

ash fiber



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THE PROPERTIES OF ASBESTOS. II. THE DENSITY AND STRUCTURE OF CHRYSOTILE¹

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Received August 26, 1955

It is shown that the tubular structure hypothesized for chrysotile asbestos is not compatible with experimentally determined density values for sealed, solid blocks of asbestos fiber. The data indicate that the fundamental fibers are packed together efficiently with very little void space. The only void space observed appears to be associated with the volume occupied by sorbed water. Sorption and desorption of water probably causes reversible swelling of the fiber bundles. It is hypothesized that the fundamental fibers may exist as sheet- or ribbon-like structures possessing a certain degree of distortion due to limited curvature about the fiber axis.

The unusual nature of serpentine minerals ($3\text{MgO} \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) which occur in massive, pseudo-fibrous and fibrous (chrysotile) forms has led numerous investigators to attempt a structural

analysis of the various species. Chrysotile was classified first as an amphibole structure with a repeating $\text{Si}_4\text{O}_{11}^{-4}$ unit,² but this was revised later to a layer- or sheet-type structure with a repeating

(1) Preceding paper in this series, F. L. Pundsack, *THIS JOURNAL*, 89, 892 (1955).

(2) B. E. Warren and W. L. Bragg, *Z. Krist.*, 76, 201 (1930).

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Si_2O_5 unit.¹ Although there appears to be general agreement that chrysotile has a sheet- or layer-type structure, many workers have pointed out that the fundamental sheet structure must be distorted in some way to account for the X-ray diffraction patterns which are observed.⁴⁻⁸ In recent years interest in the structural characteristics of chrysotile has been stimulated by the almost simultaneous publication by Bates, Sand and Mink⁹ in this country and Noll and Kircher¹⁰ in Germany of electron photomicrographs of chrysotile which appear to show the fibers in the form of hollow tubes. Hillier and Turkevich¹¹ had previously noted this phenomenon in passing. Recently a number of attempts have been made to correlate X-ray diffraction data from chrysotile with the hypothesized tubular structure.¹⁰⁻¹²

It is apparent that a tubular structure of the type hypothesized for chrysotile will contain considerable void volume (i.e., space not occupied by chrysotile) when the fibers are packed into solid bundles of the type found in nature. Thus, if the density of naturally occurring blocks of fiber is determined in a liquid which does not penetrate the fiber blocks, the magnitude of the void volume can be ascertained, and the existence of a tubular structure can be shown to be either possible or highly improbable.

Experimental

Materials.—The chrysotile fiber used for the density determinations in water was selected from a supply of No. 1 Danville Crude from Canada. The analysis of this material has been reported previously.¹ Portions of the selected solid fiber blocks were broken off into unopened bundles about 2.4 cm. long and 0.4–0.5 cm. in diameter. The samples were examined carefully for flaws and imperfections. Density determinations on these specimens are referred to as density values for "blocks of fiber." After the experimental runs had been completed on these blocks of fiber, they were opened carefully by hand and found to be free of any foreign inclusions which might otherwise invalidate the measurements.

The density determination in air was carried out with an essentially flawless, translucent specimen of chrysotile from Arizona. This sample was in the form of a slightly irregular block about 5 cm. $\times$ 3 cm. $\times$ 1.6 cm. with a mass of approximately 58 g.

Distilled water with a specific resistance $>5 \times 10^6$ ohms was used for density determinations in an aqueous medium.

Density Measurements.—Two 25-ml. capacity pycnometers fitted with thermometers and side-arm capillary tubes were calibrated to ± 0.002 cc. with the liquid being used in the density measurements. Samples were weighed out into the pycnometer flasks, and then they were outgassed in accordance with a method described by Tschapek¹³ and later used successfully by Culbertson and Weber.¹⁴ The procedure consists of adding enough liquid to the flask to cover the sample and then evacuating the system in a vacuum desiccator to just below the vapor pressure of the liquid.

- (3) B. E. Warren and K. W. Hering, *Phys. Rev.*, **89**, 925 (1941).
- (4) V. A. Fock and V. A. Kolpinsky, *J. Phys. U.S.S.R.*, **3**, 125 (1940).
- (5) B. E. Warren, *Am. Mineralogist*, **27**, 235 (1942).
- (6) E. Aruja, *Mineralog. Mag.*, **27**, 65 (1944).
- (7) T. F. Bates, L. B. Sand and J. F. Mink, *Science*, **111**, 512 (1950).
- (8) W. Noll and H. Kircher, *Naturw.*, **37**, 540 (1950).
- (9) J. Hillier and J. Turkevich, *Anal. Chem.*, **21**, 475 (1949).
- (10) E. J. W. Whittaker, *Acta Cryst.*, **7**, 327 (1954).
- (11) E. J. W. Whittaker, *ibid.*, **8**, 261, 265 (1955).
- (12) H. Jagodzinski and G. Kunze, *Neues Jahrb. Mineral. Monatsh.*, **96**, 113, 137 (1954).
- (13) M. W. Tschapek, *Kolloid-Z.*, **63**, 343 (1933).
- (14) J. L. Culbertson and M. K. Weber, *J. Am. Chem. Soc.*, **60**, 2695 (1938).

This method effectively removes adsorbed air from the system. After the system had been outgassed a sufficient length of time (determined by repeated runs until a constant density was attained) the vacuum was broken and the flask filled with liquid and allowed to come to room temperature, $25 \pm 1^\circ$. The pycnometer unit was assembled and the density determined. The actual temperature of the system was read to within 0.1° from the thermometer in the pycnometer flask. After the density values had been obtained for the unsealed specimens the samples were collected, dried and the density calculated on both an "as-is" (i.e., original sample weight which includes sorbed water) and a dry basis.

For the "sealed block" density determinations unopened blocks of chrysotile were weighed and then dipped in molten paraffin at about 78° . This procedure formed a relatively smooth, even coating of solidified paraffin over the entire block of fiber. Subsequent gas adsorption measurements showed that the coating was impervious. The density of the "sealed blocks" was determined in water, and then the value was corrected for the density of the paraffin present. Sorbed water content of the blocks was determined by dehydration runs on untreated fiber blocks from the same source. The untreated blocks were weighed under the same conditions of relative humidity as the blocks used in the density determinations. The density of the paraffin, 0.901 g./cc., was determined independently by coating glass rods of known volume with the molten paraffin.

The density determination in air on the specimen of fiber from Arizona was carried out simply by mapping the contours and profile of the block on graph paper and calculating the volume on the basis of the mapped dimensions. The block was weighed and then the sorbed water content was determined on a small portion of the block by the procedure described below.

Water Determinations.—Experiments showed that reversibly sorbed water could be removed from chrysotile by drying the material at temperatures between 175 and 200° . At temperatures much above 200° a slight, non-reversible water loss occurs in chrysotile. Therefore, for purposes of calculating the density of the fiber samples on a dry sample basis the water loss up to 175° was considered sorbed water. As an approximation the sorbed water was assumed to occupy the same volume as an equal quantity of free water, and this correction was used to obtain the density of the solid fiber. Although the sorbed water may actually occupy a volume slightly less than that of free water, this assumption is not critical to the conclusions reached in this work.

Theoretical

When hollow cylindrical tubes with an outer radius r_1 and an inner radius r_2 are placed together in hexagonal close-packing the ratio of the gross volume of the bundle of tubes, V_0 , to the volume of the solid, V_s , is

$$\frac{V_0}{V_s} = \frac{2\sqrt{3}}{\pi} \left(\frac{r_1^3}{r_1^3 - r_2^3} \right) \quad (1)$$

Equation 1 may be rearranged and reciprocal density values D substituted for corresponding volumes to give

$$D_s = \frac{2\sqrt{3}}{\pi} D_0 \left(\frac{r_1^3}{r_1^3 - r_2^3} \right) \quad (2)$$

where

D_s = absolute density of the solid

D_0 = observed gross density of the fiber bundle

Equation 2 reflects the relationship of the density of the solid to the observed bundle density when the liquid fails to penetrate the void volume. If the fibers are solid (i.e., $r_2 = 0$), or the liquid penetrates the intrafibril pores but not the interfibril pores, equation 2 reduces to

$$D_s = \frac{2\sqrt{3}}{\pi} D_0 \quad (3)$$

When the liquid penetrates all pores

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D_0 , which is essential to the utilization of the preceding equations, can be calculated readily from X-ray diffraction unit cell data available in the literature. The data on the dimensions of a unit cell of the composition $Mg_3(OH)_2Si_4O_{10}$ are summarized in Table I. Using the average values $a = 5.33$ Å., $b = 9.24$ Å., and $c = 7.33$ Å. the absolute density of chrysotile is 2.56 g./cc. Since the samples used in this work contained about 2% $FeO + Fe_2O_3$ isomorphously substituted for magnesium,¹ the theoretical density of 2.56 can be corrected to 2.58 g./cc. to take this into account. This correction is incidental since it is within the range of experimental error.

TABLE I
UNIT CELL ($Mg_3(OH)_2Si_4O_{10}$) DATA FOR CHRYSOTILE

Axis	Warren and Bragg ¹	Warren and Hering ¹	Aruja ²	Whittaker ³	Padurew ⁴
a	5.33	5.33	5.32	5.33	5.33
b	9.25	9.24	9.2	9.2	9.26
c	7.33	7.33	7.31	7.33	7.36

The magnitude of D_0 to be expected for hollow tubes of the dimensions which have been suggested,¹¹ $r_1 = 175$ Å. and $r_2 = 75$ Å., can be calculated from equation 2 by using $D_s = 2.58$. In this case $D_0 = 1.91$ g./cc. assuming a sealed block in which no penetration of liquid into the void volume occurs.

Results and Discussion

The data for a series of density measurements on both sealed and unsealed blocks of fiber are summarized in Table II. It is clearly evident from the data on the paraffin-sealed blocks that they do not contain the void space required by a hollow tube structure. In fact, the results strongly suggest that the only appreciable void space in the solid blocks of fiber is that occupied by sorbed water. Furthermore, the void space is not constant, but increases as the sorbed water content increases. That is, the blocks of fiber must swell as water is sorbed. The only exception among the sealed blocks is sample

TABLE II
DENSITY OF SEALED AND UNSEALED SOLID BLOCKS OF FIBER

Sample	Sorbed H_2O , %	Gross sample, g./cc.	Chrysotile, g./cc.
Sealed 1	0	2.57	2.57
Sealed 2	0	2.55	2.55
Sealed 3	0	2.56	2.56
Sealed 4	0	2.56	2.56
Sealed 5	2.2	2.48	2.57
Sealed 6	1.3	2.48	2.53
Sealed 7	0.8	2.53	2.56
Unsealed 8	1.0	2.51	2.55
Unsealed 9	1.0	2.53	2.57
Unsealed 10	0.7	2.56	2.58
Arizona ¹	2.0	2.45	2.53

¹ Density of gross sample including sorbed water but excluding paraffin. ² Calculated on the assumption that sorbed water occupies a volume of 1 cc./g. ³ The density of this sample was determined in air.

(15) E. J. W. Whittaker, *Acta Cryst.*, **8**, 143 (1952).

(16) N. N. Padurew, *ibid.*, **3**, 204 (1950).

(17) G. J. Young and F. H. Healey, *This Journal*, **68**, 381 (1954).

no. 6 which has a density slightly lower than one would expect. In view of the consistent behavior of the other values it seems likely that the value for no. 6 may have been low because of a slight imperfection in the otherwise solid block of fiber.

The fact that the sealed samples which contain essentially no sorbed water have density values closely approximating the theoretical absolute density of chrysotile indicates that the fibers in a desorbed condition are packed together with very little void space. This behavior is not compatible with a hollow tube structure. In order to account for the close-packing of the fibers it seems more plausible to view them as strip or ribbon-like structures which may be distorted by limited curvature about the fiber axis.¹⁸ This type of structure awaits confirmation by X-ray diffraction studies.

The density values obtained for the unsealed blocks of fiber in water indicate the consistent nature of the measurements. In the unsealed blocks the only appreciable void space measured is also that occupied by sorbed water. Taken alone the values for the unsealed blocks could not conclusively establish the improbability of a tubular structure. However, the results on sealed blocks indicate that when unsealed blocks of fiber are placed in water, the blocks probably sorb water and swell although initially the only appreciable void space present is that occupied by water sorbed prior to immersion.

Measurement of the density of the block of Arizona chrysotile in air furnishes additional confirmation of the improbability of the existence of a tubular structure in chrysotile. Considering the crudeness of the method, the results are in good agreement with the premise that the only significant void space in bundles of fiber is that occupied by sorbed water. This void space is much less than would be required by a tubular structure.

A series of studies of the amount of water sorbed by chrysotile as a function of relative humidity indicates that the maximum amount of sorbed water retained by blocks of fiber at 100 per cent. relative humidity and 25° is approximately 2.5 per cent. If, as seems probable, sorbed water causes the fiber bundles to swell, the maximum degree of swelling can be calculated using the sorbed water value at 100 per cent. relative humidity. One gram of desorbed fiber occupies

$$\frac{1}{2.58} = 0.388 \text{ cc./g.}$$

When 1 g. of chrysotile sorbs the maximum amount of water the gross sample will weigh 1.026 g. and occupy a volume of

$$0.388 + 0.026 = 0.414 \text{ cc./g. chrysotile}$$

The apparent change in volume of the block of fiber is 0.026 cc./g. chrysotile. The percentage increase in volume over the range of complete desorption to complete sorption would be

$$\frac{0.026}{0.388} \times 100 = 6.7\%$$

Experimental work is now in progress to observe directly the swelling of fiber bundles and to establish

(18) Such a limited curvature has been suggested for antigorite, a so-called massive variety of serpentine, by J. Zussman, *Mineralog. Mag.*, **30**, 498 (1954).

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whether the swelling is of the predicted order of magnitude.

No satisfactory explanation of the hollow-tube appearance of chrysotile fibers when viewed in the electron microscope¹⁹ can be offered other than to suggest the obvious: the sample viewed in the electron microscope no longer bears a one to one relationship with the native fiber. Whether this is the result of the treatment the fibers have received

(19) R. K. Her, "The Colloid Chemistry of Silica and Silicates," Cornell University Press, Ithaca, N. Y., 1953, p. 208.

during the preparation or of the exposure to the electron beam in a high vacuum remains to be determined.

Acknowledgment.—The successful execution of this work is due in large part to Mr. George Reimschuessel who made many of the density measurements reported here. Mr. Marion Badollet and Mr. William Streib made available certain excellent specimens of chrysotile which were measured in the course of this investigation.

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