

The thermal decomposition of chrysotile

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SUMMARY. The decomposition of chrysotile fibres heated in air has been studied in the range 100–1400 °C by electron microscopy and infra-red absorption. The first observable change in the structure occurred at 580 °C, where cavities started to open up between the (001) layers of chrysotile as the fibres were dehydrated, giving rise to strong low-angle diffraction. There was no evidence of any structure in the remaining material but some degree of the original atomic arrangement was preserved for the magnesium silicates, forsterite, and enstatite, later developed in certain preferred orientations. The manner of this crystallization was determined by the thermal treatment, for in samples held between 600 °C and 800 °C forsterite developed slowly with little further disruption of the fibre while above 800 °C the remaining amorphous areas rapidly recrystallized to a mixture of forsterite and enstatite. It is suggested that the mechanisms described by other investigators to explain the development of forsterite in preferred orientations may serve simply to nucleate the crystallization and a similar mechanism to account for the nucleation of the enstatite crystallization is considered. At high temperatures a possible doubling of some of the lattice parameters of the silicates was observed.

THE thermal decomposition of chrysotile and other serpentine minerals has been studied by a number of authors using X-ray diffraction techniques (Brindley and Zussman, 1957; Ball and Taylor, 1963). These investigations have shown that a mixture of the two magnesium silicates, forsterite and enstatite, is formed topotactically from the chrysotile, i.e. in definite orientations with respect to the chrysotile lattice. Mechanisms have been proposed to explain the topotactic development of the forsterite (Ball and Taylor, 1963; Brindley and Hayami, 1965; Johns, 1965), which involve the formation of two separate phases, one ordered and the other amorphous, between which an exchange of ions occurs, but the formation of enstatite, which appears to vary with the conditions of treatment, has not been described in any detail.

In the present investigation chrysotile fibres were studied with a Philips 301 electron microscope by the lattice-imaging technique (Yada, 1967) coupled with selected-area diffraction. This, together with infra-red absorption measurements, which enabled changes in the atomic bonding to be monitored during the intermediate stages in the decomposition, allowed a fairly complete picture of the process to be built up. The sequence of reactions thought to be occurring is outlined and reasons given for the variations with different thermal treatments.

Experimental procedure. Samples of chrysotile from a number of mines were used: a soft silky green fibre from the Cassiar mine in Canada, a harsh brittle green/black fibre from the Shabanie mine in Rhodesia, and other specimens from the King mine in Rhodesia and the Coalinga mine in the United States, but no essential differences in behaviour were found between any of them.

The fibres were separated out into small bundles with cross-sections between a tenth and a hundredth of a square millimetre and the ends removed to avoid contamination with material from the bulk rock. A series of runs was then carried out at temperatures ranging from 100 °C to 1400 °C in which the fibre samples were heated in air at a rate of 1 °C per minute up to the temperature of the treatment, left there for a period of 24 h, and quickly cooled by removal from the furnace. Specimens were separated out for examination in the electron microscope by ultrasonic dispersal in chloroform or distilled water and then suspended on carbon films. For

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the infra-red absorption the fibres were ground to a fine powder, dispersed in nujol, and examined using the pressed-KBr-disc technique with a Perkin-Elmer 257 grating spectrophotometer.

Results and discussion

The dehydration of chrysotile. The serpentine minerals $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ are made up from alternate half-layers of silicate and magnesium hydroxide or brucite. There is a slight misfit between these two half-layers, which produces a curvature of the lattice with the brucite on the outside. Chrysotile is a form of serpentine in which the lattice curves around upon itself to form tubular fibres, which are spiral or circular in cross-section (Yada, 1967 and 1971). The electron-diffraction pattern from a chrysotile fibril contains reflections corresponding to two zones, the *hko* set, which forms layer lines stretching across the fibre axis, and the *hol* set, which is present only in alternate layers. The atomic layers are stacked regularly in the *a*-direction along the fibre axis but in the *b*-direction around the circumference there is complete translational disorder and as a result the *hko* reflections extend along the layer lines and the *hkl* reflections are absent (Whittaker and Zussman, 1971).

When the fibres were heated above 550°C a strong, sharp reflection appeared on the zero-order layer line extending from about 10 \AA to at least 50 \AA , which has previously been observed in X-ray diffraction studies (Brindley and Zussman, 1957; Ball and Taylor, 1963). This was coupled with a strengthening of the diffuse scattering around the median of the second and fourth order layer lines. Direct observation in the electron microscope showed that long cavities were opening up between the (001) planes in the fibre wall and extending along the fibres for a few hundred to over 1000 \AA (fig. 1*a*), which could be associated with the dehydration of the fibres. The low-angle reflection may represent diffraction from these cavities, which have widths ranging from 10 \AA to around 100 \AA . In fibrils treated for one hour between 550°C and 650°C there had been insufficient time for large cavities to open up and the reflection was peaked at around $12\text{--}13\text{ \AA}$, but in the rest there was no fall-off in intensity at the low-angle end below at least 40 \AA . As the temperature was increased the streak was progressively curtailed at high angles as the cavities grew.

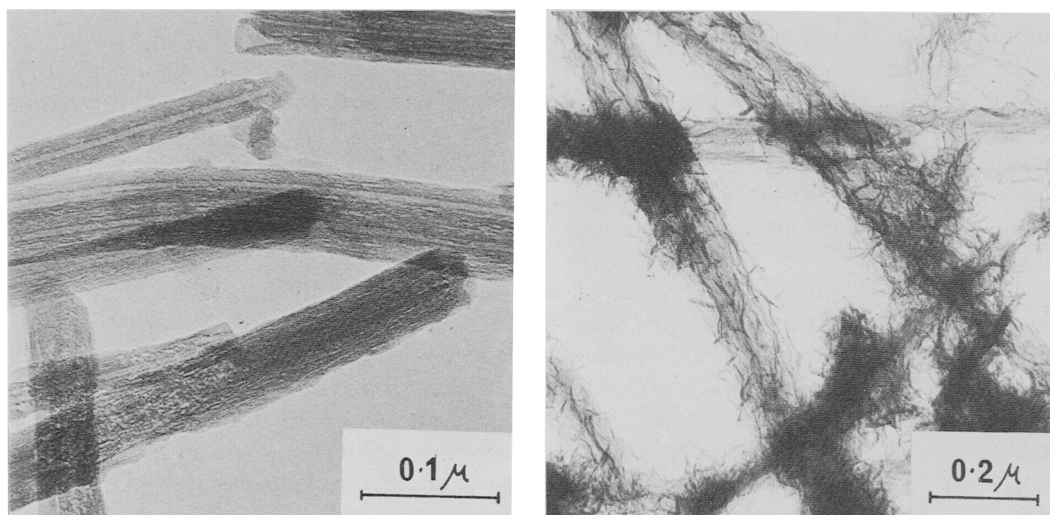


FIG. 1. *a* (left). Cavities opening up in the walls of fibres treated at 600°C . *b* (right). Fibres treated at 600°C after adsorption of water.

As the low-angle reflection was increasing in intensity all the reflections with non-zero Miller indices in the l position, namely the 001, 201, and 401 reflections, disappeared, while the 020, 040, 110, and 130 ones remained, although becoming more diffuse, and a new diffuse spot appeared on the zero-order layer line corresponding to a spacing of 3.1 Å. By 800 °C all that remained was the diffuse scattering, which still sharply defined the second-order layer line showing that a degree of order was still maintained along the fibre axis.

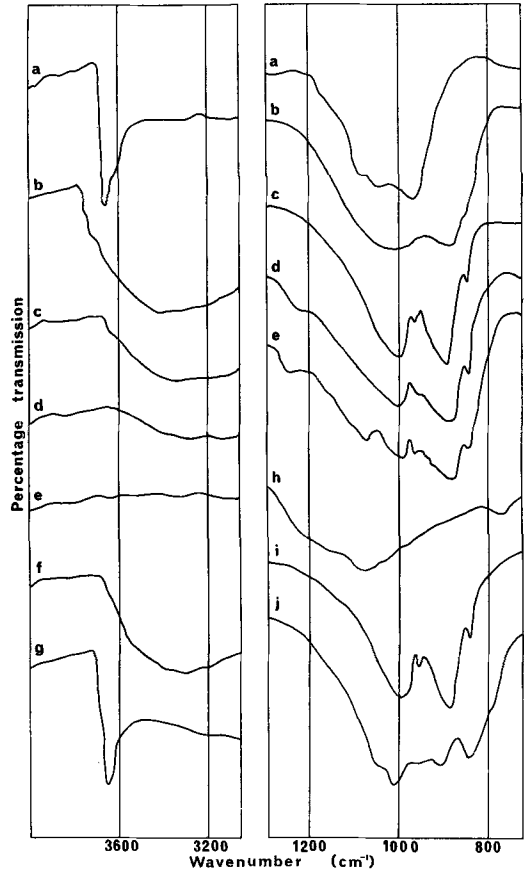
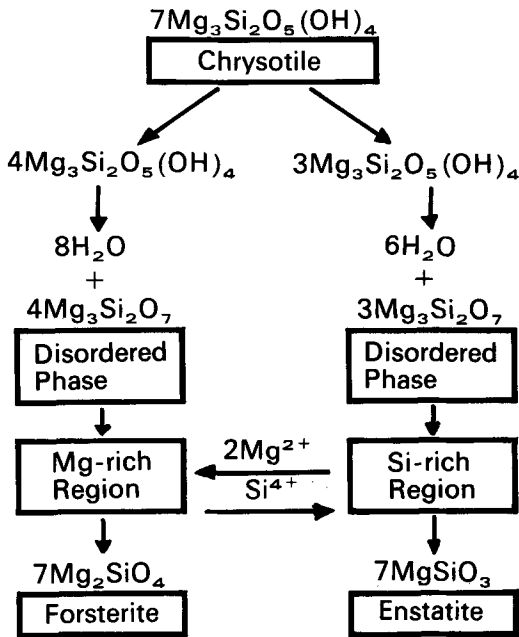
The formation of forsterite. A few small crystallites of forsterite began to appear at 620 °C and the number and size of these steadily increased as the treatment temperature was raised, until in the specimens treated at 750 °C about half of the material had been converted. The present results confirmed earlier observations that forsterite occurs chiefly in two preferred orientations, with the direction of the fibre axis in the chrysotile becoming either the forsterite b or a direction 60° away from this in the bc plane, but a third orientation was sometimes seen with the forsterite b vector in a position 30° away from the fibre axis in the bc plane. This had been observed by Ball and Taylor (1963) in samples treated hydrothermally. Brindley and Hayami (1965) suggested that where this topotactic development occurs the framework of close-packed oxygen atoms is maintained essentially intact. The protons move away and are replaced by magnesium and silicon ions and the region follows an ordered development to forsterite. The other regions are disrupted by the replacement of their Mg and Si ions by the hydrogen ions, which combine with the hydroxyls already present to form water and are liberated from the structure leaving amorphous silica. The cavities opened up between the 002 planes of chrysotile are thought to be the regions from which the evolution of water had occurred. For they appeared more frequently between the two or three outer layers of the fibres or near breaks in the fibres.

Because of the curvature of the lattice it would be difficult for large volumes to change to forsterite by the ordering mechanism: but several fibres in which the 5.1 Å 020 planes of forsterite had been imaged running perpendicular to the fibre axis did appear to have been partially unrolled during the crystallization. This mechanism probably serves primarily to nucleate crystals of forsterite in the designated orientations, because all the diffraction patterns obtained from the crystallites of forsterite were extremely sharp and had well-defined orientations and in many cases lattice imaging showed that a single orientation extended through the whole fibre diameter. If the forsterite had developed from the chrysotile structure in a more ordered fashion with the close packing of the oxygen atoms maintained over large volumes, a whole series of crystallites with slightly different orientations would have formed around the fibre circumference.

Intermediate stages in the decomposition. Some samples were treated for periods of 2, 10, and 24 h at temperatures between 580 °C and 700 °C to find whether the dehydration and forsterite crystallization took place simultaneously. No trace of a regular lattice was visible initially in the electron micrographs and the diffraction pattern was diffuse although the layer lines were still visible. Infra-red absorption spectra of the samples were taken to show changes in the atomic bonding and to find out when the dehydration was complete.

The essential features of the infra-red spectrum of chrysotile are a series of peaks associated with the Si-O bonds in the range 900-1150 cm^{-1} and a double peak at 3630 and 3670 cm^{-1} due to the stretching of the O-H bond in the brucite half-layer (fig. 3). No change in the spectrum was observed as the treatment temperature was raised until just below 600 °C, where the O-H peaks disappeared quickly in a range of about 20 °C as the dehydration occurred.

The electron micrographs had shown that cavities were beginning to open up between the atomic layers at temperatures around 580 °C but only a limited amount of dehydration can have occurred in this region, probably just in the fibres on the outsides of the bundles. Above 600 °C a broad absorption band appeared between 3200 and 3500 cm^{-1} , which decreased in size as the



FIGS. 2 and 3: FIG. 2 (left). A mechanism for the rapid recrystallization of magnesium silicates from chrysotile above 800 °C. FIG. 3 (right). The infra-red absorption spectra from chrysotile treated at (a) 580 °C, (b) 620 °C, (c) 700 °C, (d) 800 °C, (e) 1000 °C, (f) 700 °C after the adsorption of water, (g) from brucite, (h) from amorphous silica, (i) from olivine, and (j) from enstatite.

treatment temperature was raised (fig. 3). This is almost certainly associated with water molecules adsorbed by the disorganized material, as it resembles the absorption band present in most hydrated salts. Samples treated in the range 600–800 °C were rather reactive and specimens left in distilled water for a few hours were torn apart by the adsorption of the water throughout the fibre (fig. 1b). The hydration peak in these fibres was more pronounced (fig. 3f), and the diffraction pattern showed that the structure was almost completely amorphous.

The chrysotile absorption bands around 1000 cm^{-1} also remained intact until 600 °C where the spectrum changed rapidly. The specimens treated for an hour or two at 620 °C closely resembled pure silica but when the treatment was continued for between 12 and 24 h the spectrum began to show traces of the absorption peaks at 1000 cm^{-1} and 895 cm^{-1} associated with forsterite while specimens treated at 700 °C had spectra almost identical to ones of natural olivine. Thus in between the dehydration of the chrysotile and the crystallization of forsterite an intermediate state exists made up of semi-amorphous material, preserving some of the original lattice order, which later assists the crystallization of the magnesium silicates in preferred orientations.

Samples placed in a furnace already at a temperature between 620 and 750 °C remained

amorphous for much longer than ones heated slowly up to temperature, probably because the structure was disrupted by the rapid dehydration. Above 800 °C the spectra showed that a mixture of forsterite and enstatite was present with the specimens that had been heated rapidly having a larger fraction of enstatite.

The crystallization of enstatite. After a 24-h heat treatment at 800 °C, extensive recrystallization of the remainder of the dehydrated chrysotile occurred. Differential thermal analysis curves for samples of chrysotile from a large number of sources have shown that an exothermic reaction occurred at 810 °C when the specimens were heated at rates of 10 °C per minute (Martinez, 1961). The electron-microscope observations revealed that crystallites of enstatite were interspersed with the forsterite in the newly recrystallized areas, suggesting that the sudden increase in activity around 800 °C is caused by a reaction within the remaining disordered material to form a mixture of forsterite and enstatite (fig. 2).

The formation of forsterite below 800 °C uses up all the Mg ions in a given area leaving regions of SiO₂, which may inhibit further recrystallization. But in the second reaction, regions of forsterite and enstatite can develop simultaneously maintaining the correct ionic balance by counter-migration of Mg and Si ions. The chrysotile fibrils treated between 800 °C and 900 °C contained some crystallites, thought to result from the low-temperature developments, which extended for several hundred Å with apparently constant composition. These could often be identified as forsterite by the characteristic 5.1 Å 020 lattice planes running at 90° and 30° to the fibre axis and they frequently contained a number of cavities with sizes of 40 to 90 Å, which appeared to have evolved from the hollow cavities running down the fibre centres. The other regions of the fibre were filled with masses of crystallites of both forsterite and enstatite with sizes in the range 150–300 Å.

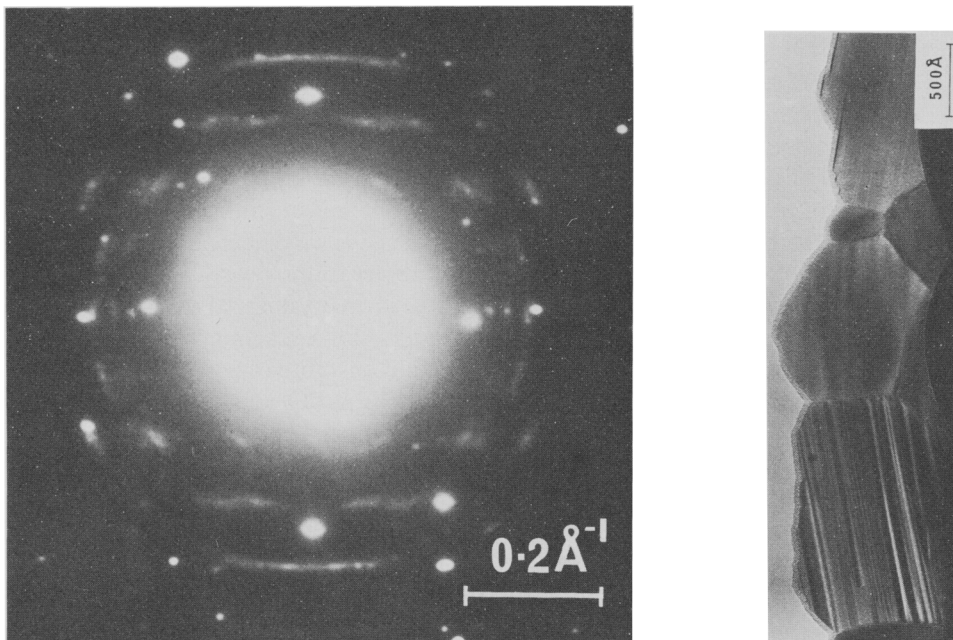
The orientation relationships for enstatite. Electron diffraction studies of these fibrils showed that there was some degree of preferred orientation in the enstatite as well as in the forsterite (fig. 4). There was a tendency for the *c* vector to align along the fibre axis, as was observed by Ball and Taylor (1963), or in the crystallographically equivalent position at 60° away from this in the *bc* plane. But in contrast to the sharp reflections of the forsterite, the enstatite diffraction peaks were diffuse and showed a spread in orientation of ±7° on either side of these positions, which was similar for the crystallites within each individual fibril, as shown by the 020 reflections in fig. 4.

The most probable orientation relationships between the chrysotile (C) and enstatite (E) lattices is:

$$2c_C(28.64 \text{ \AA}) \rightarrow 3a_E(27.33 \text{ \AA}), b_C(9.20 \text{ \AA}) \rightarrow b_E(8.81 \text{ \AA}), a_C(5.31 \text{ \AA}) \rightarrow c_E(5.17 \text{ \AA}).$$

Comparison of the orientations of the silica tetrahedra in the two lattices suggests that the reaction may be nucleated around the silicate chains in the chrysotile structure, but the precise mechanism for the development is complex involving an extensive amount of ion migration. Comparison of the number of atoms in equivalent volumes in the two structures, namely: $2V_C = 12\text{Mg}, 8\text{Si}, 36\text{O}, 16\text{H}$, $3V_E = 12\text{Mg}, 12\text{Si}, 36\text{O}$, would imply that the transformation of enstatite occurred by an addition of tetrahedra to the silica layers, but some Mg ions are probably liberated as well.

Some preferred orientation of the forsterite also occurred in these newly recrystallized areas. It probably takes up magnesium ions from the enstatite and liberates some excess silicon, so the lattice will be disrupted more than in the low-temperature development. It is thought therefore that the original lattice order need only be maintained over a few lattice spacings to nucleate the recrystallization in preferred orientations. In fibres heated quickly to temperature the orientation relationships were less pronounced, probably because the lattice order had been too



FIGS. 4 and 5: FIG. 4 (left). Diffraction pattern from a group of fibrils treated at 900 °C showing the development in preferred orientations of sharp reflections from the forsterite crystals and a diffuse pattern from the enstatite ones. FIG. 5 (right). Fibres treated at 1200 °C.

disrupted by the rapid dehydration, and many more of the fibres appeared to have recrystallized by the second mechanism. This implies that the recrystallization to a mixture of forsterite and enstatite (fig. 2) is the chief reaction occurring above 800 °C, but does not occur to any significant extent at lower temperatures. So it must have a much higher rate constant, as well as a higher activation energy than the low-temperature reaction.

High-temperature changes. Enstatite has a number of polymorphs with slight structural variations, which are stable over different temperature ranges (Smyth, 1974). The stable form below about 900 °C down to at least 560 °C is the orthorhombic variety, but a second form clinoenstatite is produced in stressed conditions. Clinoenstatite had a monoclinic lattice and is formed when slip occurs parallel to the c axis, changing the angle β from 90° to 108°. Above about 900 °C a third form, protoenstatite, is stable, which changes to clino, or a mixture of ortho and clino on cooling. The proto to clino conversion is a martensitic transition and quenching produces pure twinned clino but slower cooling rates may give rise to as much as 50% orthoenstatite, which develops from a slower order-disorder transition. In many of the crystallites in the samples treated above 900 °C and in a few of the 800 °C samples, twinning had occurred along a direction parallel to the fibre axis (fig. 5) and sometimes at an angle of 60°. The individual twins were often only two or three atomic layers wide and it is probably the size of this dimension that is partly responsible for the diffuse nature of the diffraction pattern (fig. 4).

As the temperature was increased the crystals of forsterite and enstatite grew from sizes of 200–400 Å at 1000 °C up to around 400–1200 Å at 1400 °C until the isolated fibrils resembled strings of silicate beads (fig. 5) and the crystallization had traversed the original fibre boundaries. In the forsterite diffraction pattern the $0k0$ and $0kl$ reflections with odd values of k appeared (fig. 4), which are forbidden in the space group $Pbnm$, and in addition extra $0kl$ reflections were occasionally seen with half integer values of k . These are similar but not identical to

observations made by Brindley and Zussman (1957). The odd reflections could arise from double diffraction but the reflections at half-integer k values suggest that a new unit cell with a double b axis may be formed. The characteristic diffraction pattern from the enstatite changed into a series of disordered spots stretching along the layer lines perpendicular to the fibre axis, which were spaced at a distance of 9.9 Å. It showed the more extensive development of the preferred orientation within the larger crystals, but the extra reflections make it difficult to speculate about any other structural changes.

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REFERENCES

- Ball (M. C.) and Taylor (H. F. W.), 1963. *Mineral. Mag.* **33**, 467-82 [M.A. 16-624].
Brindley (G. W.) and Hayami (R.), 1965. *Ibid.* **35**, 189-95 [M.A. 17-134].
— and Zussman (J.), 1957. *Am. Mineral.* **42**, 461-74 [M.A. 13-545].
Johns (W. D.), 1965. *Ceram. Bull.* **44**, 682-6.
Martinez (E.), 1961. *Am. Mineral.* **46**, 901-12 [M.A. 15-544].
Smyth (J. R.), 1974. *Ibid.* **59**, 345-52 [M.A. 26-283].
Whittaker (E. J. W.) and Zussman (J.), 1971. *The Electron Optical Investigation of Clays*, (ed. J. A. Gard). London (Mineralogical Society), ch. 5, 173-5 [M.A. 23-65].
Yada (K.), 1967. *Acta Crystallogr.* **23**, 704-7 [M.A. 20-529].
— 1971. *Ibid.* **A27**, 659-64 [M.A. 23-1816].

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