

Mechanism of formation of forsterite and enstatite from serpentine

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Summary. Forsterite formed from serpentine powders at various temperatures up to 800°C has been measured quantitatively by X-ray diffraction. The results are considered in relation to a reaction mechanism proposed by Ball and Taylor and are shown to be inconsistent with the details of this mechanism. An alternative mechanism is proposed by which after nearly all the Mg ions together with some of the Si ions liberated in the reaction zones where water is formed migrate into regions where forsterite is formed. This mechanism is in closer accord with the experimental results. The retarded development of enstatite until temperatures above 1000°C are used is attributed to the nature of the reaction by which it is formed, namely a reaction between forsterite and silica.

THE dehydration and subsequent recrystallization of serpentine minerals, both platy and fibrous forms, have been the subject of numerous investigations.¹ The principal recrystallization product, forsterite, is formed topotactically, i.e., with well-defined crystallographic orientations with respect to the parent crystal structure. Considerable interest has been taken in possible mechanisms by which these topotaxial relations are developed. Brindley and Zussman (1957) studied a platy form of serpentine, lizardite, and interpreted their data in terms of a homogeneous reorganization of cations within a largely constant oxygen framework, with an expulsion of Si ions in excess of requirements for the formation of forsterite.

More recently, Ball and Taylor (1961, 1963), Taylor (1962), and independently Brindley (1961, 1963) have suggested that more satisfactory explanations for this and for other topotactic reactions in hydroxides, silicates, and other materials can be given in terms of heterogeneous rather than homogeneous processes. Reactions initiated at favorable sites such as external surfaces, dislocations, &c., are maintained by appropriate diffusions of cations up to and away from the reaction front. Dehydroxylation of a mineral such as serpentine may proceed by migration of H⁺ ions to a reaction site where water is formed and

¹ Ball and Taylor (1963) give references to earlier work.

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liberated, with a converse migration of other cations, Mg^{2+} and Mg^{2+} , to maintain electrical neutrality.

Ball and Taylor (1963) have given a detailed description of the heterogeneous processes by which the dehydroxylation and recrystallization of serpentine (both chrysotile and platy forms) may take place. They considered the formation of forsterite and also, at higher temperatures, of enstatite, and, under hydrothermal conditions, of talc.

Although the crystallographic relations provide strong pointers of how these 'ordered' reactions may occur, they scarcely give quantitative information. Since the reactions probably occur on a fine scale, possibly within domains of the order of 10^{-4} cm in size, it is not easy to obtain any direct information on the ionic (mainly cationic) migrations by which they are considered to take place. The present writers have sought further information by making quantitative measurements on the development of forsterite and, as will be shown here, the results suggest a somewhat different sequence of events than those postulated by Ball and Taylor.

Experimental

A massive serpentine from Quebec Province, of fine grain size and pale buff colour, was used. No mineral impurities were detected by X-ray diffraction. The mineral appears to be a layered structure with considerable stacking disorder. Powders with particle sizes in the range $< 60, > 100$ -mesh screen size were heated in air in uncompact form on a thermobalance at 570°C for periods of about 30 hours. From the loss of weight compared with the maximum loss at higher temperatures, it was determined that the mineral was about 90% dehydroxylated by this treatment. X-ray diffraction data showed no residual reflections from unreacted serpentine and no detectable forsterite. Subsequent heat-treatments were carried out in air in temperature-controlled furnaces at temperatures ranging from 650° to 800°C for periods up to 100 hours. A few experiments were carried out at higher temperatures up to 1400°C to study the formation of enstatite.

Forsterite was determined quantitatively by integrated X-ray diffraction measurements using boehmite as an internal standard. Four forsterite reflections and two boehmite reflections were measured with a scanning speed of $1^\circ/20\text{ min}$.

The results are shown in Fig. 1 where the amount of forsterite formed is expressed as a percentage of the weight of the final fired material, i.e., as a percentage of completely anhydrous material. The maximum

amount of forsterite developed is about 80% of the weight of the fully anhydrous material and is obtained after heating at 850°C for periods of 30 hours or longer. The internal standard, boehmite, was calibrated with respect to a nearly pure, well-crystallized, 'fused-cast' forsterite. The latter contained just detectable amounts of MgO and clinopyroxene, estimated at 5 to 7% total impurity. Determinations made without allowance for these impurities may be over-estimated by a few percent.

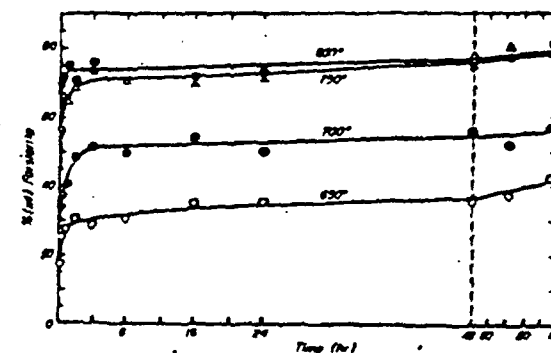


Fig. 1. Weight percent of forsterite formed from powdered serpentine in periods up to 100 hours when heated isothermally at temperatures shown in $^\circ\text{C}$.

so that the value of 80% forsterite may need to be reduced to about 75 to 76%.

It was observed that the reflections from the forsterite derived from serpentine were broadened with respect to those from the high-temperature-produced forsterite. The broadening was approximately the same irrespective of the time (1 to 96 hours) or temperature (650 to 800°C) of the heat-treatment. If this broadening is attributed to small crystal size, and if a correction for instrumental broadening is based on the reflections from the high-temperature-produced forsterite, then a value of the order of 4×10^{-4} cm is obtained for the crystal size of the forsterite obtained from serpentine.¹ If the broadening arises partly from lattice

¹ The correction used for instrumental broadening is:

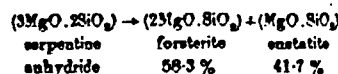
$$B_{\text{corrected}} = B_{\text{total}} - B_{\text{instrumental}}$$

The crystal size is calculated from the Scherrer formula: $t = \lambda / B \sin \theta$ and $\cos \theta$.

distortion, the crystal size broadening will be correspondingly less and the estimated crystal size will be larger. At present, 4×10^{-3} nm must be taken as a lower limit to the crystal size. However, the fact that there is no noticeable diminution of the broadening within the time-temperature limits of the experiments suggests that the distortional contribution to the broadening may be small so that the crystal size may indeed be as small as 10^{-4} nm. This result implies that the diffusion processes that occur in these topotactic reactions take place over quite short distances and this is compatible with the relatively low temperatures at which the reactions proceed to completion as compared with the higher temperatures required when forsterite is formed from mixed powders of MgO and SiO₂.

Discussion

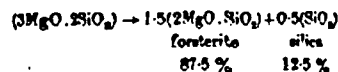
Chemical equations for formation of forsterite. From the MgO-SiO₂ equilibrium diagram, forsterite and enstatite would be expected as reaction products from the recrystallization of dehydroxylated serpentine. The equation can be written:



The intimate mixing of the 'oxides' in the serpentine after dehydroxylation would be expected to favour the attainment of equilibrium and any residual 'water' might assist the reaction since water often provides a catalytic effect. The non-appearance of crystalline enstatite until higher temperatures ($> 1000^\circ\text{C}$) are reached raises doubts as to the validity of this equation, but it is not conclusive evidence because if enstatite is slow in crystallising an amorphous phase of enstatite composition may be formed.

The fact that the amount of forsterite found experimentally, 75 to 80 %, is much greater than the amount predicted by this equation indicates that the reaction is probably not proceeding directly towards the ultimate equilibrium.

A second equation can be written on the supposition that all the MgO in the serpentine composition goes into forsterite, leaving a residue of amorphous silica:



This equation gives the maximum amount of forsterite, 87.5 %, which is not greatly in excess of the measured amount. That the observed amount, about 75 to 80 %, is somewhat less is not surprising since a small proportion of MgO might well be retained in the amorphous silica phase. What seems most important is that the measurements point much more strongly towards the second equation than towards the first. The criticism of Ball and Taylor (1953, p. 474) that in previous work silica was introduced 'merely to balance the chemical equations' was a valid criticism, but the present results seem now to provide at least a partial justification.

Consideration of the inhomogeneous mechanism proposed by Ball and Taylor (1953)

They considered that the dehydroxylation and recrystallization of serpentine in air may proceed in four stages as follows:

Dehydroxylation: Protons migrate to reaction zones where water molecules are liberated. Mg and Si ions counter-migrate keeping the Mg:Si ratio more or less unchanged at 3:2, while the oxygen framework remains largely unchanged. This means that after the loss of water from regions that become pores, the remaining oxygens accommodate all the Mg and Si ions. The anhydride product is a partly disordered material giving an essentially 'amorphous' X-ray powder diagram.

Cation reorganization. A partial separation into Mg-rich and Si-rich regions begins, which requires Mg and Si ions now to move in opposite directions.

Forsterite crystallization. An ordering of cations and a change in oxygen ion packing in the Mg-rich regions leads to formation of forsterite.

Enstatite formation. The Si-rich regions change to enstatite but this stage occurs less readily than the others for reasons that are not at all clear.

The present experiments confirm the first stage, namely dehydroxylation and formation of an 'X-ray amorphous' phase. The degree of disorder in this phase must not be over-exaggerated since topotaxial relations between serpentine and forsterite require persistence of some degree of order. It has been shown that as recrystallization proceeds, forsterite (but no enstatite) appears in fine-grained form, increasing in amount with time and temperature until about 75 to 80 % of the product is forsterite, which requires that practically all the Mg of the serpentine composition goes to form forsterite. This does not support the second and third stages described by Ball and Taylor, in which Mg-rich

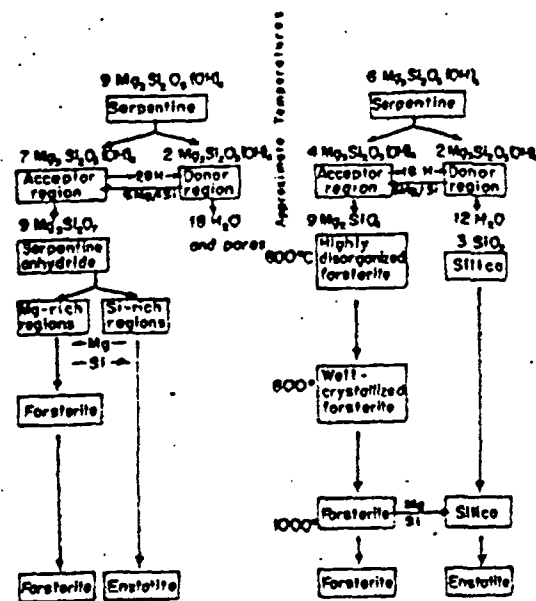


Fig. 2. Comparison of reaction schemes proposed by Ball and Taylor and by the present writers.

and Si-rich regions are developed giving rise respectively to forsterite and enstatite.

An alternative form of the 'donor-acceptor' mechanism

It has been shown previously (Brindley, 1961, 1963) that the topotactic relationship between serpentine and forsterite leads to the conclusion that eight unit cells of serpentine become nine unit cells of

forsterite, and in these corresponding volumes, namely 8V and 9V, there are the following numbers of ions: 8V contains 48 Mg, 32 Si, 144 O, 64 H; 9V contains 72 Mg, 36 Si, 144 O. Thus the overall cation 'exchange' is: $24 \text{ Mg} + 4 \text{ Si} \rightleftharpoons 64 \text{ H}$, or $6 \text{ Mg} + 1 \text{ Si} \rightleftharpoons 16 \text{ H}$.

On this view, the 'donor' regions where water molecules are formed donate (6 Mg + 1 Si) to the 'acceptor' regions in exchange for 16 protons. A highly disordered situation arises in which the 'donor' regions are probably largely siliceous and the 'acceptor' regions have a composition approximating to that of forsterite. With heat-treatment the 'acceptor' regions become organized in small domains of forsterite, which accommodate practically all the Mg ions of the original serpentine. The domains show little tendency to enlarge their size with the heat-treatments employed.

The difficulty of forming enstatite is seen as arising from the nature of the reaction involved, namely a reaction between a more-or-less stable forsterite and excess silica.

The two mechanisms proposed are set out schematically in fig. 2, which shows the quantitative relations involved and the approximate temperatures at which reactions occur. The mechanism proposed by the present writers takes into account the high proportion of the MgO content that enters into forsterite and offers a simple explanation for the delayed appearance of enstatite.

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