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CHRYSOTILE MORPHOLOGY

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ABSTRACT

Bundles of chrysotile fibers embedded in "Araldite" were cut with a diamond knife. Electron micrographs showed predominantly circular cross sections, many rings, and also end-on views of concentric tubes. Areas of intermediate electron optical density within tubes and between tubes were seen. The data support the explanation of high density values as being caused by amorphous-appearing material plugging voids, and strongly indicate that chrysotile fibers are tubes in their massive form. The ultramicrotomy method and the electron micrographs obtained are discussed: several unusual morphological features revealed by cutting cross sections are pointed out.

INTRODUCTION

Pundsack (1) and Kalousek and Muttart (2) have found the density of massive chrysotile to be too high for a tubular morphology. These findings have promoted the concept that the ultimate fibers are laths or solid cylinders in the bulk and that tubes which are routinely seen in the electron microscope (2–7) are artifacts (1, 2) or the result of selective sampling (8). The usual techniques of grinding fibers, the high vacuum, and the effect of the electron beam have been considered by some to explain hollow fibers.

Bates and Comer (6) recently reviewed the evidence for a tubular shape and published micrographs of replicas of cleaved surfaces of massive chrysotile. Although the replica technique avoids both grinding and the introduction of the actual material into the electron microscope, chrysotile cleaves primarily along the long axis of the fibers and few cross sectional views were found. Nevertheless they were able to conclude (correctly in our opinion) that the presence of amorphous material in voids between tubes and within hollow fibers would explain high density values.

The present study was initiated following the publication of Pundsack's high density data. It was felt that the methods of ultramicrotomy (developed primarily for electron microscopical examination of biological materials) would allow cutting of thin cross sections of relatively large bundles of chrysotile fibers, and that micrographs of these sections would provide a much clearer picture of fiber morphology than previous studies afforded. Noll and Kircher (7) previously attempted to cut thin sections but obtained only a few isolated fiber cross sections.

METHODS

General

Early attempts to cut thin cross sections of chrysotile using metha-

crylate embedding and glass knives resulted in too few usable sections to be practical. The methacrylate resin did not adhere to the fiber bundle sufficiently well to prevent the bundle from "popping out" when cut by the knife. "Araldite," an epoxy resin first employed as an embedding medium by Glauert, Rogers, and Glauert (9, 10), was found to be superior to methacrylate for embedding chrysotile. Preliminary results with a number of different samples of chrysotile embedded in "Araldite" and cut with glass knives showed close packed circular cross sections which were too thick for detailed high resolution studies. The use of a diamond knife enabled sections to be cut thin enough to demonstrate details within the predominantly circular cross sections.

All micrographs in this paper are from a specimen of a silky fibrous chrysotile (Transvaal) No. M14676, Manchester University Dept. of Geology collection. Samples were prepared for sectioning as described below and cut with a diamond knife mounted on a Servall Porter-Blum ultramicrotome.*

Embedding

Thin strands of silky chrysotile were teased apart with fine needles under a 30 power dissecting microscope until the teased fibers were approximately 50 to 100 microns in diameter. Loosely tangled masses of the teased fibers were placed in small test tubes and treated according to the following schedule:

(1) Three changes of absolute ethanol during 24 hours at room temperature.
(2) 50% ethanol-50% epoxy resin mixture without accelerator for 24 hours at room temperature.
(3) Three changes of epoxy resin mixture without accelerator during 24 hours at 50° C.
(4) The fibers were then transferred to No. 4 gelatin capsules in which the long axis of the fibers was roughly oriented to the long axis of the capsules which were filled with the resin mixture complete with accelerator. If air bubbles formed they were removed by placing the filled capsules in a vacuum. One day at room temperature was allowed for infiltration.
(5) The capsules were then incubated at 50° C. for two to four days during which polymerization occurred.

The modified Glauert, Rogers, and Glauert mixture consisted of 10 ml. "Araldite" 502 (resin), 10 ml. dodecenyl succinic anhydride (hardener), 1.5 ml. dibutyl phthalate (plasticizer), and 0.4 ml. tridimethylaminophenol (accelerator).

After removal of the gelatin in warm water the polymerized blocks were trimmed so that the area to be sectioned contained one or two fiber bundles oriented approximately perpendicularly to the front plane of the

* The mounting for the diamond knife was custom made by Mr. Nils Jernberg of Rockefeller Institute; however, a similar mounting can now be purchased complete with diamond knife from Ivan Sorvall Inc., Norwalk, Conn.

trimmed block. The sections floating in the knife trough were picked up on 400 mesh nickel or copper grids and coated with a thin film of evaporated carbon.

Microscopy

The sections were then examined in an RCA EMU-3D electron microscope equipped with a 50 micron objective aperture. Advantage was taken of 100-KV operation for scanning at high (100,000 ×) magnifications but all photographs were taken with 50-KV electrons at the lowest intensity consistent with adequate focussing. Several series of micrographs were taken of specimens held in the beam for periods of time ranging from a few seconds to 5 minutes in order to ascertain whether some of the peripheral structure seen on cross sections was caused by contamination. We have concluded on this basis that none of the structures seen in the micrographs can be attributed to contamination.

Results

The fibers, as seen by this method, are arranged in bundles or groups ranging from a few fibers to hundreds or thousands of fibers comprising bundles a micron or more in diameter. Previous observations suggested that the shape of cross sections tends towards a circle when the fiber is cut perpendicularly to the major axis. This indication is completely confirmed by the improved embedding and sectioning techniques.

Examination of numerous micrographs shows an overwhelming proportion of circular cross sections. One such micrograph is seen in Fig. 1. In the upper portion of the micrograph a group of about 100 fibers is seen cut perpendicularly to the major fiber axis. To the lower left and to some extent the upper right and center right a more longitudinal cut was obtained. This micrograph shows the characteristic lack of perfect fiber alignment over areas larger than a few thousand Angstroms in diameter.

An interesting and important feature of Fig. 1 is the relatively large amount of void space both within and between the cross sectioned fibers. Only in thin sections could the central holes be photographed. Most of the sections were estimated to be about 400 Å thick but some were much thinner. Some of the sections such as that shown in Fig. 1 may be wedge shaped. This interpretation would explain the relative faintness of the central holes in the circular cross sections in the lower and right portions of the micrograph as compared with the upper left region. Although the sections' varying thicknesses might account for varying densities, there are examples of cross sections without central holes in areas of predominantly "doughnut shaped" cross sections. The important question of the relative amount of void space will be discussed later.

Many cross sections of concentric tubes with central holes and annular

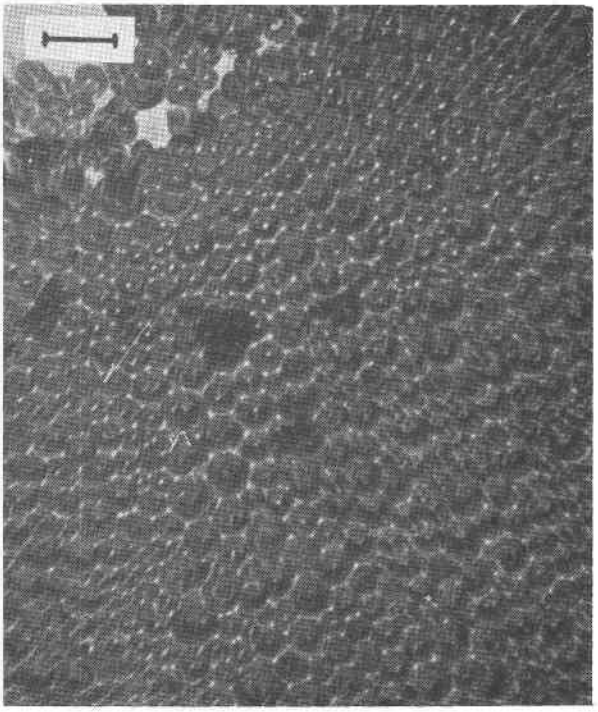

FIG. 1. Electron micrograph of a cross section of a chrysotile fiber bundle. In the upper left area the major fiber axes were perpendicular to the knife edge. In this and subsequent micrographs the line indicates a distance of 1000 Angstroms. Magnification 97,000×.

spaces of varying optical densities were photographed. Figure 2*a* shows a compact bundle of about 60 fibers sliced at an angle somewhat less than 90° to the major fiber axis. Areas with mixtures of single tubes and concentric tubes were not frequently observed and Fig. 2 is representative in this respect. In a few instances only annular voids or only central holes are seen within tubes but generally both central holes and annular voids were of low optical density. Figure 2*b* is another area showing concentric tubes cut both across and parallel to (arrow) the major fiber axes. An enlargement of a portion of Fig. 2*b* is seen in Fig. 2*c*. Among the structural features shown here are:

(1) Walls of the inner tube thicker than the outer tube walls.
(2) Radial lines extending from the inner tube wall to the outer tube wall. (Arrows labeled A)
(3) Polygonal walls of the outer tube. (Arrow labeled B)

Figure 3 is a cross section of a bundle of chrysotile fibers showing views of tubes within tubes, radial lines (arrows labeled A) as described above and additional structural features. Some of these structures are incom-

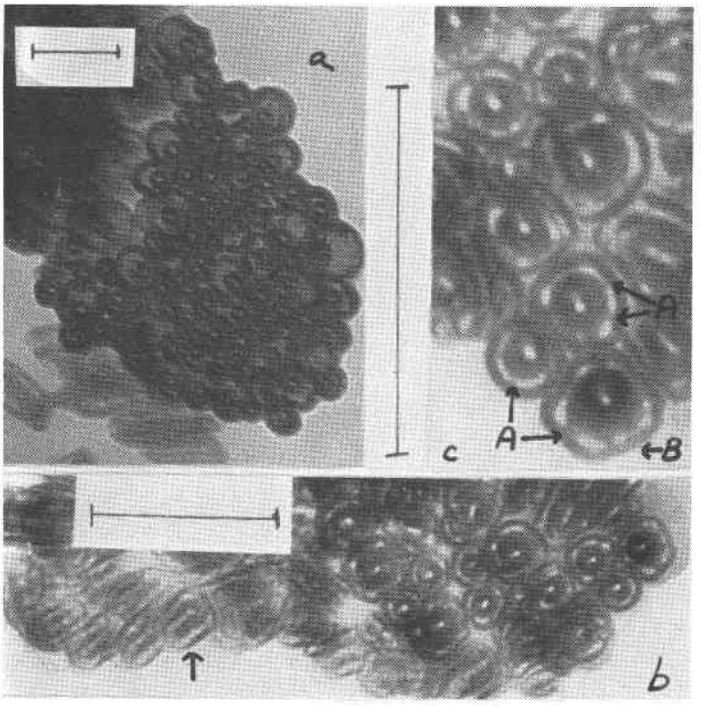

FIG. 2. A composite of three electron micrographs showing cross sections of concentric tubes found in chrysotile: (a) 119,000×. (b) arrow points to longitudinal sections. 119,000×. (c) an enlargement of a portion of b. Refer to text for meaning of arrows. 485,000×.

plete walls of inner tubes within outer tubes with complete walls (arrows labeled B), incomplete inner walls within incomplete outer walls (arrow labeled C), complete inner walls within incomplete outer walls (arrow labeled D), and an incomplete inner wall apparently attached to or originating from the outer wall (arrow labeled E). This micrograph also shows areas of varying electron optical density both within and between tubes.

Diameters (O.D.) of outer tubes vary between 200 Å and 500 Å with an average of 340 Å based on a limited number of measurements. Inner tube diameters (I.D.) range from 15 Å to 150 Å with a rough average of about 80 Å. Outer tube and inner tube wall thicknesses are about 40 Å and 70 Å respectively. In some regions inner tube wall thicknesses were about the same as outer tube walls (40–50 Å).

DISCUSSION AND CONCLUSIONS

We feel that this investigation, although not completed, demonstrates the value of ultramicrotomy of relatively hard materials utilizing a dia-

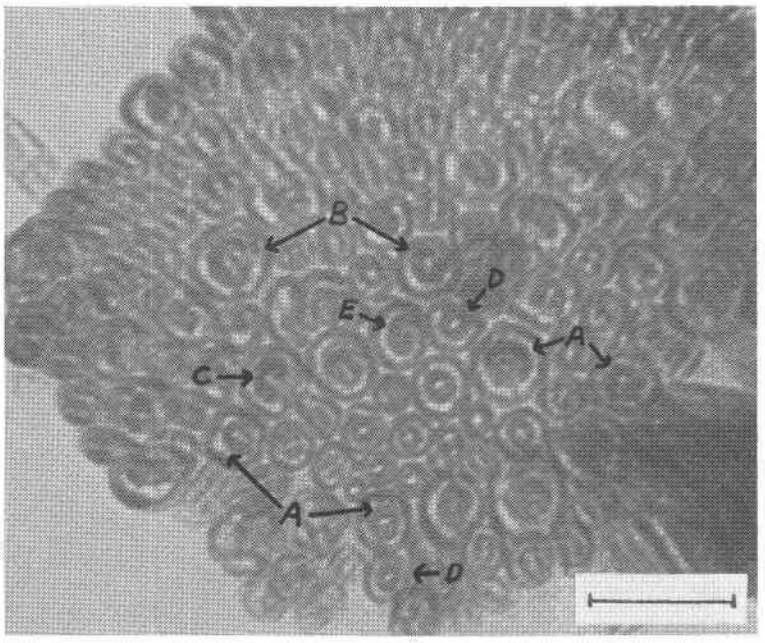

FIG. 3. Electron micrograph of chrysotile cross section showing several unusual structures. Refer to text for meaning of arrows. 195,000×.

mond knife and "Araldite" embedding. It should be noted that Fernandez-Moran has published micrographs of sections of metals using a diamond knife (11).

We conclude from an examination of electron micrographs such as shown in Figs. 1–3 that most of the chrysotile fibers and especially the sample of silky chrysotile from Transvaal are cylindrical in shape in the massive form. It is inconceivable that such large areas of fibers in such close array could be changed from laths, curved or otherwise, to cylinders by any of the described manipulations.

It is also evident that a large number of the close packed arrays of cylinders are hollow for some part of their length. Areas of low optical density are also apparent between individual tubes forming interfiber void spaces. However, much of the two types of open areas is actually of electron optical density intermediate between the fiber walls and the background of embedding polymer. We have for some time interpreted these areas of intermediate density as relatively unorganized or amorphous material. Therefore the results presented here are in agreement with the recent conclusions of Bates and Comer (6) concerning amorphous material.

Whereas the existence of hollow tubes in massive chrysotile would seem

to be firmly established, at present it is difficult to estimate the proportion of hollow to filled cylinders. The difficulty arises in the selection of the area of a section to be recorded in the electron microscope. Although all regions of sections thin enough to produce an image have shown circular cross sections some of these have had only faint indications of holes. The presence of amorphous material also complicates interpretations of the amount of hollow cylinders. Routine production of extremely thin sections and series of serial sections through an appreciable depth of fiber bundles will be necessary to sort out the possibilities that most of the fibers are either entirely hollow, partially filled with amorphous-appearing or crystalline material, or completely filled with amorphous-appearing or crystalline material. From the micrographs obtained so far it seems probable that some of the tubes (such as shown in Figs. 2 and 3) may have their inner volumes completely filled for some depth; somewhat farther down the material may only partially block the hole and at other locations be absent. On the other hand tubes may be found that have about the same amount of material plugging their inner voids through a large depth of fiber. In spite of the fact that a determination of actual amounts of tube varieties must await further work, it is interesting to consider the structures brought out so far by ultramicrotomy.

Figures 2 and 3 show a preponderance of cross sections of concentric tubes. Arrangements of more than two tubes in this manner have not been seen so far. In some micrographs (see Figs. 2*b*, 2*c*, and 3) the walls of the inner tube are much thicker than either the outer tube walls or the walls of other inner tubes. For several reasons it is rather unlikely that the thickness could be due to embedding polymer shrinking away from the outer tube walls. Most importantly, a consideration of embedding conditions suggests that the epoxy resin does not penetrate either into the intrafiber void space or between individual fibers. The resin probably flows between relatively large fiber bundles. In view of the difficulty experienced by Young and Healy (12) in getting non-polar gases past "water sorbing plugs" in their study of gas absorption of chrysotile, it seems impossible that the viscous mixture used for embedding reached the internal regions of the tubes. Secondly, the relatively high electron density of the thick inner tube walls suggests material of higher electron scattering power than a hydrocarbon polymer. The above reasoning can also be cited to explain the areas of intermediate electron optical density found within tubes and between tubes. It appears more probable that such areas are of the previously postulated amorphous material.

Although many of the tube-in-a-tube cross sections appear to be almost perfect concentric arrangements of rings, some are distorted. Thus some of the inner tubes are off center and some of the outer tubes appear to

have polygonal walls rather than circles. The latter may be compared to the much larger tubes of halloysite with polygonal outlines found by Bates and Comer (6). It is possible that some of the elliptical shapes of tubes are caused by the force of the knife but it is doubtful this could be the cause of polygonal outlines.

Models, constructed from sections of transparent tubing with voids filled with wax to simulate concentric tubes with amorphous material, have been useful aids for interpreting cross sections. The interpretations described above have been verified with such models and they have indicated that the radial lines (labeled A) seen in Figs. 2*c* and 3 could be lower edges of the sliced tubes seen through the depth of the section of tubing. These radial lines could also be visualized as narrow sheets connecting the inner and outer tubes. Such sheets might be of crystalline or of amorphous material. Thinner sections and serial sections may help clear up this point and also the significance of the various arc shaped structures seen in Fig. 3. It is possible that the latter structures may have some significance for interpretation of the growth of chrysotile.

Although concentric tube arrangements have been reported in electron micrographs of various samples of chrysotile, particularly of synthetic material, we have more frequently seen tube-within-a-tube arrangements in thin sections than in dispersions of whole tubes of this sample. Whether the discrepancy is due to a subjective factor in selecting areas in the microscope or is simply a reflection of the greater capability of ultramicrotomy must await further work.

The sizes of the tubular structures found in cross section by ultramicrotomy agree in general with the observations on dispersed fibers and of replica studies (6) and with the calculations of Whittaker (8) based on *x*-ray diffraction patterns.

The preponderant evidence deduced from electron micrographs of chrysotile prepared by sectioning, dispersing, or replicating fibers in addition to *x*-ray and electron (13, 5) diffraction and gas absorption all points to a tubular structure partially filled or blocked with amorphous or crystalline material. An explanation of the growth of tubular crystals has been advanced by Bates and can be summarized from the recent publication of Bates and Comer (6): " . . . it is to be expected that the arrangement of atoms will become less regular both inward and outward from some point within the wall of the tube. It is hypothesized that, in the process of crystallization, material 'trapped' inside and subsequent layers outside the 'ideal tube' will have less regularity in atomic arrangement finally filling 'intertube' and 'intratube' areas with 'amorphous-appearing' material."

It would seem that cutting cross sections of various fibrous and platy

minerals would profitably add to knowledge concerning their morphology and origin. We plan to continue ultramicrotomy of massive chrysotile using samples known to have different appearances in the dispersed state and to attempt to obtain serial sections of bundles to elucidate some of the structures observed.

Summary

(1) Cross sections of massive chrysotile embedded in "Araldite" were cut with a diamond knife.

(2) A preponderance of cross sections of a number of different samples, but primarily of silky chrysotile (Transvaal), were circular when examined in the electron microscope.

(3) Many sections showed rings with central holes which strongly indicates a tubular morphology.

(4) The sample examined most extensively had many concentric tube arrangements.

(5) Material of intermediate optical density was found both in interfiber voids and intrafiber voids and is interpreted as amorphous material.

(6) Some new arrangements which may be related to tubular crystal growth were photographed.

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