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Hydration and melting reactions in the system $MgO–SiO_2–H_2O$ at pressures up to 100 kbar

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Abstract

The proposed model for the system $MgO–SiO_2–H_2O$ ties subsolidus and melting reactions into an internally-consistent *P–T* net. None of the hydrous magnesium silicates considered is stable at the temperature of the solidus for forsterite + enstatite + H_2O; however, brucite is stable at solidus temperatures and at pressures greater than 50 kbar. In the presence of H_2O enstatite melts incongruently to forsterite plus a silica-saturated liquid at pressures up to 90 kbar. At 90 kbar the hydration reaction $Fo + H_2O \rightarrow En + Br$ intersects the solidus, and at higher pressures forsterite and H_2O do not coexist. The melting of forsterite + enstatite in the presence of a small amount of H_2O is vapor-present at pressures up to 90 kbar and generates a vapor-saturated, silica-saturated liquid. At higher pressures melting of the same bulk composition generates a silica-saturated, vapor-undersaturated liquid.

Introduction

Forsterite and enstatite are major constituents of the earth's upper mantle, and they are present in significant amounts in basic and ultrabasic igneous rocks. Because of this, the phase equilibria in the system $MgO-SiO_2$ have received much attention since Bowen and Andersen (1914) first discovered that enstatite melts incongruently at one atmosphere to forsterite plus a silica-saturated liquid. Among recent studies of the effects of water on the melting relations of forsterite and enstatite at high pressures are those of Kushiro *et al.* (1968), Hodges (1973), Nakamura and Kushiro (1974), and Eggler (1975).

The phase relations in the system $MgO-SiO_2-H_2O$ are a fundamental part of the model mantle system $CaO–MgO–Al_2O_3–SiO_2–H_2O–CO_2$, and must be understood in order to progress toward a full understanding of melting and crystallization processes in the upper mantle. Few experimental data are available at pressures greater than 30 kbar. In this paper a model is presented for the subsolidus and melting relations in $MgO–SiO_2–H_2O$ to 100 kbar, based on the available experimental evidence, thermodynamic data, and Schreinemaker's rules.

The system $MgO–SiO_2$

The 1 atmosphere melting relations involve the minerals periclase, forsterite, enstatite, and quartz. For convenience, all polymorphs of SiO_2 will be referred to as quartz and all polymorphs of $MgSiO_3$ as enstatite. At 1 atmosphere there are eutectics between enstatite and quartz at 1543°C, and between periclase and forsterite at 1860°C. There is a liquid miscibility gap between two SiO_2-rich liquids at temperatures above 1695°C, which we assume is closed by the addition of H_2O under pressure. At 1890°C forsterite melts congruently, and at 1557°C enstatite melts incongruently to forsterite plus a silica-saturated liquid. The melting temperature of forsterite has been determined at pressures up to 50 kbar by Davis and England (1964). Boyd *et al.* (1964) found that at pressures greater than 5 kbar enstatite melts congruently, so that a eutectic between forsterite and enstatite is present at high pressures. The position and temperature of the eutectic has been determined by Taylor (1973) and by Chen and Presnall (1975).

The system $MgO–H_2O$

Phase equilibria in this system have been modeled in detail by Ellis and Wyllie (1979), as shown by the array of curves around the invariant point (Fo,En,Q) in Figure 1. On the basis of experimental data at pressures up to 33 kbar, and water fugacities pre-

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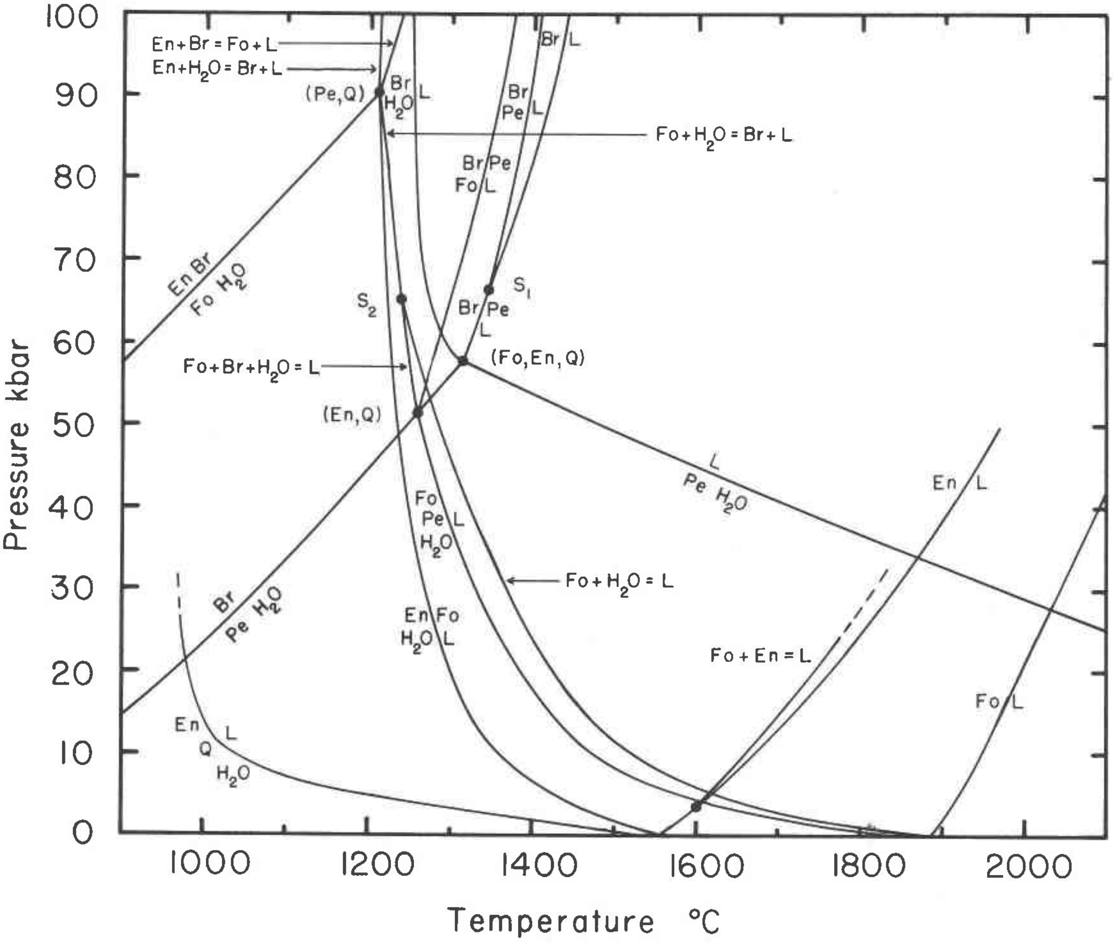

Fig. 1. P–T net for selected melting relations in the system $MgO-SiO_2-H_2O$. For sources and assumptions see text. Abbreviations: Pe = MgO, Q = polymorphs of SiO_2, En = polymorphs of $MgSiO_3$, Fo = Mg_2SiO_4, A = $Mg_7Si_8O_{22}(OH)_2$, T = $Mg_3Si_4O_{10}(OH)_2$, S = $Mg_3Si_2O_5(OH)_2$, Br = $Mg(OH)_2$, H_2O = H_2O vapor.

dicted by the MRK equation of state (Holloway, 1976, 1977), they predicted that there is no temperature maximum on the reaction

$$\text{Brucite} \rightarrow \text{Periclase} + H_2O$$

as reported by Yamoaka *et al.* (1970). The calculated position of the reaction $Br \rightarrow Pe + H_2O$ is shown in Figure 1. Brucite was predicted to melt at an invariant point where the reaction

$$\text{Brucite} \rightarrow \text{Periclase} + H_2O$$

meets the reaction

$$\text{Periclase} + H_2O \rightarrow \text{Liquid}$$

This invariant point was arbitrarily located near 58 kbar and 1310°C in order to be at a temperature higher than that of the reaction

$$\text{Forsterite} + H_2O \rightarrow \text{Liquid}$$

in the system $MgO-SiO_2-H_2O$. The reasons for this decision became clear with consideration of the ternary phase relations as illustrated in Figures 1 and 3.

The system SiO_2-H_2O

This system was investigated by Kennedy *et al.* (1962) at pressures up to 9.5 kbar. Invariant points were determined at 1160°C—1.5 kbar and 1470°C—400 bars, involving the phase assemblages quartz-tridymite-L-V and tridymite-cristobalite-L-V respectively. A critical end point was located on the univariant reaction

$$\text{Quartz} + H_2O \rightarrow \text{Liquid}$$

at 1080°C and 9700 bars. The existence of the critical end point is not accepted by Stewart (1967) or Warner (1973) in their interpretations of experiments at 10 kbar. Nakamura and Kushiro (1974), however, show that H_2O-SiO_2 is indeed supercritical at 15 kbar.

Subsolidus relations in the system $MgO-SiO_2-H_2O$

The known compounds in this system are: quartz, SiO_2; enstatite, $MgSiO_3$; forsterite, Mg_2SiO_4; periclase, MgO; brucite, $Mg(OH)_2$; talc, $Mg_3Si_4O_{10}(OH)_2$; serpentine, $Mg_3Si_2O_5(OH)_4$; sepiolite, $Mg_4Si_6O_{15}(OH)_2 \cdot 6H_2O$; anthophyllite, $Mg_7Si_8O_{22}(OH)_2$; hydroxyl-clinohumite, $Mg(OH)_2 \cdot 4Mg_2SiO_4$; hydroxyl-chondrodite, $Mg(OH)_2 \cdot 2Mg_2SiO_4$; phase A, $3Mg(OH)_2 \cdot 2Mg_2SiO_4$; 10A phase, $Mg_3Si_4O_{10}(OH)_2 \cdot 2H_2O$; and H_2O. The stability fields of many of these hydrous minerals are not well established.

In order to be able to construct an internally-consistent subsolidus *P–T* net, a smaller number of phases had to be considered. The phases picked were quartz, enstatite, forsterite, talc, serpentine, anthophyllite, brucite, and water. Experimental data on reactions among these phases have been given by Bricker *et al.* (1973), Chernosky (1976), Evans *et al.* (1976), Greenwood (1963, 1971), Hemley *et al.* (1977a,b), Johannes (1968), Kitahara *et al.* (1966), Moody (1976), Scarfe and Wyllie (1967), Skippen (1971), Bowen and Tuttle (1949), and Yoder (1967).

The experimental studies were used to indicate the relative positions of reactions in order to derive the subsolidus *P–T* net. The topology proposed by Greenwood (1971) and by Hemley *et al.* (1977b) for the reactions limiting the stability of anthophyllite at low pressure has been accepted here. The low-pressure topology proposed by Evans *et al.* (1976) and Chernosky (personal communication, 1978) has been accepted for the reactions limiting the stability of serpentine.

The topology derived from the subsolidus reactions is shown schematically in Figure 2. The primary features of interest are that at very high pressures serpentine is predicted to be stable at higher temperatures than anthophyllite, and that there are two reactions which extend to higher temperatures:

$$\text{Brucite} + \text{Enstatite} \rightarrow \text{Forsterite} + H_2O \qquad (1)$$

and

$$\text{Brucite} + \text{Quartz} \rightarrow \text{Enstatite} + H_2O \qquad (2)$$

Reactions (1) and (2) must reach the solidus, because none of the other phases considered is stable at the temperatures of these reactions.

The position shown for reaction (1) in Figure 1 was calculated from the data of Robie and Waldbaum (1968) and the water fugacities predicted by the MRK equation of state (Holloway, 1976, 1977). The calculated curve passes through the points 70 kbar and 1020±40°C, 80 kbar and 1115±40°C, and 90 kbar and 1210±40°C. Reaction (2) is not shown in Figure 1, because it is estimated to occur at temperatures below 900°C in the pressure range considered.

Delany and Helgeson (1978) have presented partial *P–T* diagrams for the system $MgO-SiO_2-H_2O$ at pressures up to 100 kbar. The topology of the invariant points they illustrate corresponds to points shown in the complete *P–T* net given in Figure 2. However, the calculated *P–T* paths of important reactions differ. Delany and Helgeson base their calculations of *P–T* paths on the estimates of thermodynamic properties of minerals by Helgeson *et al.* (1978), and estimates of the fugacities of H_2O generated from equations given by Helgeson and Kirkham (1974). They are not able to reproduce the experimentally-determined path of the reaction Brucite→ Periclase + H_2O at pressures below 0.5 kbar or between 2.0 and 33 kbar. The calculations of Ellis and Wyllie (1979), using the H_2O fugacities predicted by the MRK equation of state, reproduce the experimentally-determined *P–T* path of the reaction within the experimental error at all pressures yet studied. For this reason we believe that the reaction positions predicted using the MRK equation of state and tabulated values are more reliable than the positions predicted by Delany and Helgeson. According to the calculations of Delany and Helgeson, the reaction Brucite + Enstatite→ Forsterite + H_2O would never intersect the solidus in this system. However, we believe that the position shown in Figure 1 for the reaction Brucite + Enstatite→Forsterite + Vapor is a better estimate and that the reaction intersects the solidus at the invariant point (Pe,Q) at 90 kbar.

Melting relations in the system $MgO-SiO_2-H_2O$

Figure 1 shows the melting reactions involved with the extension to high temperatures of reaction (1) and the dehydration of brucite. The solidus reactions involve the melting of periclase, brucite, forsterite, enstatite, H_2O, and combinations of these phases. Melting reactions involving polymorphs of SiO_2 are excluded. Isobaric liquidus diagrams for selected pressures are shown in Figure 3.

The melting reaction of enstatite in the presence of H_2O was studied by Kushiro *et al.* (1968) at pressures between 5 and 30 kbar. They showed that H_2O greatly reduces the temperature at which enstatite melts, that the rate at which melting temperature decreases with increasing pressure is less at high pres-

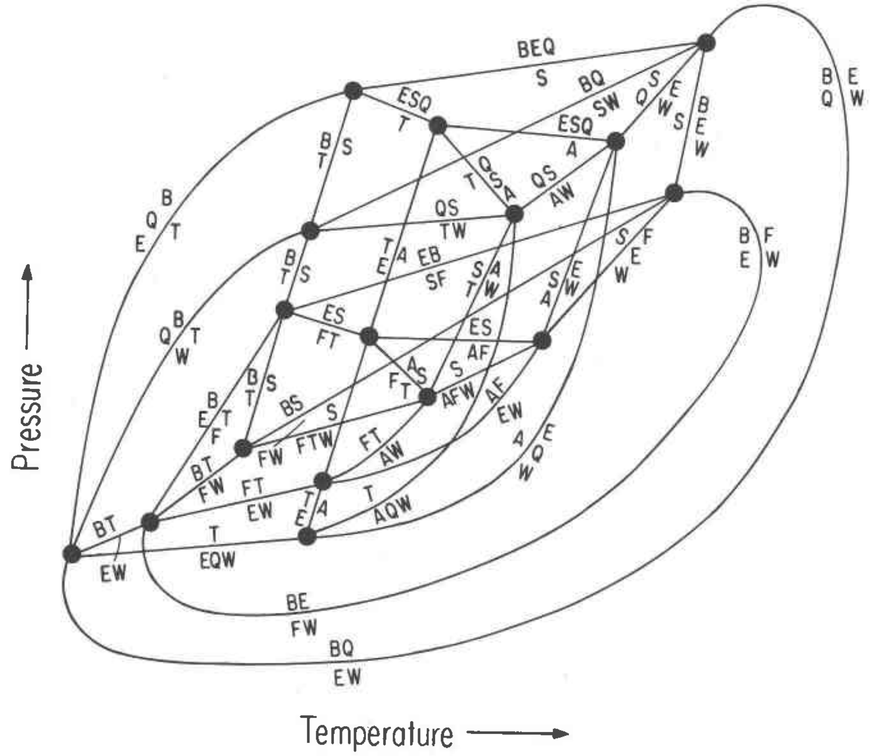

Fig. 2. Schematic *P–T* net showing the topology of subsolidus reactions in the system $MgO-SiO_2-H_2O$. To facilitate labeling all reactions in the limited space available, enstatite has been abbreviated as E, forsterite as F, brucite as B, and H_2O as W.

sures, and that in the presence of excess H_2O enstatite continues to melt incongruently at pressures up to 30 kbar (Fig. 1). The H_2O content of the first melt formed at 10 kbar was estimated as 11 weight percent. Eggler (1975) confirmed the melting relations observed by Kushiro *et al.* at 20 kbar and estimated that the first liquid formed contained 21.5±1.5 weight percent H_2O. Nakamura and Kushiro (1974) studied the composition of the vapor phase coexisting with forsterite and enstatite at 15 kbar. They found that the vapor phase contained very little MgO, and that the maximum SiO_2 solubility, 22 weight percent, occurred at the solidus at 1315°C. The vapor coexisting with enstatite alone contained as much as 40 weight percent SiO_2 and very little MgO.

The anhydrous melting curve for forsterite shown in Figure 1 was studied at pressures up to 50 kbar by Davis and England (1964). The water-saturated melting reaction illustrated in Figure 1 was located at pressures up to 30 kbar by Kushiro and Yoder (1968). Hodges (1973) confirmed that forsterite melts in the presence of excess H_2O at 1425°C at 20 kbar and determined that the melt formed may contain 20.2±1.0 weight percent H_2O (66 mole percent).

The melting of forsterite in the presence of H_2O is not a simple univariant reaction. The data of Nakamura and Kushiro (1974), showing a significant SiO_2 content in vapor which coexists with forsterite, require the melting reaction to be divariant. The position shown for the melting reaction is actually a maximum temperature on the ternary liquidus, as discussed and illustrated by Boettcher and Wyllie (1969) for a hypothetical system $MO-SiO_2-H_2O$.

In order to complete our proposed *P–T* net for subsolidus and melting relations, several assumptions were made about melting relations. We assume that critical phenomena do not become important in any of the melting reactions of the Mg-silicates. This is consistent with all published phase diagrams, which indicate that very little MgO is contained in the vapor. We also assume that the melting curves with H_2O maintain a slight negative slope throughout the pressure interval considered. We have assumed that the melting curves do not pass through temperature minima in the pressure interval considered. So far no such temperature minimum has been recorded experimentally. The conclusions reached on the basis of Figure 1 would not be changed even if shallow temperature minima do exist at high pressures.

Figure 1 shows the reactions for the system MgO–

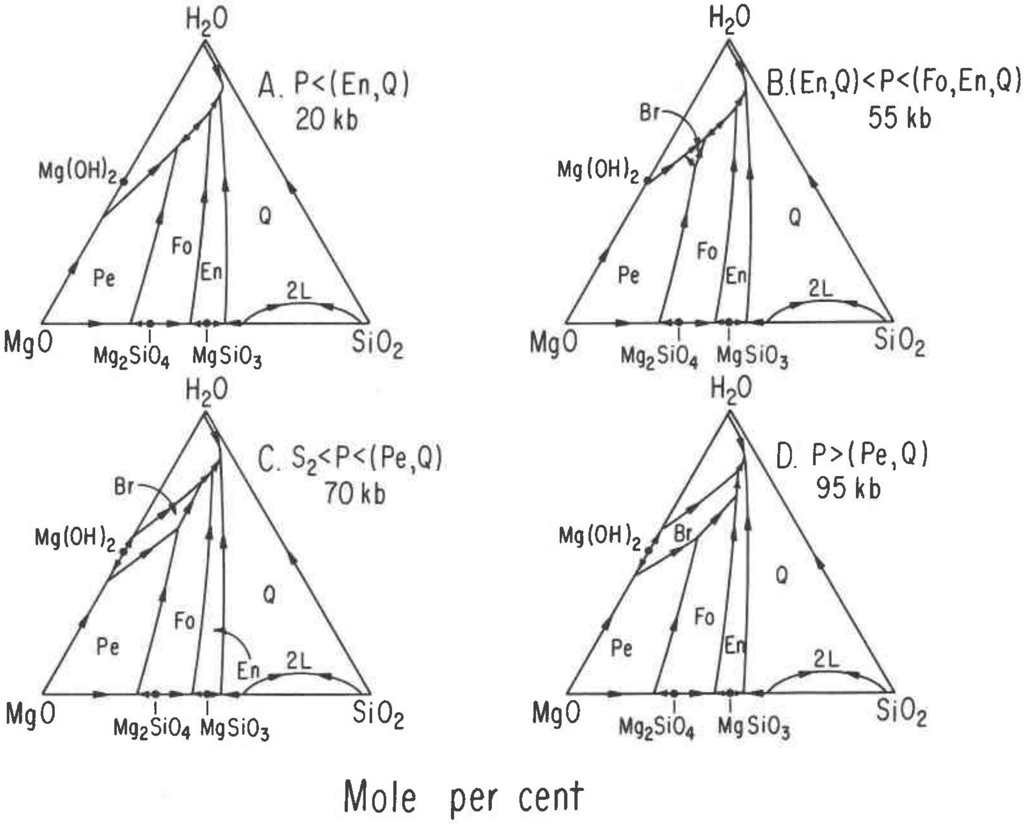

Fig. 3. Isobaric liquidus diagrams at various pressures for the system $MgO-SiO_2-H_2O$, partly schematic. Derived from sources described in the text, and the phase relations shown in Fig. 1. Details of temperature relations on the vapor surface are not shown.

H_2O emanating from the invariant point (Fo,En,Q), according to Ellis and Wyllie (1979). This provides a framework for the proposed ternary *P–T* net, which is based on the calculated position of subsolidus reaction (1), and the melting reactions for forsterite and enstatite with excess H_2O extrapolated from experimental measurements at pressures to 30 kbar. By analogy with the dry system at 1 bar, we assume that the melting reaction

$$\text{Forsterite} + \text{Periclase} + H_2O \rightarrow \text{Liquid} \quad (3)$$

remains at somewhat lower temperature than the reaction

$$\text{Forsterite} + H_2O \rightarrow \text{Liquid}$$

An invariant point (En,Q) is generated near 1265°C and 52 kbar, where melting reaction (3) meets the binary reaction for the hydration of periclase; these two reactions are replaced by three other reactions at pressures above (En,Q). The reaction connecting (En,Q) and (Fo,En,Q) is degenerate, representing the dehydration of brucite on the H_2O-saturated ternary liquidus surface (see Fig. 3B).

A second invariant point, (Pe,Q), is generated near 1210°C and 90 kbar where the melting reaction

$$\text{Enstatite} + H_2O \rightarrow \text{Forsterite} + \text{Liquid}$$

meets the subsolidus reaction (1). At higher pressures, forsterite may no longer coexist with vapor, as shown in Figure 3D. Figure 1 shows the three additional reactions emanating from the point (Pe,Q), as required by Schreinemaker's rules. One of these,

$$\text{Forsterite} + H_2O \rightarrow \text{Brucite} + \text{Liquid}$$

is obviously an extension of the low-pressure reaction

$$\text{Forsterite} + H_2O \rightarrow \text{Liquid}$$

with the change occurring at a singular point (S_2 in Fig. 1) where the curve for the hydrous melting of forsterite merges with the reaction (3) for the hydrous melting of the assemblage forsterite + brucite. The singular point is located between invariant points (En,Q) and (Pe,Q), 50–90 kbar, as shown in Figure 1.

The series of isobaric liquidus diagrams given in Figure 3 illustrate the relationships among the melting reactions plotted in Figure 1. The H_2O contents of the H_2O-saturated liquidus field boundaries are based on the solubility data cited above from enstatite and forsterite up to 30 kbar. Expressed in mole percent, solubilities do not increase greatly at pressures above 20 kbar. The solubility of H_2O in liquids formed by the melting of periclase plus forsterite is inferred to increase more than the solubility in other liquids, because of the more negative slope of the reaction

$$\text{Periclase} + H_2O \rightarrow \text{Liquid}$$

At pressures greater than 50–60 kbar, the H_2O solubility increases only slightly, as indicated by the slight negative slopes of the solidus curves.

The transition from liquidus field boundary to vaporus field boundary near the side SiO_2-H_2O, *via* a critical point, is based on the results of Nakamura and Kushiro (1974) at 15 kbar. It is not possible to illustrate the details in mole percent diagrams. The arrangement of liquidus and vaporus field boundaries, and the tie-lines crossing the miscibility gap between liquid and vapor fields, was illustrated in detail in a series of schematic diagrams in weight percent for a hypothetical system $MO-SiO_2-H_2O$ by Boettcher and Wyllie (1969). In that example, the critical point migrated across the diagram from SiO_2-H_2O towards the side $MO-H_2O$ with increasing pressure. From the solubility data presented by Nakamura and Kushiro (1964), we conclude that for $MgO-SiO_2-H_2O$ the critical point probably remains close to the SiO_2-H_2O side to very high pressures.

At pressures below that of the invariant point (En,Q) in Figure 1, Figure 3A shows that two eutectics exist: between periclase, forsterite, and H_2O, and between enstatite, quartz, and H_2O. Enstatite with H_2O melts incongruently to forsterite plus a silica-saturated liquid. In all three reactions, the liquids are H_2O-saturated.

At the pressure of the invariant point (En,Q), the brucite stability curve just reaches the solidus (Fig. 1). At higher pressures, between the invariant points (En,Q) and (Fo,En,Q), brucite occurs on the liquidus surface between the fields for periclase, forsterite, and vapor, as shown in Figure 3B. With increasing pressure, the size of the brucite liquidus field increases.

At the pressure of the invariant point (Fo,En,Q), the brucite field just reaches the $MgO-H_2O$ side-line, on the H_2O-side of brucite. With increasing pressure, the width of the brucite liquidus field on the join $MgO-H_2O$ increases and, at the singular point S_1, brucite just begins to melt congruently. At higher pressures, the binary brucite field is as shown in Figures 3C and 3D.

We do not know the relative pressures of the singular points S_1 and S_2 in Figure 1, but we have assumed that S_2 occurs at lower pressure than S_1. The singular point S_2 indicates a significant stage in the enlargement of the brucite liquidus surface.

As the pressure reaches S_2, the field of brucite just reaches the line connecting forsterite and its coexisting H_2O-vapor. At higher pressures, as shown in Figures 1 and 3C, forsterite melts incongruently with H_2O to produce brucite plus liquid. Expansion of the brucite field toward higher SiO_2/MgO ratios eliminated the eutectic between forsterite, brucite, and H_2O.

At the invariant point (Pe,Q) in Figure 1, the expanding liquidus field for brucite just reaches that for enstatite, separating the liquidus field for forsterite from coexistence with vapor. The arrangement of liquidus fields at pressures greater than the point (Pe,Q) is shown in Figure 3D. Enstatite melts incongruently in the presence of H_2O, producing a SiO_2-normative liquid by the reaction

$$\text{Enstatite} + H_2O \rightarrow \text{Brucite} + \text{Liquid}$$

The only eutectic in the system at very high pressures is located between enstatite, quartz, and H_2O, producing a SiO_2-normative, H_2O-saturated liquid. This is not depicted in Figure 1 at pressures over 25 kbar.

Discussion

The model proposed for the system $MgO-SiO_2-H_2O$ ties the subsolidus and melting relations together into one internally-consistent $P-T$ net. This net allows prediction of melting relations at pressures up to 100 kbar. The model predicts that enstatite will continue to melt incongruently in the presence of H_2O up to 90 kbar. Brucite becomes stable on the liquidus surface near 50 kbar, and its primary field of crystallization expands with increasing pressure, so that at pressures greater than 90 kbar forsterite is no longer stable in the presence of H_2O.

The incompatibility of forsterite and H_2O at high pressures is analogous to the incompatibility of forsterite and CO_2 at high pressures observed by Newton and Sharp (1975) and modeled in the system $MgO-SiO_2-CO_2$ by Wyllie and Huang (1976). In contrast to the system $MgO-SiO_2-CO_2$, the hydration of forsterite takes place at a much higher pressure than its carbonation. Also in contrast, there is no rapid increase in the solubility of H_2O in the coexisting silicate liquids when the reaction for the hydration of forsterite intersects the solidus. The greatest change in the solubility of H_2O occurs in the pressure interval below 10 kbar.

The proposed *P–T* net shows that none of the hydrous magnesium silicates considered are stable at the temperature of the solidus. The work of Yamamoto and Akimoto (1977) indicates that the most stable mineral may be hydroxyl-clinohumite. Figure 4 shows that the maximum temperature at which Yamamoto and Akimoto found hydroxyl-clinohumite to be stable is still below that of the solidus for forsterite plus enstatite in the proposed model.

The melting of the assemblage forsterite plus enstatite at pressures below 5 kbar produces a quartz-normative liquid under both dry and hydrous conditions. At higher pressures, wet melting of forsterite plus enstatite continues to produce a quartz-normative liquid, but dry melting now produces a forsterite-normative liquid, due to the congruent melting of enstatite reported by Boyd *et al.* (1964). At pressures greater than 90 kbar, three possibilities exist for the melting relations: (1) dry melting produces a forsterite-normative liquid, (2) melting of brucite plus enstatite in the presence of excess H_2O produces a quartz-normative vapor-saturated liquid, and (3) the vapor-absent melting of forsterite plus enstatite plus brucite produces a quartz-normative vapor-undersaturated liquid. Thus, at pressures lower than that of the invariant point (Pe,Q) shown in Figure 1, the first liquid formed by the melting of forsterite plus enstatite is always vapor-saturated, but at pressures above (Pe,Q) this is no longer true.

The addition of small proportions of H_2O to the assemblage forsterite plus enstatite may cause large degrees of partial melting only at temperatures near the dry solidus. For example, at 20 kbar the first liquid formed by the melting of forsterite plus enstatite contains 21.5 weight percent H_2O. The melting of forsterite plus enstatite plus 0.1 weight percent H_2O will therefore produce about 0.5 weight percent of melt. If one assumes a simple linear relation between the H_2O content of liquid between the wet and dry solidi, an increase in temperature of 100°C will result in the amount of melt only increasing to 0.65 weight percent. An increase in temperature of 200°C will increase the amount of melt only to 0.83 weight percent. At higher pressures the rate of increase of partial melting with increasing temperature must be considerably slower, due to the greater separation of the wet and dry solidi.

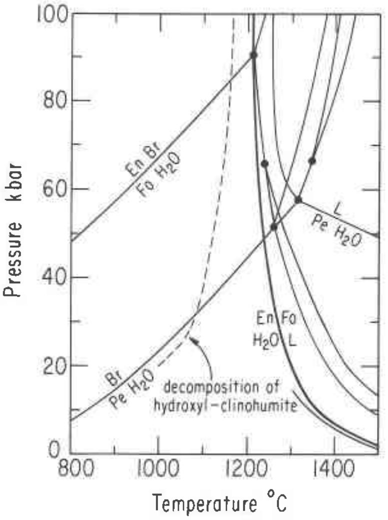

Fig. 4. The maximum thermal stability of hydroxyl-clinohumite (dashed line) determined by Yamamoto and Akimoto (1977) compared to the predicted solidus for the assemblage Fo + En + H_2O (heavy line) in the system MgO–SiO_2–H_2O (compare Fig. 1).

Nakamura and Kushiro (1974) suggested that the silica-rich vapor which coexists with forsterite is capable of transporting silica upwards through mantle peridotite, producing a differentiated mantle. Our model indicates that the range of depths over which this process of mantle metasomatism could operate is limited, due to the instability of H_2O vapor in the presence of forsterite plus enstatite at high pressures (Fig. 1). In the mantle, H_2O would react to produce hydrous minerals, such as amphibole and phlogopite, at pressures lower than 90 kbar. However, amphibole and phlogopite can contain only a limited amount of H_2O. If a greater amount of H_2O were present, the brucite-producing reaction at 90 kbar would provide an absolute upper pressure limit for the existence of free H_2O in the mantle.

The crystallization of melts containing small amounts of H_2O at pressures above and below that of the invariant point (Pe,Q) would give products with distinctly different textures. At lower pressures, the small amount of liquid remaining near the solidus follows the boundary between the forsterite and enstatite fields until the solidus is reached. There the silicates remaining in the melt will crystallize on the earlier forsterite and enstatite crystals, and the H_2O will form a separate vapor phase. At pressures above (Pe,Q) the forsterite and enstatite would again precipitate on the earlier crystals, but the H_2O would react with the forsterite crystals to form brucite, and the final liquid would precipitate brucite, forming a matrix for the earlier crystals. The texture would perhaps resemble that of kaersutite in some mantle-derived rocks (Best, 1975).

Acknowledgments

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