpentine were embedded in epoxy resin, then sectioned and ion-beam thinned using standard procedures. These were examined in a Philips EM301 TEM operating at 100 kV. The areas that were thinned to electron transparency were found to contain chrysotile only (Cressey 1977). Antigorite–chrysotile interfaces are obviously difficult to sample and preserve throughout the thinning process, because of the easy parting at these boundaries and because samples consist predominantly of chrysotile between extremely thin plates of antigorite. However, experiments with thin flakes simply pulled off the "cube" cleavage faces and held in folding TEM specimen-support grids produced more informative images. Viewed in a Siemens 101B TEM operating at 80 kV, these cleavage flakes were found to be sufficiently thin at their edges to be transparent to electrons without any further preparation. Figure 4A shows the edge of one such cleavage flake, reproduced at a magnification comparable to that of the SEM image shown in Figure 3. With the complementary information from SEM images, this TEM image can be interpreted as showing matted layers of chrysotile above and below a thin plate of antigorite oriented approximately perpendicular to the electron beam. The antigorite plate has irregularly curved broken edges and has the appearance of an almost transparent support film to the chrysotile fibers. Selected-area diffraction (SAD) from this support plate clearly shows superlattice reflections (Fig. 4B) and confirms it to be antigorite with the a^*b^* reciprocal lattice plane normal to the beam. Furthermore, the plate of antigorite shown in this image is only part of the single crystal extending over the whole of the cleavage fragment (about 1 mm × 1 mm square) placed in the TEM. This was confirmed from the orientation of a series of SAD patterns taken from different areas along the edge of the cleavage fragment.

From TEM images, such as that shown in Figure 4A, it can be appreciated that orientations of chrysotile fibers are not random where they are associated with antigorite. Undisturbed fibers of chrysotile in contact with antigorite are observed to lie predominantly with their *X* fiber axes close to two main directions at 60° to one another and at ±30° to the *Y* crystallographic axis of the antigorite single-crystal sheet. In addition, chrysotile

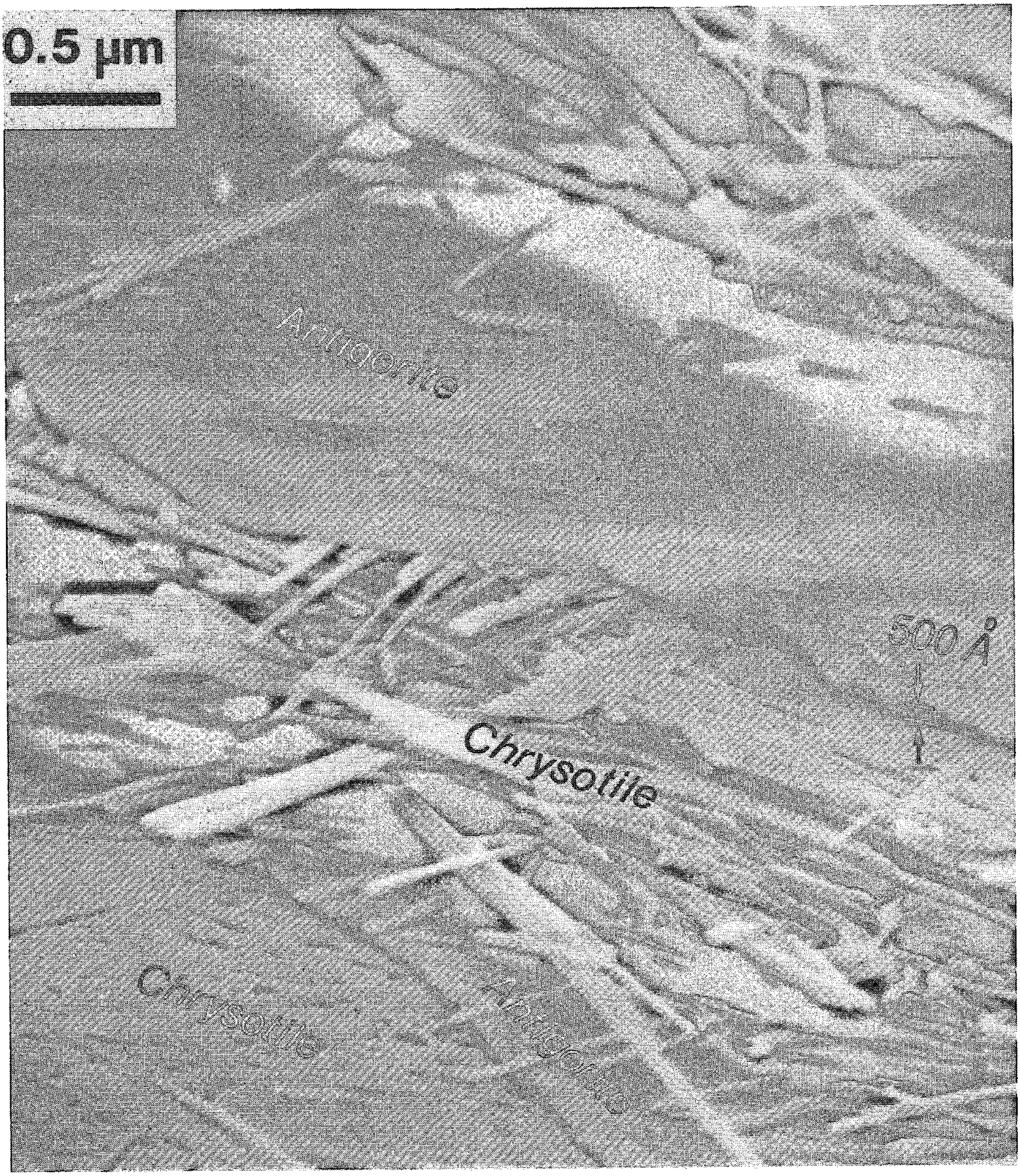

FIG. 3. High-magnification SEM image of Tilly Foster serpentine. Chrysotile fibers are seen to form matted layers parallel to the thin single-crystal plates of antigorite.

fibers also are commonly observed to lie with their *X* fiber axes almost parallel to the *Y* axis of the antigorite. However, *X* fiber axes of chrysotile are only rarely aligned anywhere near parallel to the *X* axis of the antigorite. The typical relative abundance and distribution of these fiber orientations can be seen in Figure 4A. In this micrograph, one of the chrysotile orientations at 30° to *Y* of the antigorite is less abundant in this area. Lineations in the antigorite plate itself also mark the positions of chrysotile fibers that have been plucked

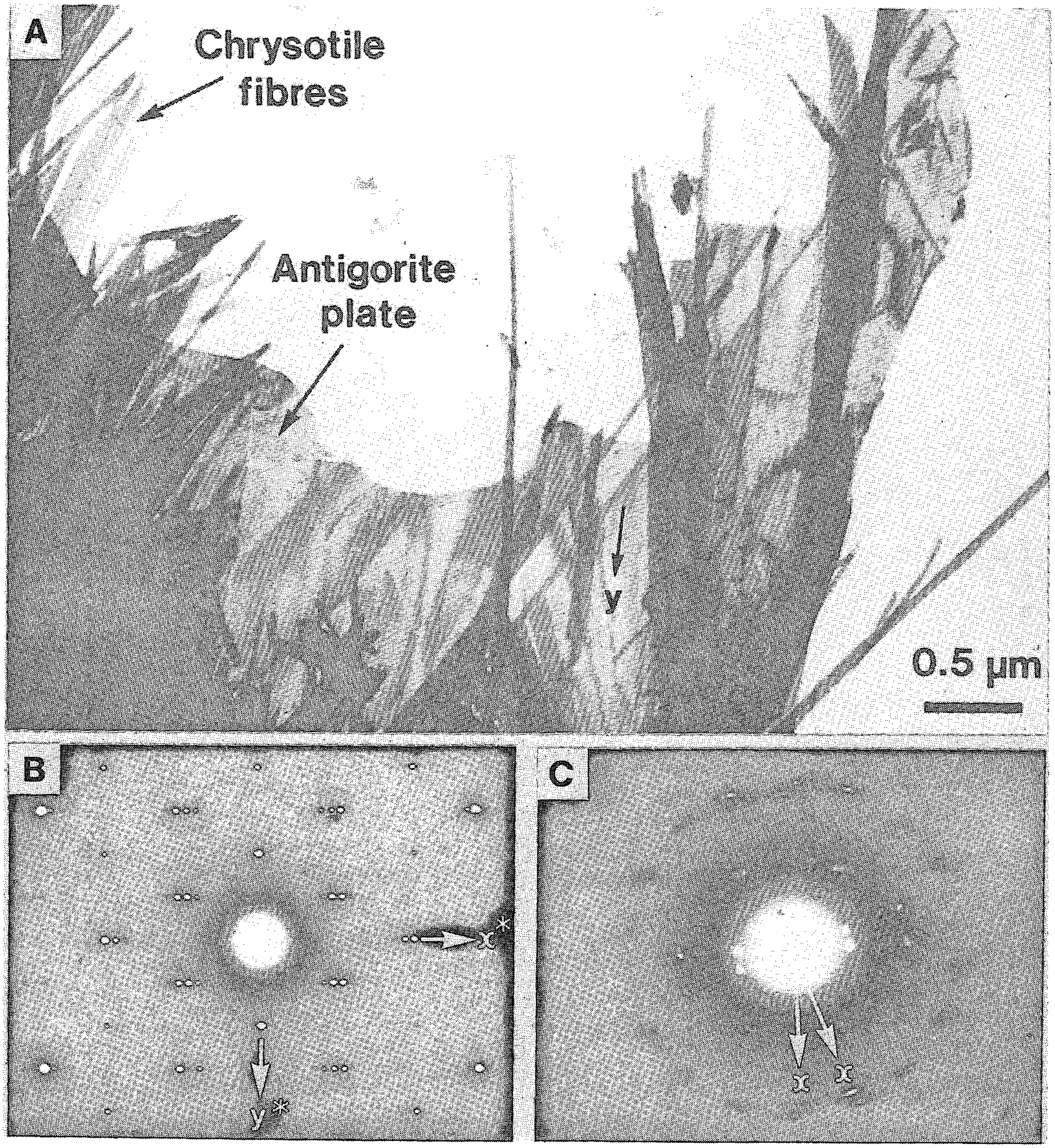

FIG. 4. A) The edge of a thin cleavage flake of Tilly Foster serpentine, imaged in the TEM. The micrograph shows the layer of chrysotile fibers that have grown in contact with a thin single-crystal plate of antigorite. The direction of the *Y* axis of the antigorite is indicated by an arrow. B) Selected-area electron diffraction (SAD) pattern from the single-crystal plate of antigorite, showing superlattice reflections parallel to X^*. C) SAD pattern from a bundle of clinochrysotile fibers, showing two dominant directions of the *X* fiber axes.

away from the antigorite, leaving grooves in the plate of antigorite. These grooves show up as contrast features due to variations in thickness in the antigorite plate. The spacing between these grooves, which commonly occur in parallel sets, is about 160–200 Å, *i.e.*, the approximate width of an individual fiber of chrysotile in a group of parallel fibers in edge-contact with one another. It is likely that such grooves are the origin of the parallel lines, with a separation of about 160 Å, reported by Aumento (1967).

Chrysotile–antigorite crystallographic relationships have been verified by SAD and from images in which the *a* superlattice of antigorite (approximately 40 Å) is visible in the image. The chrysotile fibers typically produce SAD patterns such as shown in Figure 4C. It should be noted that diffraction patterns indicate that only clinochrysotile (fiber axis = *X*) is present; no parachrysotile (fiber axis = *Y*) has been observed, even where the chrysotile fiber axes are parallel to *Y* of antigorite.

X-ray diffraction

A thin micaceous cleavage plate of the Tilly Foster serpentine, of dimensions about 1 mm × 1 mm square, was placed flat on a ("zero-background") single-crystal silicon substrate in a Philips diffractometer operating at 45 kV and 45 mA. The resultant diffractogram (produced using Ni-filtered Cu radiation) contains peaks that can only be indexed as either 00*l* ($d_{00l} = 7.3/n$ or $14.6/2n$ Å) or 0*k*0 ($d_{0k0} = 9.2/2n$ Å). Such a pattern showing enhanced orientation is consistent with the interpretation that the Tilly Foster serpentine forms an intergrowth in which axes of chrysotile fibers are coplanar with sheets of antigorite parallel to the surface of the cleavage flake. Once powdered, such flakes produced diffraction patterns similar to that of clinochrysotile.

Specimens of Tilly Foster serpentine were chosen optically for the single-crystal X-ray investigations. Selected samples consisted of very thin, rectangular micaceous flakes that exhibit approximate single-crystal biaxial optics, with extinction angles of about 5° relative to the edges of the rectangular "crystal". Fragments examined generally do not extinguish sharply between crossed polars, indicating that they consist of several layers of single crystals, each in slightly different azimuthal orientations. From our subsequent X-ray experiments, we were able to confirm that the direction of slow vibration of these flakes corresponds to the *Y* crystallographic axis of the antigorite in these cleavage fragments.

Our precession photographs of cleavage fragments of Tilly Foster serpentine show features that are essentially the same as those observed by Aumento (1967), *viz.* superlattice reflections along X^*, and streaking of certain reflections along Z^* indicative of $\pm a/3$ and $\pm b/3$ displacements in the stacking of the serpentine layers. These reciprocal-space features can be attributed to the antigorite, but the presence of multiple orientations of chrysotile coupled with the precession movement complicates the issue, and results in a complex ring pattern. All the precession photographs published by Aumento (1967) show these rings, but he did not discuss them. Wicks (1969) has noted that these persistent rings are not explained by Aumento's interpretation of Tilly Foster serpentine. We prefer to interpret individual precession photographs as two superimposed patterns, one from antigorite, the other from various orientations of chrysotile.

In order to elucidate the orientation relationships between the chrysotile and antigorite, we have recorded transmission X-ray texture photographs on flat film, using Ni-filtered Cu radiation, for different stationary orientations of cleavage plates relative to the X-ray beam. Figure 5 shows a set of stationary X-ray photographs produced from a single, morphologically orthorhombic cleavage fragment with edge dimensions 1400 × 600 × 60 µm. Each morphological face, (001), (100) and (010), was set successively perpendicular to the X-ray beam. Orientations of chrysotile fibers in the plane perpendicular to the X-ray beam are easily recognized in such stationary photographs because the cylindrical lattice of chrysotile, even if stationary, produces a distinctive rotation-type set of reflections with characteristic diffuse streaks extending from 110 and 130 reflections. The fiber patterns observed also are distinctive in that they are typical of clinochrysotile. In the case of antigorite, a stationary crystal also produces many reflections because of (1) its small superlattice dimension in reciprocal space, and (2) the presence of streaking in reciprocal space parallel to Z^*, caused by $\pm a/3$ and $\pm b/3$ displacements in the stacking of the serpentine layers. By a conventional consideration of the intersection of the sphere of reflection with the reciprocal lattice, we have deduced the relative orientations of antigorite and chrysotile required to produce the various observed reflections recorded by these stationary photographs. For antigorite indexing in Figure 5, *l* is used to denote nonrational values for reflections that arise from the intersection of reciprocal lattice streaks with the sphere of reflection. Several reasonably clear orientation relationships among the cleavage morphology, the antigorite, and the clinochrysotile emerge from a study of these X-ray photographs:

(1) The antigorite *X* and *Y* axes are constrained to lie within ±10° from a morphological cleavage edge. This is illustrated by the ±10° arcs shown by the main reflections of antigorite produced with the beam parallel to Z^* of the antigorite plates (Fig. 5A). Spots of strong intensity occur at the middle of the angular ranges of these arcs, indicating that a single orientation of antigorite predominates, *i.e.*, antigorite is mainly oriented with its *Y* axis parallel to the straight edge of the cleavage fragment that was aligned parallel to the horizontal axis of the camera.

(2) Some of the chrysotile fibers are present in random orientation. Collectively, these fibers produce the ring type of diffraction pattern.

(3) Populations of chrysotile with distinct ranges of fiber orientation are present, as indicated by the arcs of higher intensities superimposed on the background ring patterns. These chrysotile fibers have *X* axes aligned predominantly parallel to *Y* of antigorite and in a range up to about ±45° from *Y* of antigorite, but few fiber axes lie outside this range (Fig. 5A).

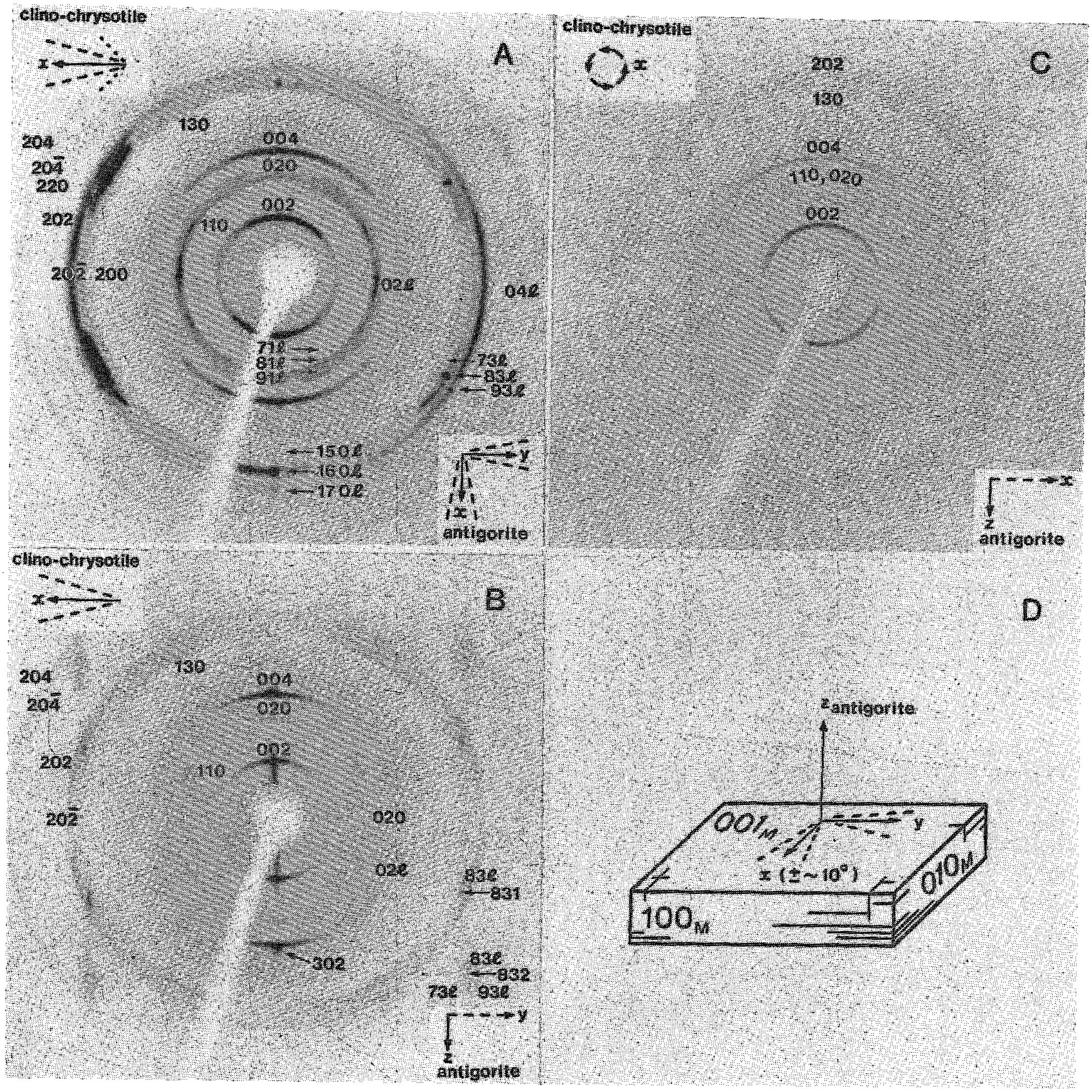

FIG. 5. A–C) X-ray transmission photographs of Tilly Foster serpentine recorded on flat film using Ni-filtered Cu radiation, showing textural and orientation relationships among antigorite, chrysotile and cleavage morphology. Photographs were produced from a single, morphologically orthorhombic cleavage fragment set successively with A: (001), B: (100) and C: (010) morphological faces perpendicular and stationary with respect to the X-ray beam. Antigorite and clinochrysotile indexing is shown in opposite quadrants. D) Diagrammatic representation of the orientation relationship between antigorite and the orthorhombic morphology of a cleavage fragment; subscript M denotes morphological indexing.

(4) The majority of chrysotile fibers are aligned with their axes coplanar with the *X–Y* plane of antigorite (Fig. 5B).

(5) Distinct populations of chrysotile with fiber axes parallel to *X* of antigorite are absent (Fig. 5C).

All of these observations are consistent with information obtained from our SEM and TEM investigations. These X-ray results represent the typical fabric of a single block (see Fig. 2) consisting of interlayered antigorite–chrysotile. In some samples, investigated by

X-ray diffraction in this way, two distinct orientations of antigorite can be shown to be present, with their *Y* axes rotated through 90° to one another in the *X–Y* plane. In such cases, the proportions of antigorite crystals oriented in each of these directions can be estimated from the relative intensities of reflections produced by the two antigorite orientations. In such samples, antigorite is considered to occur with two orientations of the layers similar to those imaged in Figure 2.

"Spherulitic" Tilly Foster serpentine

A small proportion of the Tilly Foster serpentine (specimen BM47236) that we studied can be described as "spherulitic". In the optical microscope, these cleavage fragments appear to be composed of spherules or radial bundles of fibers approximately 20 μm across. In general, the "spherulitic" material tends to be slightly more brown-green in color than the apple-green of the samples already described, but both have the same macrocleavage properties. As expected, X-ray photographs of stationary "spherulitic" samples exhibit well-defined orientations of antigorite plates superimposed on powder-type rings consistent with random fibers of clinochrysotile. In the TEM, all ion-thinned "spherulitic" material was found to consist entirely of randomly oriented clinochrysotile and fibers of polygonal serpentine (Cressey 1977). The fibers of polygonal serpentine are similar to those described by Cressey & Zussman (1976). Plates of antigorite are not present in the thin edge produced by the ion-thinning process, so that the orientation of any chrysotile that may be associated with the antigorite could not be established. No evidence of a spherulitic texture was observed by TEM. SEM observations of surface topography also have failed to identify the "spherules", which leads us to believe that the spherulitic appearance in the transmission optical microscope may be an effect made up from many superimposed layers.

Formation of the pseudomorphs

From our observations of the interlayered units that occur in mutually perpendicular arrays in the Tilly Foster serpentine, we believe that the growth of this material involves the pseudomorphic replacement of a precursor with orthogonal cleavages. However, the precursor mineral has never been identified. Possible precursor minerals that have been considered by previous investigators are galena, halite and anhydrite (Dana 1874) and periclase (Dana 1892). Of these, the rectangular morphology of cleavage fragments of anhydrite most strongly resembles the "cleavage" morphology of the Tilly Foster serpentine. Dana (1874) noted that anhydrite is known, elsewhere, occasionally to form as a hydrothermal vein mineral. There is some evidence for the presence of (remobilized) sulfur in the Tilly Foster rocks, in the form of pyrrhotite. Koeberlin (1909) reported the presence of substantial secondary pyrrhotite in the Croton mines, within 4.8 km of the Tilly Foster mine. We suggest that the pseudomorphic replacement by serpentine may have taken place in three stages:

(1) Plates of antigorite nucleated and grew within cleavage planes on orthogonally oriented surfaces of the precursor, the thin and extensive platy morphology of the antigorite having been imposed by the thin planar geometry. Two distinct crystallographic orientations of antigorite relative to the precursor are recognized. The *X–Y* plane of the antigorite is always parallel to one principal crystallographic axial plane of the precursor, with the *Y* axis of the antigorite either parallel or perpendicular to a second principal axial plane of the precursor. Such orientations could be the result of preferred epitactic nucleation of antigorite on cleavage surfaces of the precursor.

(2) Following the growth of large platy single crystals of antigorite in the cleavage voids of the precursor, the first stages of the pseudomorphic replacement of the precursor by chrysotile then took place. Clinochrysotile fibers seen in contact with antigorite crystals appear to have nucleated on the antigorite predominantly with their *X* fiber axes either near to being parallel with *Y* of antigorite or rotated approximately ±60° from *X* of antigorite, but rarely with *X* fiber axes parallel to *X* of antigorite. These orientation relationships may originate from epitactic growth on the antigorite, although the orientations of both serpentine phases may have been controlled independently by the precursor structure.

(3) Eventually, the complete pseudomorphic replacement of the interiors of blocks of the precursor took place. This replacement by chrysotile contains fibers in more random orientations, but generally the *X* fiber axes are constrained in the general directions of the fiber axes of the earlier-nucleated chrysotile, *i.e.*, mainly oriented within a range of ±45° to *Y* of the antigorite.

It should be pointed out that the orientation relationships among antigorite, chrysotile and precursor cleavages are not perfectly constant. If initial orientations of growth of antigorite were indeed the result of epitactic nucleation, it is possible that subsequent overgrowths were less well constrained. This probably accounts for the relative misorientation of up to ±10° observed for the antigorite. Similarly, the orientations of the chrysotile may have become less well constrained as pseudomorphism proceeded.

CONCLUSIONS

Our observations on the Tilly Foster serpentine using modern instrumentation broadly confirm, and amplify, the conclusions of Dana (1874) based on detailed and careful observations of hand specimens. We refute the conclusion of Aumento (1967) that Tilly Foster serpentine is a new polymorph; by the techniques available to us, especially high-resolution SEM, we have been able to demonstrate clearly that this material is composed of chrysotile and antigorite. By electron and X-ray diffraction, we have elucidated the crystallographic relationship between these minerals. We suggest that the observed lower specific gravity compared with other serpentines may be due to the unusual packing arrangement in this material. Most of the optical properties can be accounted for in accordance with our SEM, TEM and XRD results, although the reason why some material exhibits an apparently spherulitic texture in transmitted light optics is not obvious.

ACKNOWLEDGEMENTS

We thank Fred Wicks, Jim Chisholm and Robert F. Martin for their interest in this work, and for their helpful comments that led to improvements in the manuscript.

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Received February 13, 1992, revised manuscript accepted August 11, 1992.