

The dehydration of chrysotile in air and under hydrothermal conditions.

By M. C. BALL, A.R.I.C., Ph.D.,
and H. F. W. TAYLOR, D.Sc., Ph.D.

Department of Chemistry, University of Aberdeen, Scotland.

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Summary. Chrysotile fibres, and also single crystals of lizardite, were dehydrated hydrothermally, and the resulting pseudomorphs studied by X-ray rotation photographs. The initial products are normally forsterite and disordered material; talc forms more slowly. At water pressures up to 600 kg/cm², both forsterite and talc show strong preferred orientation. At higher pressures the talc is oriented but the forsterite tends to be unoriented. The orientation of forsterite formed at 550° C and 500 kg/cm² differs from that found when chrysotile is dehydrated by heating in air. The orientation relationships suggest that, in the dry reaction, the forsterite orientation is controlled mainly by the octahedral layers of the chrysotile, while in the hydrothermal reaction it is controlled mainly by the tetrahedral layers. This does not support the generally accepted mechanism for the dry reaction. New mechanisms are suggested, for both dry and hydrothermal reactions, similar to that already suggested by us for the dehydration of brucite. The formation of talc in the hydrothermal reaction, and of enstatite in the dry reaction above 1000°, are also discussed. The dehydration of talc, to give enstatite, has also been studied using single crystals, and the mechanism of this process is briefly discussed.

IT has long been known that, if a fibre of chrysotile is heated in air, forsterite is formed topotactically; that is, a pseudomorph is formed that contains forsterite in one or more definite orientations (Aruja, 1943; Hey and Bannister, 1948). More recently, this observation has been confirmed and extended by studies on lizardite, a variety of serpentine that contains crystals sufficiently large for single-crystal X-ray work (Brindley and Zussman, 1957). Chiefly from the observed orientation relationships, possible mechanisms for the dehydration have from time to time been suggested. Chrysotile can also be dehydrated hydrothermally (Bowen and Tuttle, 1949), when forsterite is again a product. Up till now, studies of the hydrothermal dehydration have been made only with powders, and it is therefore not known if the reaction occurs topotactically under these conditions and if so,

whether the forsterite orientation is the same as when chrysotile is heated in air. The main object of the present work was to answer these questions. The results throw some light on the mechanism of the hydrothermal reaction, and also suggest a new approach to that of the reaction under dry conditions.

Experimental.

Chrysotile. Several samples were used; in all cases, X-ray rotation photographs showed only the reflections of clino-chrysotile. This is the monoclinic variety with a fibre spacing of about 5.3 Å (Whittaker and Zussman, 1956). For most of the runs, a nearly iron-free specimen from the Phillips Brothers' mine, Globe, Arizona, U.S.A., was used. It consisted of white fibres 1–2 cm long. The other specimens, from Jeffrey mine, Quebec, Canada, and Munro mine, Ontario, Canada, were pale green and contained more iron. With one minor exception mentioned later, no differences in behaviour were found between any of these specimens.

Fibres were treated hydrothermally with water for varying combinations of temperature, pressure, and time. Usually a cold-seal apparatus (Tuttle, 1948; Roy and Osborn, 1952) was used, but for some runs at the lower temperatures and pressures, closed bombs were employed. To reduce the danger of change in composition due to leaching, a mass of fibres was packed tightly into a stainless-steel capsule with loosely fitting ends, which was placed within the pressure vessel, and only fibres from the middle of the mass were examined after the run. A few runs were also made in which fibres were heated in air. The fibres always persisted as pseudomorphs, which were not greatly changed in general appearance. In all cases X-ray rotation photographs were made of the pseudomorphs to find what phases were present, and what preferred orientation, if any, each phase possessed. Filtered cobalt radiation was used.

Lizardite. A specimen from the original locality at Kennack Cove, Lizard, Cornwall, England (specimen M 709 in the Building Research Station collection, described by Midgley, 1951), was used. It consisted of small flakes, which proved on X-ray examination to be approximately single crystals with (001) cleavage and a tendency to elongation parallel to *a* (the 5.3 Å axis). Crystals were treated hydrothermally as for chrysotile, and X-ray single crystal photographs taken of the resulting pseudomorphs.

Results.

Products from chrysotile. Fig. 1 gives the main results, both for hydrothermal runs and for those made by heating in air. For both kinds of run, the times were usually 1-7 days.

In the hydrothermal runs, there was no reaction below 500° C. At 500°-700°, traces of chrysotile usually remained, but above 700° the

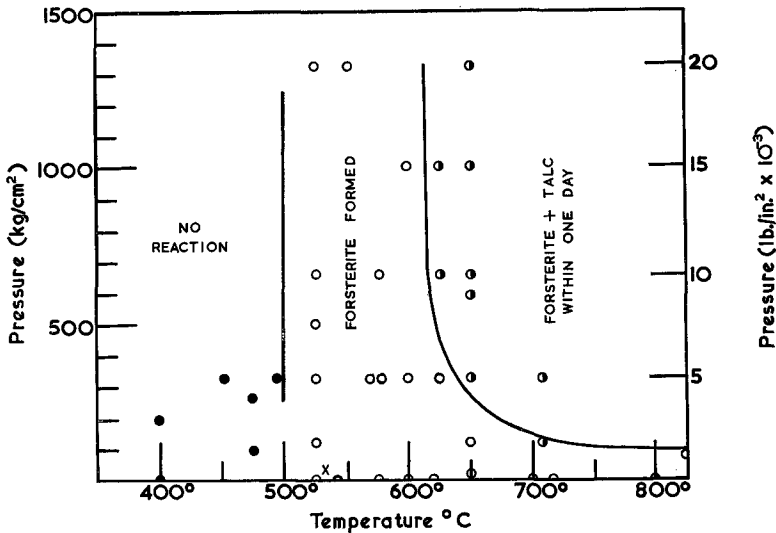


FIG. 1. Crystalline phases detected by X-rays in chrysotile fibres after 1-7-day treatment, either hydrothermally or by heating in air. ● chrysotile only. ○ forsterite, with or without residual chrysotile. ◐ forsterite and talc, with or without residual chrysotile. × unidentified phase and residual chrysotile; see text.

chrysotile had usually reacted completely within a few days. Forsterite was produced in all but two of the hydrothermal runs above 500°. It was often the only product detected with X-rays. Talc formed less readily; its formation was favoured by the combination of high pressure and high temperature (fig. 1), or by increasing the time of the run. Thus at 620° and 330 kg/cm², talc was found after 5 days but not after 1 day; but at lower temperatures, e.g. at 520° and 1330 kg/cm² or at 580° and 330 kg/cm², it was not found after 6 days. In two runs, both made with the Arizona specimen at 530° and 33 kg/cm² for 6 days, neither forsterite nor talc was formed, but an unidentified product

appeared. This had a fibre spacing of about 5.1 Å and is being further investigated. Enstatite was not formed in any of the hydrothermal runs, although phase equilibrium data (Bowen and Tuttle, 1949) predict its occurrence in some of the runs above 600°. Evidently equilibrium was not being reached.

The runs made in air below 1000° C gave results agreeing with those of Brindley and Zussman (1957). Below 500° there was no reaction, while at 520°–1000° the chrysotile disappeared within a few days, giving forsterite. In some runs above 1000°, enstatite was also formed. It was obtained at 1060°–1200° with the Munro or Jeffrey specimens, but only at 1150°–1200° with the Arizona specimen. Fibres heated in air at 570°–720° often gave, in addition to the forsterite reflections, an intense low-angle X-ray reflection similar to that reported by Brindley and Zussman. This reflection was also shown by some of the fibres which had been treated hydrothermally at or below 133 kg/cm². Brindley and Zussman reported a distinct peak at 14–15 Å for specimens low in Al. In the present work, fibre rotation photographs showed not a peak, but an intense and broad streak lying along the zero layer line. For specimens heated in air at 570°, this extended from about 10 Å to at least 50 Å without any marked variation in intensity along most of its length. With increase in temperature, the streak was progressively curtailed at its high-angle end, which at 720° corresponded to a spacing of 12–14 Å. Fibres heated at 850° or above did not give this reflection at all.

Orientation of the forsterite. Except in some of the hydrothermal runs at the higher pressures used, the forsterite always showed strong preferred orientation. The dehydration thus occurs topotactically over a wide range of hydrothermal conditions as well as in air. Several different orientations of the forsterite were observed. Fig. 2 defines these, and fig. 3 shows the conditions under which each was found. With the pseudomorphs after chrysotile, only rotation photographs can be obtained and it is therefore possible only to determine which direction in the forsterite has been formed parallel to the fibre axis. The additional information needed to determine the orientation relationships completely can be obtained from studies on lizardite.

For chrysotile fibres heated in air at 520°–1200°, the present results confirm earlier observations that forsterite is formed in at least two orientations; the fibre direction of the chrysotile becomes either forsterite *b*, or a direction 60° away from this in the *bc* plane. Both orientations are strongly developed. Studies on lizardite (Brindley and

Zussman, 1957) showed that, in either case, the normal to serpentine (001) becomes forsterite *a*. As clino-chrysotile is monoclinic, there are probably really three orientations of the forsterite (fig. 2*b*). This combination of orientations will collectively be called the dry orientation.

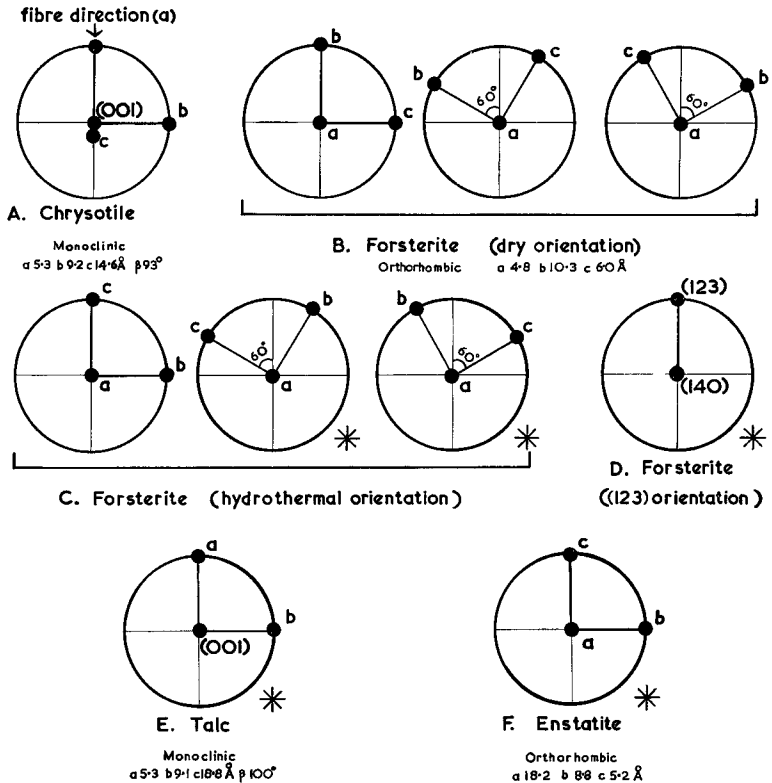


FIG. 2. Orientation relationships for the formation of forsterite, talc, and enstatite, shown in stereographic projection. In those cases marked*, only the direction in the product formed parallel to chrysotile *a* was experimentally determined, the orientation in the sense of rotation around this direction being conjectural.

It was found also in fibres treated hydrothermally at relatively high temperatures and low pressures (fig. 3).

When chrysotile is treated hydrothermally at lower temperatures and higher pressures, the dry orientation is supplemented or replaced by a second group of orientations, which will collectively be called the

the original material. These confirmed that forsterite *c* had been formed parallel to serpentine *a*, and showed also that forsterite *a* had been formed perpendicular to serpentine (001). The other constituents of the hydrothermal orientation were found only with chrysotile, and were weakly developed. They were represented by X-ray reflections which indicated that the fibre axis had become a direction 60° away from forsterite *c* in the *bc* plane. It seems reasonable to suppose that, as in the previous case, there are three constituent orientations all having forsterite *a* perpendicular to chrysotile (001) (fig. 2c). Brindley and Zussman (1957) found that the orientation with forsterite *c* parallel to chrysotile *a* sometimes occurred as a minor one in fibres heated in air, but this was not found in the present investigation.

Hydrothermal treatment of chrysotile at 670 kg/cm² or above still gave pseudomorphs, but the forsterite present in them was largely or wholly unoriented (fig. 3). In a few runs at lower pressures, yet another forsterite orientation was found, with the normal to (123) parallel to the fibre direction (fig. 2d). This will be called the (123) orientation. It occurred erratically, and attempts to obtain it reproducibly were unsuccessful. It is possibly favoured by abnormally rapid increase in both pressure and temperature at the beginning of the run.

Other products formed from chrysotile. Talc, formed in many of the hydrothermal runs, always showed strong preferred orientation. It was often better oriented than the forsterite, especially at high pressures. The talc *a*-axis was always formed parallel to the fibre direction, irrespective of the orientation of the forsterite already formed (fig. 2e). Talc probably always begins to form before the last traces of chrysotile have disappeared. Attempts were made to obtain talc by hydrothermal treatment of fibres which had previously been heated in air to cause complete decomposition to forsterite and amorphous material, but these were unsuccessful. No talc was formed, even after 16 days at 680° and 500 kg/cm². Enstatite, formed by heating in air at 1060°–1200°, also showed strong preferred orientation (fig. 2f).

Discussion.

Previous studies of the dehydration of chrysotile in air. Previous theories of the mechanism (e.g. Brindley and Zussman, 1957; Mchedlov-Petrosyan and Vorobyov, 1960) have mostly proceeded from the assumption that the elements of water and of silica are lost more or less uniformly from all parts of the structure; all unit cells have been

assumed to behave in the same way. It has also generally been assumed that SiO_4 tetrahedra are more likely to persist as entities than are MgO_6 octahedra, and that the amorphous material that is presumed to be formed in addition to forsterite below 1000° is pure silica.

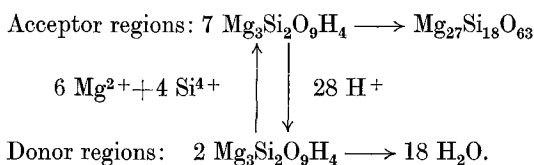
These assumptions can be criticized on several grounds. Firstly they do not lead to any explanation of the occurrence under different conditions of the dry, hydrothermal, and (123) orientations. A more general criticism is based on the results of recent studies of topotactic processes in other minerals rich in Mg or other cations of similar size, which suggest that the most stable features of these structures are the frameworks of nearly close-packed oxygen ions; migrations of cations, including Si^{4+} , occur with relative ease (Bernal, Dasgupta, and Mackay, 1959; Freeman and Taylor, 1960; Gay and LeMaitre, 1961). This suggests that no oxygen is lost, either as H_2O or as SiO_2 , from those parts of the structure where the topotactic reaction actually occurs. There is no evidence to support the assumption that SiO_4 tetrahedra are particularly stable in high temperature reactions; both the above studies and also ones on Ca and Mn silicates (Dent and Taylor, 1956; Taylor, 1960; Dent Glasser and Glasser, 1961) show that they are often less stable than are metal-oxygen polyhedra. The orientation relationships observed in the dry dehydration of chrysotile itself also indicate a correspondence of the Mg-O parts of the initial and final structures, but not of the Si-O parts. Bradley and Grim (1951) noted this fact over ten years ago, but their observation has since been largely overlooked.

The assumption that amorphous silica is formed as a separate phase is not based on any direct evidence, but has been introduced merely to balance the chemical equations; forsterite has a higher Mg:Si ratio than chrysotile. The ideas of Gay and LeMaitre (1961) perhaps offer a better starting-point for understanding the stoichiometry of the chrysotile dehydration. These workers discussed the formation of iddingsites (topotactically altered olivine crystals). They considered that this occurred by cation migration, and that the resulting products were not intergrowths of sharply defined phases, but disordered, irregular structures in which the better crystallized regions merged into regions of indefinite composition and structure. This may also be true of the product formed from chrysotile.

We have recently discussed the dehydration of brucite assuming a mechanism based on cation migration (Ball and Taylor, 1961). The following discussions of the chrysotile and talc dehydration are based

on the concepts developed in that paper, and also owe much to the ideas of Gay and LeMaitre.

A new approach to the chrysotile dehydration. It will be assumed that, for either dry or hydrothermal conditions, an inhomogeneous mechanism operates as with brucite (Ball and Taylor, 1961). The process can be broken down into four stages. In the first of these, donor and acceptor regions come into existence, and cation migrations occur. The oxygen for the expelled water comes entirely from the donor regions, which are destroyed and form pores. This stage can be represented:



This is probably only an approximation, as some protons are almost certainly left behind in the acceptor regions, especially under hydrothermal conditions. The product of this stage is a partly disordered material. The oxygen framework is more or less unchanged, but extra cations have been introduced to balance the loss of protons, and some of those originally present have possibly migrated to new sites. The Mg:Si ratio stays at 1.5.

In the second stage of the reaction, cation migrations continue, but Mg^{2+} and Si^{4+} now begin to move in opposite directions, so that Mg-rich and Si-rich regions are formed. The protons probably tend to accompany the silicon. There are probably no sharp boundaries between these regions; the oxygen framework is continuous, and variations in Mg:Si ratio are likely to be gradual.

In the third stage, the Mg-rich regions change to forsterite. This involves an ordering of cations and also a change in the type of oxygen packing, though not in the number of oxygens per unit volume. The change in the type of packing can happen in several different ways, and this is where the possibility of different orientations of the forsterite arises. This is discussed in detail later. This third stage is probably largely concurrent with the second. The crystallization of forsterite is visualized, not as a sudden process, but as a gradual one which begins in small nuclei and spreads as the cation migrations and packing changes proceed.

The fourth stage is the change of the Si-rich regions to enstatite (on

dry heating) or to talc (under hydrothermal conditions). This stage occurs less readily than the other three, and the reaction is easily halted at the end of the third stage, under either dry or hydrothermal conditions. In principle the fourth stage resembles the previous one in that it involves cation ordering and a change in the type of oxygen packing. Why it occurs less readily is not certain. Possibly the change in oxygen packing does not occur so readily at the lower Mg:Si ratio. Another possibility is that the Mg:Si ratio in the Si-rich regions drops to the appropriate range (0.75–1.00) only slowly, as the crystallization of forsterite advances.

The forsterite orientations. For all components of both dry and hydrothermal orientations, the normal to chrysotile (001) is known or assumed to become forsterite *a*. Both structures are based on nearly close-packed oxygen layers normal to these directions (fig. 4), and the preservation of these layers is evidently the most important single factor controlling the orientation. The layers in chrysotile are of two kinds, which will be called *o*- (for octahedral) and *t*- (for tetrahedral). The number of oxygens per unit area is the same in each kind of layer, but the arrangement is different (fig. 5). In each case, the most important of the parameters defining the type of packing is the orientation of the three equivalent pseudohexagonal or a_{ψ} -axes. In chrysotile, the a_{ψ} -axes of the *o*-layers are perpendicular to those of the *t*-layers. In forsterite, the layers are all of *o*-type (fig. 4), and all are similarly oriented in their own plane. The significance of the dry and hydrothermal orientations can now be stated: for all three dry orientations, the forsterite a_{ψ} -axes coincide with those of the chrysotile *o*-layers, while for all three hydrothermal orientations, they coincide with those of the chrysotile *t*-layers. This means that, under dry conditions, the oxygen packing in the products is based on that in the *o*-layers, while under hydrothermal conditions, especially around 550° and 500 kg/cm², it is based on that in the *t*-layers. In the latter case, even the *t*-layers must undergo changes, but these are relatively small inasmuch as the a_{ψ} -directions are unchanged.

Migrations of both Mg²⁺ and Si⁴⁺ must occur, whichever group of orientations is adopted. The results suggest that, under dry conditions, Si⁴⁺ is somewhat more mobile than Mg²⁺, while under the hydrothermal conditions mentioned above, the reverse is the case. Many of the MgO₆ octahedra can be preserved in the dry reaction (fig. 6). The position in the hydrothermal reaction is more complex, but it is possible to show that some of the SiO₄ tetrahedra could be preserved.

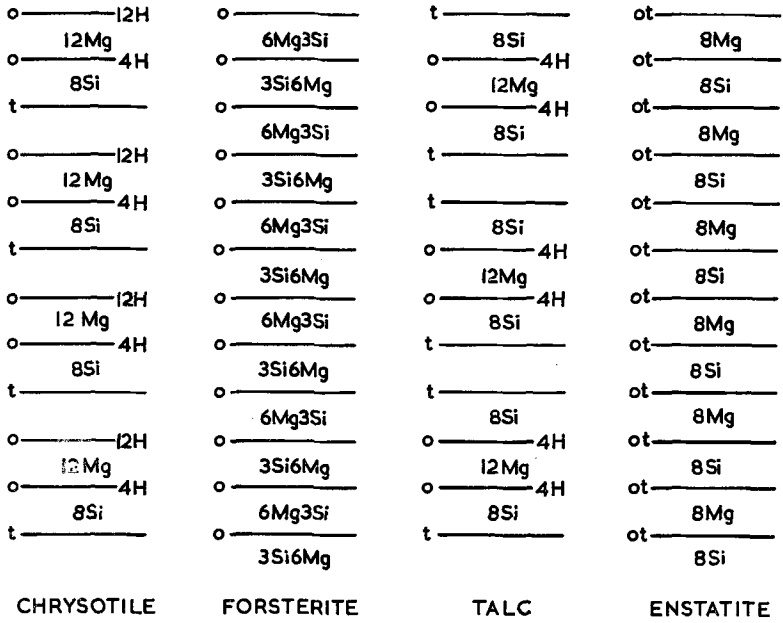


FIG. 4. Crystal structures of chrysotile, forsterite, talc and enstatite, drawn so as to emphasize the existence in all of them of nearly close-packed oxygen layers. Each horizontal line represents 12 oxygen atoms. *o*, *t*, and *ot* represent different types of oxygen layer; see text and fig. 5.

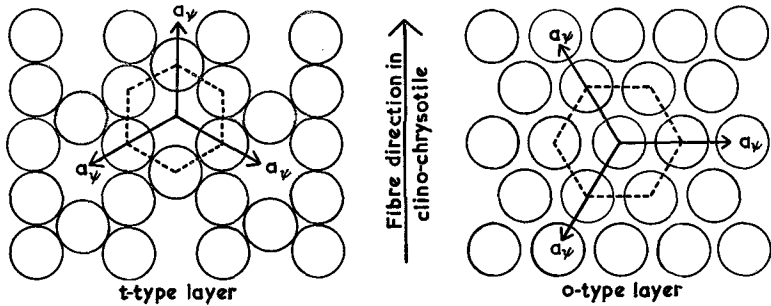


FIG. 5. Oxygen layers of *o*- and *t*-types in chrysotile and related compounds, showing the orientation of the three equivalent pseudo-hexagonal a_y -axes relative to the fibre direction in clino-chrysotile for each kind of layer.

The (123) orientation differs from the others in that forsterite a cannot be normal to chrysotile (001). Examination of a model of the forsterite structure showed that nearly close-packed oxygen planes exist parallel to (140), which is approximately perpendicular to (123). It was therefore assumed that (140) is formed parallel to chrysotile (001) (fig. 2*d*). An a_y -axis for the (140) oxygen planes lies approximately

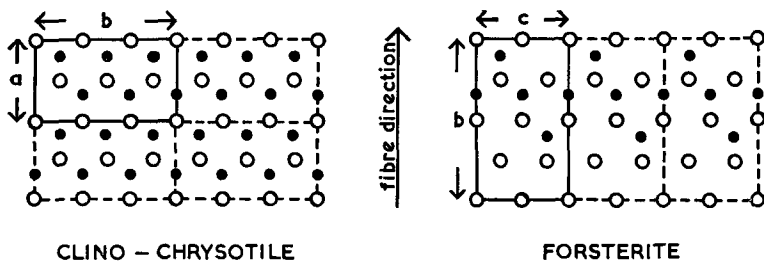


FIG. 6. Octahedral parts of the chrysotile and forsterite structures drawn in the observed relative orientations for the component of the dry orientation with forsterite b parallel to chrysotile a . A single layer of oxygens (large open circles) and an adjacent layer of magnesiums (small full circles) is shown. The chrysotile structure is viewed along the normal to (001) and the forsterite structure along a . The other two components of the dry orientation are derived from the one shown by rotations through $\pm 60^\circ$ in the plane of the drawing.

in the (123) plane and thus parallel to an a_y -axis of the chrysotile o -layers. This suggests that the (123) orientation should be regarded as a variant on the dry orientation. On the whole, this orientation appeared under circumstances where the dry orientation might have been expected.

No detailed explanation can be offered for the formation at high pressures of forsterite in random orientation. Possibly the solvent power of the fluid increases and allows recrystallization from solution. It is possibly significant that randomly oriented forsterite begins to appear at pressures where the density of oxygen atoms in the fluid is beginning to approach that in the solid; this might be expected to influence the manner in which oxygen atoms are lost by the solid. The reaction is still partly topotactic because talc, if formed, is as well oriented as at lower pressures.

The formation of enstatite and talc from chrysotile. Fig. 4 shows that both enstatite and talc have structures based on nearly close-packed oxygens, and the postulated orientation relationships (fig. 2 *e* and *f*)

are partly based on the assumption that the plane of these layers is preserved. In neither case is there a possibility of two groups of orientations analogous to the dry and hydrothermal orientations for forsterite. This possibility exists with forsterite because it is impossible for both the tetrahedra and the octahedra to have the same orientation in starting material and product. This is not the case with enstatite or talc; in each case the proposed orientation relationship is such that both tetrahedra and octahedra have the same orientation in the product as in the chrysotile.

As previously stated, it is assumed that these products are formed in the Si-rich regions of the crystal as a result of cation migrations and changes in the type of oxygen packing. With talc, one-half of the oxygen layers, as well as some of the MgO_6 and SiO_4 polyhedra, can persist from the chrysotile structure (fig. 4). With enstatite, all of the oxygen layers must undergo minor packing changes because each layer in the product contains alternate strips of *o*- and *t*-types.

Although two *groups* of orientations would not be expected with enstatite, one might expect the observed orientation to be accompanied by two others related by 60° rotations around the normal to chrysotile (001), and this was not observed. A similar effect was noted in the formation of enstatite from saponite (Midgley and Gross, 1956). Although the persistence of the oxygen framework is the main factor controlling these orientation relationships, it is evidently not the only one. In the cases under discussion, the habit or curvature of the layers seems also to be important.

The explanation of enstatite and talc formation that has been advanced here demands that these products take their orientation from the residual order that persists, mainly in the oxygen packing, in the Si-rich regions in which they are formed. The alternative possibility was considered that the Si-rich regions become completely amorphous and that the talc (or enstatite) orientation is controlled by epitaxial nucleation, either on the forsterite already formed, or on residues of chrysotile. This possibility was rejected. The forsterite cannot play this role because, in the case of talc, the orientation does not depend on that of the forsterite. Nucleation on chrysotile residues could occur with talc, but not with enstatite, which only begins to form after all the chrysotile has disappeared.

Intermediate stages in the dry dehydration of chrysotile. D.t.a. curves for serpentine minerals show an endothermic peak followed by an exothermic one, all within the range 600° – 850° (Caillère and Hénin, 1957).

Specimens heated to temperatures between these two peaks show high chemical reactivity and other characteristic properties, suggesting the existence of a recognizable intermediate state (Mchedlov-Petrosyan and Vorobyov, 1960). Brindley and Zussman (1957) obtained X-ray evidence for an intermediate state in the low-angle reflection already described, and also in the occurrence under certain conditions of a forsterite-like product with tripled values of a and c .

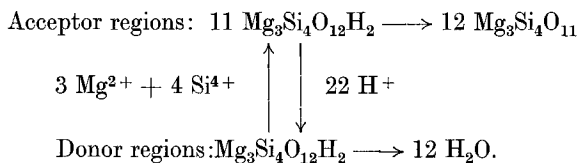
The present theory is compatible with all these observations. The endotherm can be attributed to the initial stage of cation migrations and water loss from donor regions, while the exotherm can be attributed to the change in type of oxygen packing and consequent formation of forsterite. The product of the first stage is largely disordered, and this would explain its chemical reactivity. The slightly differing low-angle X-ray effects observed by Brindley and Zussman and by ourselves each have their counterparts in those given by different specimens of iddingsite (Gay and LeMaitre, 1961). These authors attributed them to incipient crystallization in a disordered material, and this explanation could well apply in the present case. The forsterite-like product with tripled a and c appears analogous to the spinel-like phase found on dehydration of brucite (Ball and Taylor, 1961). This could alternatively be described as a periclase-like phase with doubled a , and its existence was attributed to an ordered displacement of cations out of their normal sites, which could be explained by the process of cation migration. The tripling of the forsterite a - and c -axes can perhaps be explained in a similar way.

A note on the dehydration of talc. If talc is heated in air, the main product is a polymorph of MgSiO_3 (Thilo and Rogge, 1937). It has generally been assumed that this process occurs topotactically, although there seems to be no direct evidence of this as only powders have been examined. Indirect evidence that the process is topotactic is provided by the observation of Midgley and Gross (1956) that the closely related conversion of saponite to enstatite occurs in this way.

A preliminary observation on the dehydration of talc was made in the present investigation; one end of a small crystal was heated to about 1000° , and X-ray single crystal photographs made of the product. These showed the reflections of talc and of enstatite, which was oriented in the same way as when it is formed from chrysotile (fig. 2*f*). As in that case, only one of the three equivalent orientations was found.

The dehydration of talc therefore probably occurs in the same way

as that of chrysotile, the initial stage being the expulsion of water from donor regions and formation of a partly disordered product:



Counter migrations of Mg^{2+} and Si^{4+} then occur, and the Mg-rich regions so formed are afterwards changed into enstatite through cation ordering and change in the type of oxygen packing.

Thilo and Rogge showed that different forms of enstatite were produced depending on the temperature. At 900° – 1020° they obtained the 'M₁ modification'. This was an imperfectly crystallized variety which they considered to be possibly related to clinoenstatite. In the present case, the pattern appeared more like that of enstatite, but the reflections were somewhat diffuse and the material could well have been similar to that described by Thilo and Rogge.

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