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HOLLOW CHRYSOTILE FIBERS

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INTRODUCTION

The "hollow tube" theory for chrysotile was established when Turke-
vich and Hiller (1949) published electron micrographs indicating that
single fibers were hollow tubes. This theory was further substantiated by
the work of Noll *et al.* (1958), Huggins (1962), Zussman and Brindley
(1957), Bates *et al.* (1950), Maser *et al.* (1960), and others. Conversely,
Pundsack (1956, 1961), and Kalousek and Muttart (1957), concluded
that the density of chrysotile blocks was incompatible with either tubular
or solid cylinders. More recently, Whittaker (1963) and Bates (1958)
have hypothesized that chrysotile fibers are filled with amorphous or
partially oriented material and that this accounts for the lack of voids in
the fibers. The recent publication by Huggins and Shell (1965) on density
of bulk chrysotile and massive serpentine shows that the density of
Arizona and African chrysotile is compatible with tubular structure, and
that Canadian chrysotile, which has a higher density, has at least 50 per
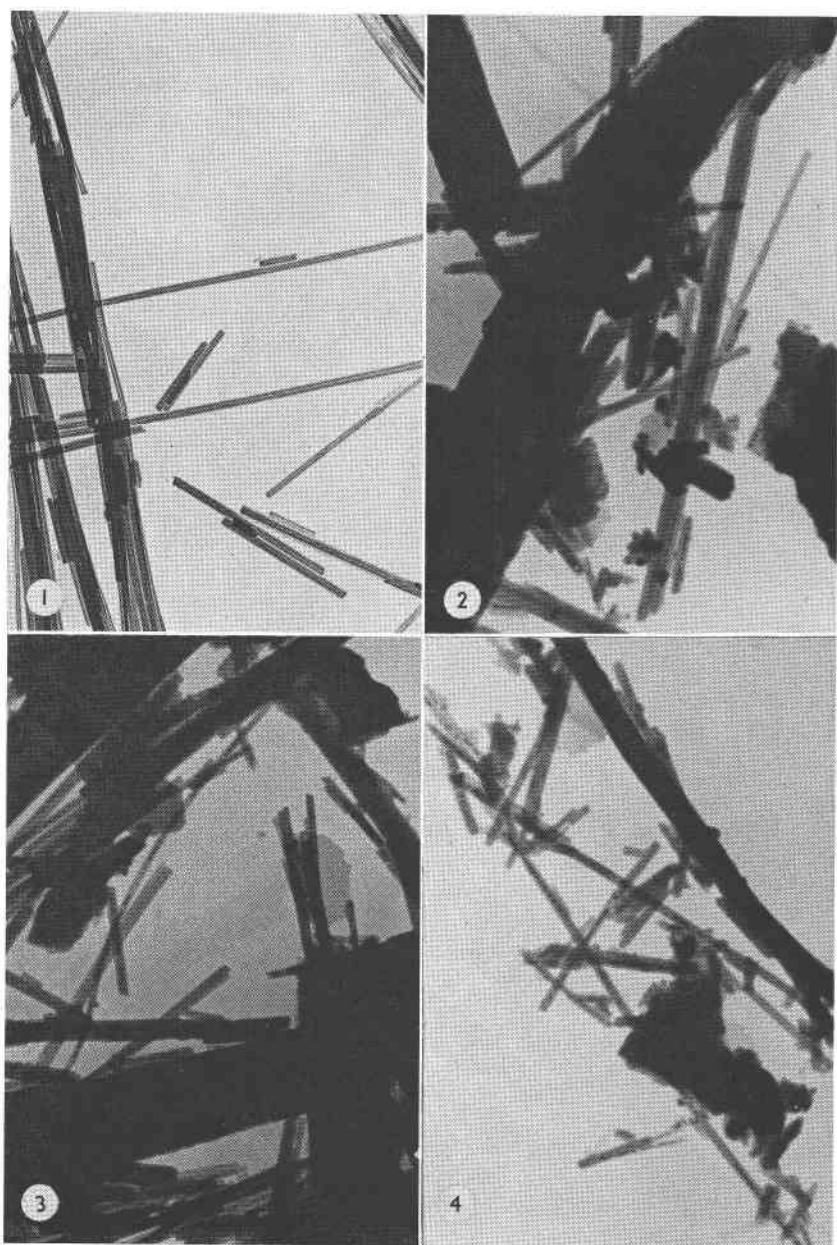cent unfilled tubes.

FIG. 1. Untreated fiberized Arizona chrystotile. ×38,000.
FIGS. 2, 3, 4. Electron micrographs of typical fibers after treatment. ×38,000.

The present investigation was initiated to determine if the hollow or tubular spaces could be filled. It was reasoned that if void areas existed in the middle of the tubes, they could be filled with lead nitrate or a similar aqueous solution, which would be very opaque to the electron beam.

EXPERIMENTAL PROCEDURE

Fiberized Arizona chrysotile was heated overnight at 450° C. to remove all sorbed water. While still hot, the chrysotile fibers were placed into a saturated aqueous solution of lead nitrate. The fibers and solution were then sealed in a platinum tube, and a hydrostatic pressure of 1500 psi was applied at ambient temperature for two days. The sample was removed, washed with hot distilled water, and then calcined at 450° C. overnight to convert the lead nitrate to lead oxide. After cooling, a portion of the sample examined with the electron microscope revealed that many tubes had been partially filled with lead oxide. The procedure was repeated a second time in order to fill the tubes more completely.

RESULTS

Untreated, fiberized Arizona chrysotile is shown by electron microscopy in Fig. 1. Figures 2, 3 and 4 are electron micrographs of typical fibers after treatment. Treated fibers unmistakably show filling of the fibers along the center with the lead-containing solution. This could only have resulted from the existence of a hollow or partially filled space along the center of the original fiber. The width of the filling is the same as that postulated for the hole diameter.

CONCLUSIONS

A "hollow tube", or in some cases a partially filled "hollow tube", is the ultimate macro-structure for single fibers of chrysotile; this offers the possibility of altering certain properties of the mineral.

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COMPLEX ALKALI TITANIUM OXIDES $A_x(B_yTi_{8-y})O_{16}$ OF THE
α-MnO_2 STRUCTURE-TYPE

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α-MnO_2, one of the numerous modifications of manganese dioxide
(Glemser *et al.*, 1961; Gattow and Glemser, 1961a,b), exhibits a particu-
larly interesting crystal structure (Byström and Byström, 1950). In this
tetragonal structure (MnO_6)-octahedra form a rather open framework
with channels in the direction of the c axis. Obviously the structure is
stabilized by large alkali or alkaline earth ions in the channels. Isostruc-
tural with α-MnO_2 are the manganese minerals cryptomelane, hollandite
and coronadite. Complete substitution of manganese by titanium and
iron or titanium and chromium has been found in the minerals priderite
(Norrish, 1951) and redledgeite (Strunz, 1963), resp. By synthesis potas-
sium-priderite (Norrish, 1951) and compounds of a series $Ba_x(Mg_xTi_{8-x})$
O_{16} (Dryden and Wadsley, 1958) could be prepared. The chemical com-
position of these various compounds indicates the tolerance of the
α-MnO_2 structure to substitutions for A-ions (channels) and B-ions
(framework). In addition, the positions of the large A-ions may be oc-
cupied incompletely leading to complex non-stoichiometric oxides. It has
been reported recently (Bayer and Hoffmann, 1965) that substitution of
sodium by potassium or by rubidium in $Na_x(B_yTi_{8-y})O_{16}$ (Na_xTiO_2-
type) results in formation of α-MnO_2-type compounds. Therefore a sys-
tematic study of ionic substitution and non-stoichiometry has been

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