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THE INFLUENCE OF SAMPLE TEXTURE ON CHRYSOTILE DEHYDROXYLATION

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ABSTRACT

Sample texture, or microporosity, has a pronounced influence on chrysotile dehydroxylation at high temperatures. Specimens of high surface area, indicating an open texture dehydroxylate to form an x-ray-amorphous phase that remains stable for at least 150° C, after the dehydroxylation has taken place. As temperature is increased further, forsterite forms rapidly over a very narrow temperature interval. Dehydroxylation does not influence the apparent surface area of the specimen, but forsterite formation has a drastic effect. With specimens of low surface area, both the dehydroxylation and the forsterite formation occur more gradually and there is little or no indication of an amorphous region.

These observations are interpreted to indicate that the dehydroxylation of chrysotile is governed by the ease with which molecular water can be removed from reaction sites. The data presented indicate that the rate of water removal is a function of the surface area of the unheated specimen. Previous work on the nature of chrysotile asbestos has indicated that surface area is a measure of the degree of cementation of the chrysotile fiber bundles: Samples having low surface areas are more completely cemented than those having high surface areas.

INTRODUCTION

Differential thermal analysis (DTA) traces for chrysotile are characterized by a major endotherm at approximately 700° C. and an exotherm at approximately 800° C. The former is due to the dehydroxylation of chrysotile, the latter to the transformation of the dehydrated chrysotile structure to a new structure: forsterite. The positions of these peaks are essentially the same for chyrsotile specimens from different localities, but peak size varies considerably from specimen to specimen (Faust and Fahey, 1962). Variations in peak size are frequently observed for reactions in which a gas is evolved, since the thermal properties of a specimen change with the composition of the gas it contains (Mackenzie, 1957). Gas composition (in this case, air and water vapor) varies with sample texture and with the tightness of sample packing due to the effect these variables have on the diffusion rates of the gases. A variation of endotherm size is, therefore, to be expected for materials with differing particle size and morphology.

The exotherm at about 800° is associated with a phase transition, and therefore should not be subject to the same factors that influence the endotherm. The size of serpentine exotherms has been shown to be somehow dependent upon the size of the temperature interval between the completion of dehydration and the initiation of recrystallization. Serpentine specimens that yield small exothermic peaks are found to contain forsterite in the temperature interval between the endotherm and exotherm, while those that yield large peaks are amorphous to x-rays in this region (Mackenzie, 1957). It has also been observed that exotherm size for certain chlorite and serpentine specimens is enhanced by weathering and fine-grinding (Mackenzie, 1957). From this it has been inferred that particle size has an influence on recrystallization.

Recently, Brindley and Hayami (1964) have shown that the rate of recrystallization of serpentine varies inversely with the rate of dehydration; *i.e.*, the faster the dehydration, the slower the recrystallization. This relationship was established by experiments in which coarse serpentine (60 to 100 mesh) was found to dehydrate more slowly and recrystallize more rapidly than a finely ground (−200 mesh) portion of the same material. The same behavior was observed for massive serpentine specimens: Surface layers dehydroxylated rapidly to form an amorphous phase, while material at depths greater than 1 mm dehydrated more slowly and transformed readily to forsterite. These results were explained on the basis of disorder introduced by rapid dehydration, the argument being that the crystalline order of serpentine, which is favorable for a topotactic rearrangement to forsterite, is disrupted when dehydroxlyation occurs rapidly.

Data will be presented to show that behavior similar to that described by Brindley and Hayami is also found with chrysotile. However, with chrysotile it is not particle size that controls dehydration and recrystallization, but rather the ease with which the water evolved during dehydration escapes from the specimen due to the microporosity of the sample. It will be shown that open-textured materials (as evidenced by high surface area), from which water can diffuse readily, are characterized by large exothermic peaks on DTA traces and dehydrate to form an x-ray-amorphous phase; while materials of low surface area, from which diffusion is slower, are characterized by small exotherms and lower temperatures of recrystallization.

EXPERIMENTAL

Chrysotile specimens from the following locations were examined:

Sample Origin	*Sample Form*
Thetford Mines, Quebec	cross-fiber block
Globe, Arizona	tangled filaments
Cassiar, British Columbia	tangled filaments
New Idria, California	matted flakes
Stragari, Yugoslavia	matted flakes

In some cases, the specimens were modified by additional treatments, including: (1) mechanical opening by grinding to −100 mesh in a Pitchford Grinder, a high-intensity, reciprocating ball mill; (2) chemical defibrillation by thrashing 0.5 to 1% slurries of chrysotile in 0.003*M* acetic acid followed by centrifugation to remove undispersed and partially dispersed aggregates (Naumann and Dresher, 1966); and (3) surface treatments with stearic (Badollet, 1937) and hydrochloric acids.

DTA traces were obtained under the following conditions:

Heating rate: 10° C./min.
Inert sample: calcined (1300° C.) kaolin
Difference thermocouple: chromel vs alumel
Temperature thermocouple: platinum vs platinum—13% rhodium embedded in the inert specimen
Sample size: Figs. 1 and 2; 0.2 grams
Figs. 3 and 4; 0.3 grams

The calibration and operation of the DTA equipment were verified by means of the quartz α-to-β transition at 573° C. Unless specified otherwise, the specimens were heated in air.

Test specimens for static heating experiments were held for 24 hours in a stream of dry nitrogen. The heating unit was a Marshall High Temperature Testing Furnace, a commercial assembly specifically designed to give close temperature control and small temperature gradients within the heating zone. Sample temperatures were measured by means of a thermocouple placed near the specimens. Checks on temperature profiles and temperature drifts indicated that temperature control was well within 10° C. of the chosen temperature for any 24-hour heating period.

X-ray diffraction patterns were obtained with a Norelco High-Angle Diffractometer using nickel-filtered copper Kα radiation. Surface areas were determined by nitrogen adsorption using a Perkin-Elmer-Shell Model 212B Sorptometer. The thermogravimetric analysis (TGA) equipment was a Stanton Instruments Ltd. Thermobalance.

RESULTS

Differential thermal analysis. DTA traces for chrysotile specimens from five localities are given in Fig. 1. The three traces of the left portion of the figure are for materials with the relatively low surface areas that are usual in naturally occurring chrysotile (Young and Healey, 1954; Pundsack, 1961). The two traces on the right are for specimens from two atypical deposits that contain chrysotile of high surface area. The temperatures of the characteristic peaks were essentially the same for all five materials; but exotherm size differed considerably, showing a regular increase in size and sharpness with increasing surface area. Similar changes in exotherm size were observed when low-surface-area materials were treated to increase their surface area. This is shown by the traces of Fig. 2, which were obtained for: course filaments from the Thetford Mines specimen, filaments of this specimen ground to −100 mesh, and filaments defibrillated in the presence of a chemical dispersant.

Note in Fig. 1 that a small endotherm at approximately 600° C. precedes the major endotherm in the traces for the New Idria and Stragari materials, and there is an indication of a similar endotherm in the trace for the completely defibrillated sample of Fig. 2. This feature was found only with samples of high surface area (approx. 50 m^2/g or more), and was recurrent for such samples. It will be shown that this endotherm can be attributed to the loss of surface OH groups. The evidence for this interpretation is given in Fig. 3. The traces for untreated New Idria chrysotile, and for portions of this material that had been reacted with (a) stearic acid to give approximately a monolayer coverage, and (b) hydrochloric acid to neutralize approximately 70% of the basicity of the exposed fibril surfaces. The treatment levels were based on 20 $Å^2$ per stearate chain and a surface area of 70 m^2/g, and amounted to 5.6×10^{-4} moles stearic acid and 2×10^{-3} moles hydrochloric acid per gram of asbestos, respectively. The secondary endotherm is well defined in the trace for the untreated material. The trace for the stearated sample shows an exotherm at approximately 200° C. corresponding to the com-

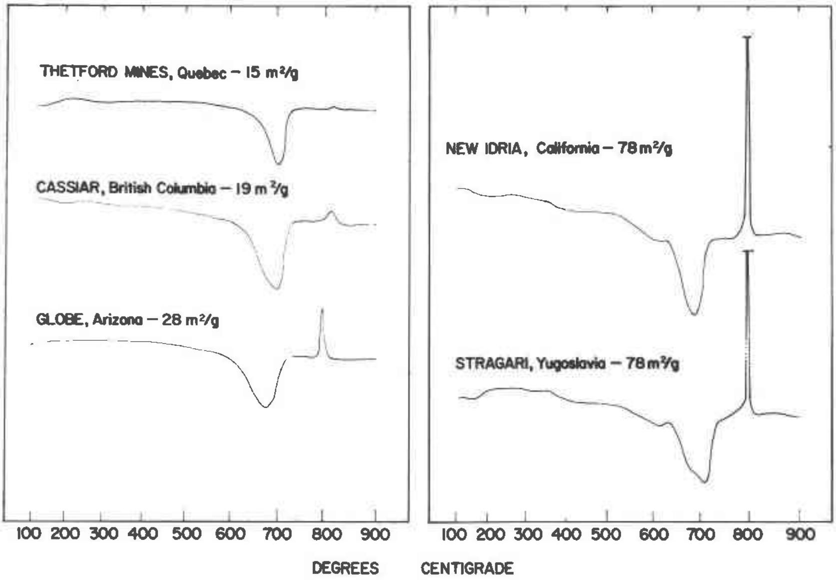

FIG. 1. DTA traces for chrysotile specimens from five localities.

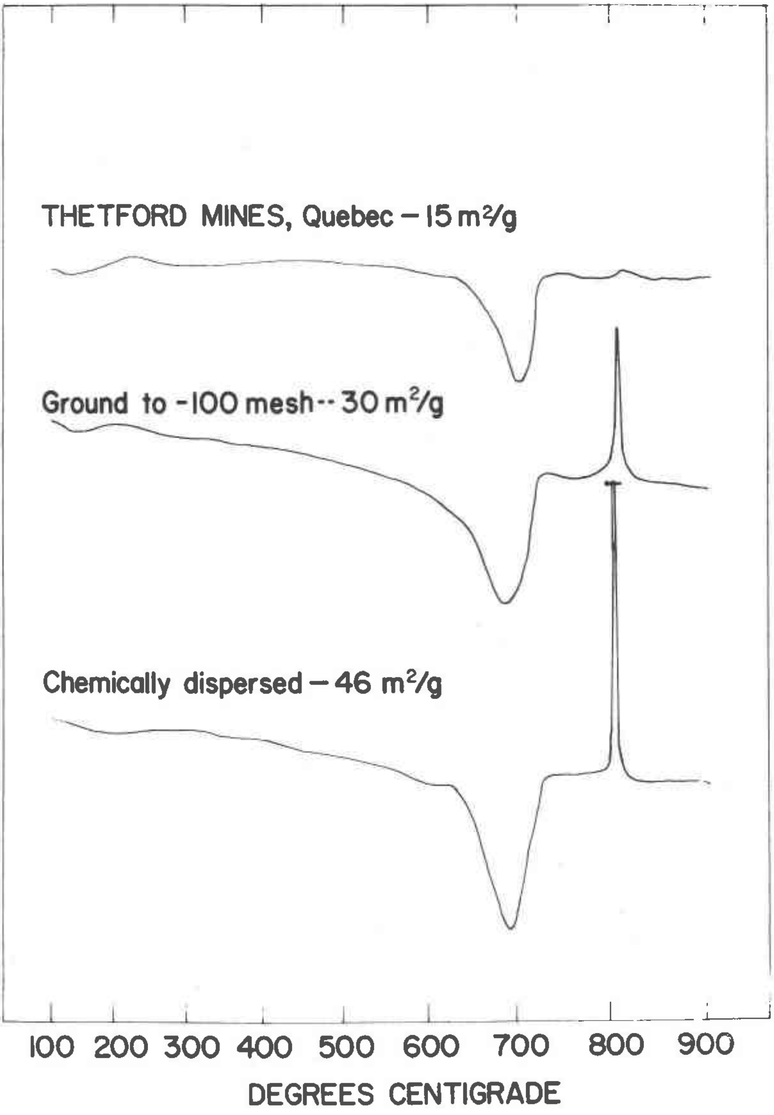

FIG. 2. DTA traces for Thetford Mines chrysotile before and after mechanical and chemical defibrillation.

bustion of the organic coating, but no indication of the 600° C. endotherm. The endotherm is weak and poorly defined in the trace for the leached sample.

The traces in Fig. 4 show the effect of sample environment. The first

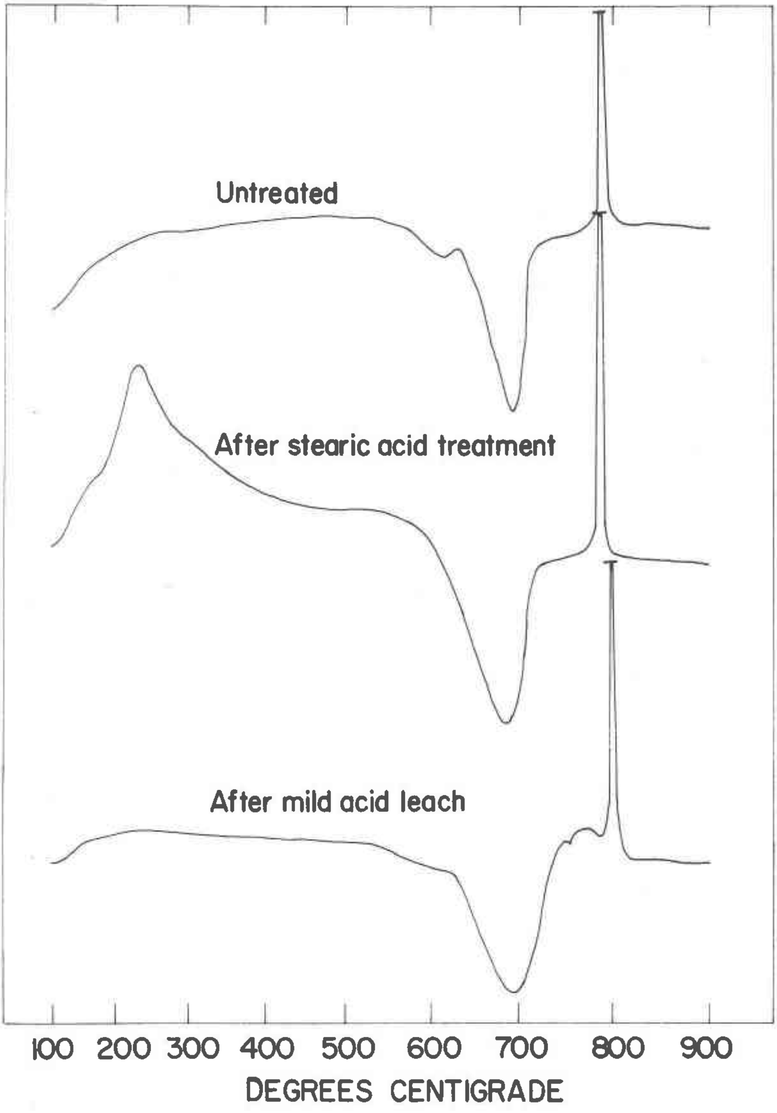

FIG. 3. DTA traces for New Idria chrysotile before and after surface modifications.

was obtained for a sample of New Idria chrysotile heated in still air (the normal mode of operation). The second trace is for a sample heated in an approximately one liter/minute stream of dry nitrogen. The third was obtained under the same conditions except that the nitrogen was

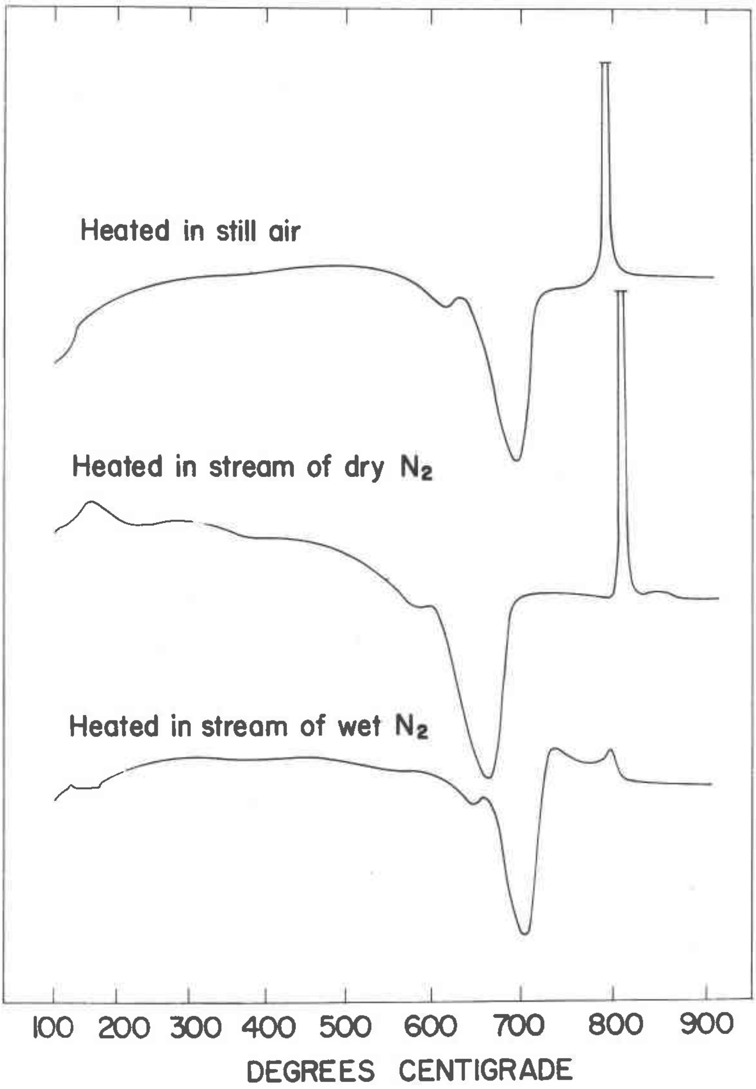

FIG. 4. Effect of sample environment on DTA traces of New Idria chrysotile.

saturated at 95° C. with water vapor. With dry nitrogen, the positions of the endothermic peaks were shifted to lower temperatures. The exotherm was unchanged in both shape and position. With wet nitrogen, peak positions were slightly raised in temperature, but the size of the exotherm was drastically reduced.

TABLE I. SUMMARY OF RESULTS FOR HEAT-TREATED CHRYSOTILE SPECIMENS

	Cassiar Chrysotile				New Idria Chrysotile	
	Untreated		Defibrillated		Untreated	
Temperature (° C.)	Surface area (m^2/g)	*x*-ray identification	Surface area (m^2/g)	*x*-ray identification	Surface area (m^2/g)	*x*-ray identification
450	9	Chrysotile	42	Chrysotile	70	Chrysotile
500	12	Chrysotile	40	Chrysotile	71	Chrysotile
550	10	Chrysotile	42	Chrysotile (trace)	69	Amorphous
600	12	Forsterite	40	Amorphous	69	Amorphous
650	11	Forsterite	45	Amorphous	70	Amorphous
700	13	Forsterite	32	Forsterite (trace)	64	Forsterite
750	14	Forsterite	33	Forsterite + Enstatite (?)	40	Forsterite + Enstatite (?)
800	18	Forsterite	25	Forsterite + Enstatite (?)	6	Forsterite + Enstatite (?)
850	14	Forsterite	18	Forsterite + Enstatite (?)	2	Forsterite + Enstatite (?)

Static Heating

A summary of the *x*-ray results for samples of a low-surface-area chrysotile (Cassiar) and a high-surface-area chrysotile (New Idria) and of surface-area determinations is given in Table I. Data were also obtained for defibrillated New Idria chrysotile, but are not included because they were nearly identical with those obtained from the undefibrillated material.

The phase transitions of the undefibrillated Cassiar samples proceeded as described by Hargreaves and Taylor (1946) and by Brindley and Zussman (1957). As temperatures increased from 450° to 550° C., the chrysotile pattern gradually weakened. At 600° C., the chrysotile *x*-ray pattern disappeared, and a weak pattern for forsterite appeared. This become more intense and additional forsterite peaks appeared as the temperature was raised about 600° C. A slight increase in surface area with increasing temperature was indicated, but the significance of this trend is questioned. As has been discussed in a previous paper, the surface area of most chrysotile specimens varies with the physical handling and openness of the material (Naumann and Dresher, 1966). Because of this,

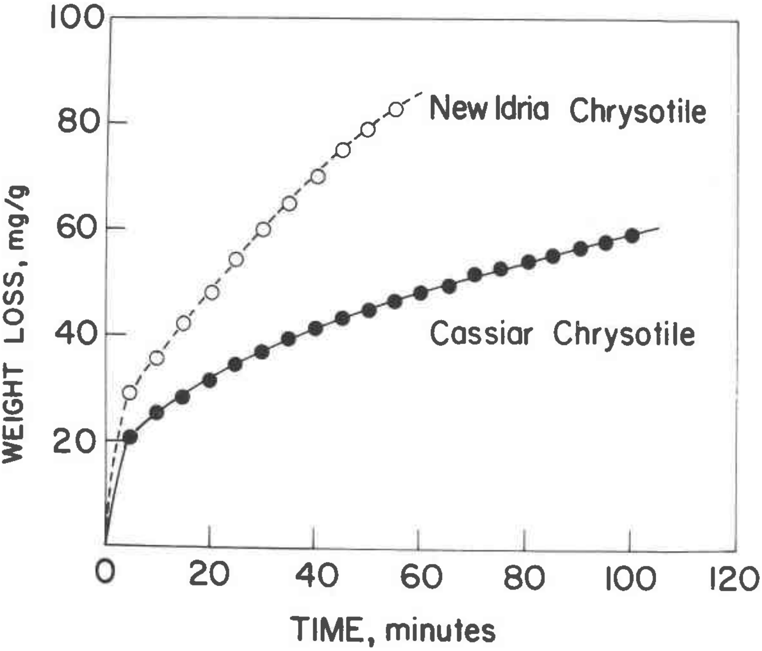

FIG. 5. Weight loss as a function of time for chrysotile specimen held at 600° C.

it is difficult to obtain good reproducibility with asbestos filaments. The variations observed with the undefibrillated Cassiar samples are as would be expected with such samples.

The samples of New Idria chrysotile and defibrillated Cassiar chrysotile decomposed at approximately 550° C. to form *x*-ray-amorphous phases that remained stable to approximately 700° C. There was little or no change in surface area associated with this loss in structure. Transformation to forsterite occurred at approximately 700° C.; and, in both materials, the transformation was accompanied by a decrease in surface area. Weak, broad peaks in the positions corresponding to the strongest reflections of enstatite were found in both materials after treatment at 750° C. or higher. This is of interest, because there has been a diversity of observation concerning the temperature at which enstatite formation begins (Hargreaves and Taylor, 1946).

In the pattern for a sample of New Idria chrysotile heated at 600° C. in nitrogen saturated with water vapor at 25° C. peaks of both chrysotile and forsterite were observed indicating a different dehydration process than that which occurs in dry nitrogen.

TGA data showing weight loss as a function of time for samples of New Idria and Cassiar chrysotile are given in Fig. 5.

DISCUSSION

The ultimate particles of chrysotile are cylinders of large length-to-diameter ratio, having diameters generally in the range of 250–350 Å (Whittaker, 1957). A material made up of particles of this size should be of high surface area and porosity. It is found in practice that the potential area of the fibrils is realized in some chrysotile specimens, but not in others, the latter being more common (Naumann and Dresher, 1966). Surface area and porosity are reduced in these materials by extra-fibril solid matter that fill a significant portion of the spaces between the fibrils (Bates and Comer, 1959; Martinez and Comer, 1964).

All of the experimental results confirm that the manner in which asbestos dehydrates is determined by the ease with which water vapor diffuses from the sample: Materials of open texture and high surface dehydrate to form an *x*-ray-amorphous phase that rearranges abruptly to form forsterite. This was seen both with the materials from the localities that inherently had high surface areas, and with low-surface-area materials that were treated to increase their surface area. When the diffusion of water was hindered by the presence of extra-fibril solid matter within the specimen, or by water vapor in the environment surrounding the sample, both dehydration and recrystallization occurred over a greater temperature interval. *X*-ray diffraction patterns from these samples showed no amorphous region, and the size of the DTA exotherm, associated with the rearrangement to forsterite, was greatly reduced. The TGA results confirm that dehydration occurs more gradually from a low-surface-area material (Cassiar) than from one of high area (New Idria).

Little if any change in surface area accompanied the dehydroxylation of the chrysotile specimens. This indicated two things: (1) that there was no immediate collapse of the structure due to the removal of water and (2) that the voids formed by the loss of water were too small for nitrogen absorption. Similar results have been reported for kaolin and illite clays (Nelson and Hendricks, 1943). Muscovite, on the other hand, undergoes a slight surface-area decrease when finely divided, but delamination and a several-fold increase in area occur when sheets of the mineral are heated rapidly (Gaines and Vedder, 1964). Brucite, the mineral most closely related to the hydroxyl layer of chrysotile, undergoes a pronounced surface-area increase when dehydrated (Razouk and Mikhail, 1959). Thus, the dehydration of chrysotile must follow a mechanism similar to that of kaolin and illite. In these minerals, the voids formed during dehydration are sufficiently small (less than approximately 16 Å^2) that nitrogen molecules are excluded. The dehydration behavior of brucite, on the other hand, gives rise to an open structure, which permits the internal penetration of nitrogen. It is also interesting to note that the response of kaolin to dehydration in the presence of water vapor is similar to that of low-surface-area chrysotile, *i.e.*, a reduction of the temperature interval between dehydroxylation and recrystallization, and a reduction in exotherm size (Stone and Rowland, 1955).

The surface-area results appear to rule out a delamination of the layers of the tube walls (similar to the delamination found when muscovite sheets are dehydrated rapidly) or any other gross disruption of the chrysotile lattice. These findings are more in line with the views of Brindley and Hayami concerning the dehydration of serpentine than those of Taylor and co-workers (Balland Taylor 1963). Brindley and Hayami suggest a disruption of crystalline order to explain the formation of an *x*-ray-amorphous phase and the retardation of forsterite formation, but such a disruption of order need not lead to the formation of large voids. The mechanism of Taylor, *et al.* involves a migration of H^+ to "donor" regions that transform into pores, and a migration of Mg^{2+} and Si^{4+} to "acceptor" regions that then transform into forsterite. Such a mechanism would give rise to a surface-area increase as is found, for example, with brucite.

A decrease in area did occur, however, when the temperature was raised enough to cause an anhydrous phase to be formed. Forsterite, and possibly enstatite, were formed at 600° to 700° C., depending upon the physical nature of the specimen. It was observed that the greatest decrease in surface area and the smallest final surface area were obtained for the sample having the highest initial surface area. The area decrease can be attributed to the sintering and the growth of forsterite crystals. The reason for the extreme surface area reduction experienced with specimens having a high initial surface area is not clear.

It is concluded that the rate of dehydroxylation and the temperature zone over which forsterite is formed, are functions of the degree of association of the chrysotile fibrils. Relatively loosely associated fibrils exhibit a high surface area, dehydroxylate rapidly, and recrystallize to the forsterite phase over a narrow temperature zone. Tighter-packed fibrils have a lower initial surface area, dehydroxylate slowly, and recrystallize to forsterite over a broad temperature zone, frequently with some dehydroxylation and recrystallization occurring simultaneously.

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