Phase relations and their petrological implications in the system MgO-SiO$_2$-H$_2$O-CO$_2$ at pressures up to 100 kbar

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Abstract

A comprehensive model has been developed for phase relations in the system MgO-SiO$_2$-H$_2$O-CO$_2$ on the basis of Schreinemakers' rules and subsolidus thermodynamic data. The assemblage forsterite plus enstatite can melt in the presence of vapor of any H$_2$O/CO$_2$ ratio at low pressures, in the presence of vapor whose H$_2$O/CO$_2$ ratio is buffered by magnesite at intermediate pressures, and at a vapor-absent eutectic at high pressures. Forsterite and H$_2$O-CO$_2$ vapor cannot coexist at pressures greater than 90 kbar. A thermal maximum is postulated to exist on the reaction Fo + En + V → L at pressures greater than 35 kbar. Thermal maxima on vapor-present melting reactions may be responsible for the eruption of kimberlitic magma from the upper mantle.

Introduction

H$_2$O and CO$_2$ are the most abundant volatile compounds in the earth's crust. It is now apparent that they also play important roles in upper mantle processes, although their abundance in the mantle is apparently low. Subsolidus reactions involving small amounts of carbonates and hydrates plus the silicate minerals of the earth's upper mantle can buffer the composition of the vapor phase, as reviewed by Wyllie (1978) and Eggler (1978). The thermodynamic basis for such buffering has been reviewed for reactions occurring at lower pressures by Greenwood (1962, 1967), Kerrick (1974), and Kerrick and Slaughter (1976).

Eggler (1975) reported on experimental studies in the system MgO-SiO$_2$-H$_2$O-CO$_2$ at 20 kbar. Mysen and Boettcher (1975a,b) have discussed experimental results on the effects of H$_2$O, CO$_2$, and H$_2$O-CO$_2$ mixtures on the melting of peridotite at 20 kbar. The effects of H$_2$O, CO$_2$, and H$_2$O-CO$_2$ mixtures on the phase relationships of peridotites have been investigated in several laboratories, with emphasis on melting relationships at pressures up to 35 kbar (Breay and Green, 1975, 1976; Eggler, 1974, 1976a, 1978; Mysen and Boettcher, 1975a,b; Wyllie and Huang, 1975, 1976). Differences in experimental results and interpretations have been extensively discussed (Eggler, 1976b; Green, 1976; Mysen and Boettcher, 1975a,b; Nehru and Wyllie, 1975; Wyllie, 1978; Wyllie and Huang, 1975, 1976).

Phase relations in the system MgO-SiO$_2$-H$_2$O-CO$_2$ are a fundamental part of the model mantle system CaO-MgO-Al$_2$O$_3$-SiO$_2$-H$_2$O-CO$_2$ and understanding them is an essential step in progress toward full understanding of melting and crystallization processes in the upper mantle. Phase relations in the simple systems MgO-SiO$_2$-CO$_2$, MgO-H$_2$O-CO$_2$, and MgO-SiO$_2$-H$_2$O have been modeled, respectively, by Wyllie and Huang (1976), Ellis and Wyllie (1979a), and Ellis and Wyllie (1979b). We have used those models plus calculations of subsolidus and melting relations whenever possible to derive a model for the system MgO-SiO$_2$-H$_2$O-CO$_2$. Compositions in the system MgO-SiO$_2$-H$_2$O-CO$_2$ are clearly different from those of the earth's upper mantle. However, the system contains olivine, pyroxene, hydrate, carbonate, vapor, and liquid. It therefore indicates the general features of phase relationships possible between those types of compounds in the upper mantle.

In this paper phases in the system MgO-SiO$_2$-H$_2$O-CO$_2$ will be referred to by using the names of corresponding minerals. The following abbreviations for mineral names have been used to write reactions...
and to label all figures: periclase (MgO) = Pe, magnesite (MgCO₃) = MC, brucite [Mg(OH)₂] = Br, polymorphs of silica (SiO₂) = Q, enstatite (MgSiO₃) = En, forsterite (Mg₂SiO₄) = Fo, liquid = L, pure H₂O vapor = H₂O, pure CO₂ vapor = CO₂, and mixed H₂O–CO₂ vapor = V.

The bounding ternary systems

The framework for this study is given by the invariant curves for ternary and quaternary reactions in Figure 1. Invariant points are identified by parentheses enclosing the crystalline phases that are not present: three phases for ternary points and two phases for quaternary points. Ternary and quaternary reactions involve four and five phases, respectively. Only reactions with free vapor are plotted; some vapor-absent reactions are indicated by short lines from invariant points.

\[ SiO₂–H₂O–CO₂ \]

The system SiO₂–H₂O was investigated by Kennedy et al. (1962) at pressures up to 9.5 kbar. A criti-

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Fig. 1. Schematic P-T net showing subsolidus and melting reactions in the system MgO–SiO₂–H₂O–CO₂. Only vapor-present reactions are shown. Some vapor-absent reactions are indicated by short lines extending from invariant points. The positions of thermal maxima are shown by dashed lines. See Introduction for explanation of abbreviations.
cal end-point on the univariant reaction $Q + H_2O \rightarrow L$ was placed at $1080^\circ C$ and 9.7 kbar. Neither Stewart (1967) nor Warner (1973) accepted the existence of this critical end-point in their interpretations of experiments at 10 kbar, but Nakamura and Kushiro (1974) showed that $SiO_2-H_2O$ is supercritical at 15 kbar.

Phase equilibrium studies and beta-track solubility measurements by Mysen and Seitz (1975) and Mysen et al. (1976) indicate that the solubility of CO$_2$ in silicate liquids remains low up to high pressures and that the solubility of CO$_2$ in silicate liquids decreases as the silica content of the liquid increases. These data indicate that the solubility of CO$_2$ in molten SiO$_2$ is much lower than that of H$_2O$, and we assume that the solubility of CO$_2$ in the supercritical fluid in SiO$_2$-H$_2$O above 9.7 kbar is negligible. Schematic phase relationships in the system SiO$_2$-H$_2$O-CO$_2$ have been illustrated for various pressures by Wyllie and Haas (1965), Boettcher and Wyllie (1969), and Eggler (1975). Similar diagrams are used in the following pages, but there are no univariant reactions for this system plotted in Figure 1.

**MgO-H$_2$O-CO$_2$**

This system was modeled in detail by Ellis and Wyllie (1979a) at pressures up to 100 kbar. Irving and Wyllie (1975) and Huang and Wyllie (1976) determined that the magnesite dissociation reaction $MC \rightarrow Pe + CO_2$ is terminated by melting at an invariant point (Br,En,fo,Q) in Figure 1 at 23 kbar and $1550^\circ C$. Ellis and Wyllie (1979a) postulated that brucite melts similarly at an invariant point (En,fo,Q,MC), estimated to be near 57 kbar and $1310^\circ C$, and that the ternary reaction for dissociation of the assemblage magnesite plus brucite is terminated by melting at the invariant point (En,fo,Q), estimated to be near 46 kbar and $1210^\circ C$. At pressures above this invariant point, brucite, magnesite, and vapor, buffered to high H$_2$O/CO$_2$, melt together in a eutectic reaction. The composition of the eutectic liquid on the vapor-absent join Mg(OH)$_2$-MgCO$_3$ was estimated by Ellis and Wyllie (1979a) to be 73 mole percent Mg(OH)$_2$, plus 27 mole percent MgCO$_3$.

There are divariant surfaces for dissociation and melting reactions occurring in the presence of H$_2$O-CO$_2$ vapor that connect the lines meeting at the three invariant points discussed above. Ellis and Wyllie (1979a) derived thermodynamic parameters from ln fugacity vs. $1/T$ diagrams and calculated the locations of contours of constant vapor phase composition on these surfaces. Their Figure 5 showed contours on surfaces for the reactions $MC \rightarrow Pe + CO_2$ (with H$_2O$ present) and $MC + H_2O \rightarrow Br + CO_2$. Vapor in the presence of magnesite is buffered to high values of H$_2O/CO_2$ except for a narrow pressure interval just above the reaction $MC \rightarrow Pe + CO_2$.

**MgO-$SiO_2-H_2O$**

Ellis and Wyllie (1979b) presented a model for hydration and melting reactions in this system up to 100 kbar. Subsolidus and melting relations were tied together into an internally consistent $P-T$ net, reproduced in part in Figure 1. The solidus curves for forsterite plus vapor, forsterite plus periclase plus vapor, and forsterite plus enstatite plus vapor extend to lower temperatures with increasing pressure, and they are intersected by hydration curves bringing brucite to the liquidus at the invariant points (En,Q,fo,mc) and (Pe,Q,MC) at pressures near 50 and 90 kbar, respectively. The incongruent melting curve for enstatite, $En + H_2O \rightarrow Fo + L$, terminates at the 90 kbar invariant point. At pressures above 90 kbar, forsterite cannot coexist with H$_2O$ because it must react to produce brucite, and the assemblage enstatite plus vapor melts incongruently to produce brucite plus liquid.

**MgO-$SiO_2-CO_2$**

Wyllie and Huang (1976) combined experimental data available to 33 kbar in this system and estimated
the phase relationships to 70 kbar. Univalent reactions with vapor are reproduced in Figure 1, and the solidus reaction is extended to 100 kbar. With increasing pressure, there are three successive carbonation reactions which terminate on the solidus at the invariant points (Br,En,Q), (Pe,Br,Q), and (Pe,Br,Fo). The silicate mineral melting with magnesite and CO₂ along the solidus curve changes at each invariant point, from forsterite to enstatite to quartz, with increasing pressure.

The system MgO-SiO₂-H₂O-CO₂

General remarks

A network of binary, ternary, and quaternary univalent reactions is given in Figure 1 as a framework for the detailed discussions that follow. The details needed to supplement the P-T projection of Figure 1 are illustrated in a series of isobaric diagrams at successively higher pressures (Figs. 2, 4, 5, 6, and 8) and a series of P-T diagrams (Figs. 3, 7, 9, and 10), showing the changes that occur at invariant points. Particular attention is paid to the changes associated with assemblages including forsterite plus enstatite.

Isobaric equilibrium liquidus diagrams shown in Figure 4 are based on the ternary relationships reviewed above and quaternary relationships related to divariant surfaces similar to those illustrated in Figures 3B and 3C. The heavy lines in MgO-H₂O-CO₂ and MgO-SiO₂-CO₂ are the vapor-saturated liquidus field boundaries, which give the compositions of liquids coexisting with crystals and with H₂O-CO₂ or CO₂ vapor. The heavy lines in MgO-SiO₂-H₂O show the compositions of H₂O-saturated liquids merging continuously through a fluid phase into the H₂O-rich vapor phase coexisting with liquids on the other side of the miscibility gap. Field boundaries have been omitted from SiO₂-H₂O-CO₂ for clarity. The limiting phase boundary in this triangle is assumed to pass from the liquidus on SiO₂-CO₂ towards the corner.

Fig. 3. Vapor-phase contours (mole fraction of CO₂) on three significant divariant surfaces in the system MgO-SiO₂-H₂O-CO₂. These three divariant surfaces meet along the heavy line, which is the buffered melting reaction MC + En = Fo + V. A shows contours on the surface for the reaction MC + En = Fo + V. B shows contours on the surface for MC + En = V + L. C shows contours on the surface for the reaction Fo + En + V = L. Note the presence of a thermal maximum (shown by a dashed line) in the contours for Fo + En + V = L.
H₂O, with very little CO₂ being dissolved in the liquid and fluid phases of SiO₂–H₂O. There is a continuous vaporus boundary close to the join H₂O–CO₂, similar to that shown for MgO–H₂O–CO₂.

The quaternary vapor-saturated liquidus surface connects the heavy lines of the bounding ternary systems, merging through a small area for quaternary fluid near the H₂O end of SiO₂–H₂O, into the narrow vaporus surface situated close to H₂O–CO₂. The geometry of a similar surface in CaO–SiO₂–H₂O–CO₂ was illustrated by Boettcher and Wyllie (1969).

Isobaric invariant points for the system MgO–SiO₂

are marked on that join, and ternary field boundaries separating liquidus areas for the crystallization of periclase, forsterite, enstatite, and quartz extend from these points to the vapor-saturated field boundaries in MgO–SiO₂–H₂O and MgO–SiO₂–CO₂. These areas extend into the quaternary system as volumes separated by surfaces which terminate as liquidus field boundaries on the vapor-saturated liquidus surface.

The field boundaries on the vapor-saturated liquidus surface are illustrated in Figure 5, where the vapor-saturated surface is projected from the MgO corner of the tetrahedron onto the face SiO₂–H₂O–CO₂.
CO₂. The projections of these surfaces in Figure 5 show both the vapor-saturated liquidus field boundaries and the intervening primary phase fields. The immiscible fields (2L) shown in MgO-SiO₂-H₂O and MgO-SiO₂-CO₂ have not been represented on the quaternary surfaces in Figures 4 and 5.

The schematic T-X, diagrams given in Figure 6 represent a series of isobaric slices through Figure 1. These diagrams are used to illustrate the details of the links between subsolidus and liquidus phase relationships indicated in Figures 1 and 3. Univariant lines are connected through the system by divariant surfaces. For example, the pair of binary reactions Fo + H₂O → L and Fo + CO₂ → L represent two ends of one divariant P-T-X surface for the ternary melting reaction Fo + V → L, which can be contoured in P-T projection by lines of constant vapor-phase composition.

Each quaternary vapor-saturated liquidus field boundary from Figures 4 and 5 is illustrated schematically in Figure 6 in terms of temperature and the composition of the coexisting vapor-phase composition. The arrows for falling temperature in Figures 4 and 5 are translated into slopes in Figure 6.

In addition, Figure 6 shows lines for the congruent melting of forsterite and enstatite in the presence of vapor, which are isobarically univariant by restriction (Ricci, 1951, p. 25). In Figures 4 and 5, these reactions are represented by temperature maxima (not marked) where the surfaces Fo-H₂O-CO₂ and En-H₂O-CO₂ intersect the vapor-saturated liquidus surface. The assemblage enstatite plus vapor melts congruently for CO₂-rich vapors, but incongruently for H₂O-rich vapors (Eggler, 1975). The change occurs at the singular point (Fig. 6) where the reaction En + V → L merges with the four-phase reaction including forsterite and where the field boundary in Figure 5A crosses the composition join enstatite-H₂O-CO₂.

Construction of these figures required considerable extrapolation from known data and repeated checking back and forth between Figures 4 and 6 and Figure 1, in order to maintain internal consistency. Although many pressures, temperatures, and compositions need to be determined precisely, we believe that the geometrical constraints are sufficient to ensure that the sequence of phase relationships illustrated provides an accurate representation of the melting and crystallization processes for phase assemblages involving forsterite and enstatite with H₂O-CO₂ vapor, magnesite, and brucite.

Subsolidus reactions in the system MgO-SiO₂-H₂O-CO₂

The ternary subsolidus reactions involving H₂O or CO₂ are univariant, and pairs of analogous reactions are connected through the quaternary system by
Fig. 6. Schematic isobaric $T$-$X_{CO_2}$ diagrams showing the interrelation of subsolidus and melting reactions in the system MgO-SiO$_2$-H$_2$O-CO$_2$ at pressures of 20, 30, 40, 50, 60, 70, and 95 kbar.

divariant surfaces corresponding to these reactions occurring in the presence of H$_2$O-CO$_2$ mixtures. The points of lowest temperature on the surfaces define the univariant reaction for dissociation of a carbonate and hydrate together (in isobaric $T$-$X_{CO_2}$ diagrams, these points occur at the intersection of two reaction lines).

There is one quaternary univariant subsolidus re-
action in Figure 1, \( \text{Br} + \text{MC} + \text{En} \rightarrow \text{Fo} + \text{V} \). Given the data of Eggler et al. (1979) plus the molar volume data of Robie and Waldbaum (1968), one may derive the reaction

\[
\ln f_{\text{CO}_2} = -21337/RT + 0.1888(P - 1)/T + 41.05
\]

This relationship may be used in conjunction with the fugacities predicted by the MRK equation (Holloway, 1976, 1977) to predict the quaternary \( T-X_{\text{CO}_2} \) relations shown in Figure 2.

The \( T-X_{\text{CO}_2} \) relations shown in Figure 2 and in Figure 3 of Ellis and Wyllie (1979a) may be used to position contours of constant vapor-phase composition for the assemblages containing forsterite plus enstatite, together with magnesite or brucite. The surface plotted by isobaric contours in Figure 2 is illustrated in Figure 3A by contours for constant vapor-phase composition. Its position in Figure 1 can be located by the positions of the invariant points \((\text{Pe},\text{Br},\text{Q})\) near 43 kbar and \((\text{Pe},\text{Q},\text{MC})\) near 90 kbar. The surface is terminated by melting along the quaternary univariant solidus curve for the reaction, \( \text{MC} + \text{En} + \text{V} \rightarrow \text{Fo} + \text{L} \), that connects these invariant points.

Note the strong buffering capacity of magnesite. If both magnesite and brucite are present, the fugacities of \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) are controlled by the reaction \( \text{MC} + \text{H}_2\text{O} \rightarrow \text{Br} + \text{CO}_2 \), and Figures 2 and 3A show that, for the quaternary reaction \( \text{Br} + \text{MC} + \text{En} \rightarrow \text{Fo} + \text{V} \) extending below point \((\text{Pe},\text{Q})\) in Figure 1, this control drives the vapor-phase composition to very high values of \( \text{H}_2\text{O}/\text{CO}_2 \). Forsterite and vapor cannot coexist at pressures greater than that of the quaternary subsolidus reaction.

**Phase relationships from 1 bar to \((\text{Br},\text{En},\text{Q})\) at 23 kbar**

The low-pressure phase relationships involving forsterite and enstatite in \( \text{MgO-SiO}_2-\text{H}_2\text{O} \) were reviewed by Ellis and Wyllie (1979b). At pressures above a few kbar, forsterite and enstatite both melt congruently, as shown in Figure 4A. Figures 4A and 5A show that they also melt congruently in the presence of \( \text{CO}_2 \), but that in the presence of \( \text{H}_2\text{O} \) forsterite melts congruently and enstatite melts incongruently. The vapor-saturated liquidus boundary between the fields giving the compositions of liquids generated from forsterite plus enstatite plus vapor is forsterite–enstatite-normative in the presence of \( \text{CO}_2 \) (with a small amount of dissolved \( \text{CO}_2 \)) and enstatite–quartz-normative in the presence of \( \text{H}_2\text{O} \) (with a high percentage of dissolved \( \text{H}_2\text{O} \)). The position of the surface between the volumes for forsterite and enstatite in Figure 4A illustrates the contrasting effects of \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) on the compositions of liquids developed from the assemblage forsterite plus enstatite. The change in liquid composition from forsterite-normative to quartz-normative occurs at the singular point shown in Figure 6A where the field boundary crosses the surface enstatite–vapor (\( \text{V} \)) is very close to \( \text{H}_2\text{O}-\text{CO}_2 \) in Figure 4A. This point, if plotted on the solidus surface in Figure 3A, would trace a line trending from \( \text{CO}_2 \) at low pressures towards \( \text{H}_2\text{O} \) at higher pressures. We have little information on the position of this important line, except for the data of Eggler (1975) at 20 kbar and the results of Mysen and Boettcher (1975a,b) on near-solidus liquids from peridotite–\( \text{H}_2\text{O-}\text{CO}_2 \).

At low pressure, the solubilities of \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) are much lower than those at 20 kbar in Figure 4A. The vapor-saturated liquidus surface is therefore further away from the edge \( \text{H}_2\text{O}-\text{CO}_2 \) and nearer to \( \text{MgO-SiO}_2 \). The liquidus and vaporus surfaces do not merge near the joint \( \text{SiO}_2-\text{H}_2\text{O} \) until the second critical end-point is reached in \( \text{SiO}_2-\text{H}_2\text{O} \) (see review above). Because there are no invariant points between 1 bar and 23 kbar in Figure 1, the relative arrangement of phase boundaries depicted at 20 kbar in Figures 4A, 5A, and 6A is maintained through the pressure interval, 1–20 kbar.

With increasing pressure the carbonation and hydration reactions shown in Figures 1 and 3A increase considerably in temperature, and the divariant surfaces therefore move upward through Figure 6A. Melting reactions with \( \text{H}_2\text{O} \) decrease in temperature with increasing pressure, whereas melting reactions with \( \text{CO}_2 \) first increase in temperature and then decrease, as shown in Figure 1. With increasing pressure in this range, the subsolidus reactions in Figure 6A move towards the melting reactions.

**Phase relationship from \((\text{Br},\text{En},\text{Q})\) at 23 kbar to \((\text{Pe},\text{Br},\text{Q})\) at 42 kbar**

Figure 1 shows that the changes occurring in this pressure interval are caused by the fact that magnesite becomes stable at and above the solidus. Details of the changes occurring in \( \text{MgO-SiO}_2-\text{CO}_2 \) were presented by Wyllie and Huang (1976). Magnesite appears first on the ternary \( \text{CO}_2 \)-saturated liquidus at the eutectic between forsterite and periclase (Figs. 4A and 5A). With increasing pressure the ternary magnesite field expands to include magnesite and expands into the vapor-absent region. The quaternary magnesite liquidus volume expands into the quaternary system as a wedge, separating the periclase volume from vapor, as shown in Figures 4B and 5B.

Phase relationships involving magnesite corre-
The three reactions which meet in the system MgO-SiO$_2$-CO$_2$ to generate the invariant point (Pe,Br,Q) must all correspond to divariant surfaces in the system MgO-SiO$_2$-H$_2$O-CO$_2$. Those three surfaces meet along the quaternary univariant reaction MC + En + V → Fo + L. The positions of H$_2$O-CO$_2$ contours on the subsolidus reaction MC + En → Fo + V have been calculated from the data of Eggler et al. (1979) and are shown in Figure 3A. The place where each calculated contour on the MC + En → Fo + V surface meets the quaternary univariant reaction MC + En + V → Fo + L determines where contours on the other two surfaces, shown in Figures 3B and 3C, must meet that line. In the absence of any data, the contours shown on the MC–En–L–V surface in Figure 3B are simply assumed to be roughly parallel to the reaction MC + En + CO$_2$ → L.

Vapor composition contours on the divariant surface Fo + En + V → L are represented by the crests of thermal ridges on the liquidus surface, sliding conformally with the solidus, as shown in Figure 4B (compare with Fig. 4A). This surface meets the magnesite phase volume at the invariant point (Pe,Br,Q) and, at higher pressures, the forsterite volume does not reach the CO$_2$-saturated liquidus at all, as shown in Figures 5C and 5D. Associated with this migration of the liquid derived from forsterite plus enstatite plus CO$_2$ is a marked increase in CO$_2$ solubility (Fig. 4B), a marked decrease in reaction temperature (Fig. 1), and a change in the melting of forsterite plus CO$_2$ from congruent to incongruent (Fig. 4B).

At some pressure near 35 kbar a new and previously undescribed feature of the system MgO-SiO$_2$-H$_2$O-CO$_2$ appears, due to the abrupt lowering of melting temperatures by CO$_2$. This feature is a thermal maximum on the reaction Fo + En + V → L. Its postulated location is shown in Figures 1 and 3A as a dashed line which passes just above the invariant point (Pe,Br,Q) and terminates very close to the point (Pe,Q,MC). The location of the thermal maximum is shown in other ways in Figures 4, 5, and 6. The origin of this significant feature, identified as the one which originates in MgO-SiO$_2$-CO$_2$ near 35 kbar. The detailed phase relations near the points (Pe,Q) and (Pe,Q,MC) are shown in Figure 7B. Analysis of phase relations at these points by Schreinemakers’ rules requires that both pressure and temperature maximum exist on the Br–Fo–En–L–V reaction. This thermal maximum terminates the one which originates in MgO-SiO$_2$-CO$_2$ near 35 kbar. The explanation given in later sections of the way in which phase relations change at high pressures gives the details of the disappearance of the thermal maximum.

Physically, the thermal maximum on the forsterite–enstatite–vapor solidus is a thermal ridge on the solidus surface, as shown in Figure 3C, where the solidus meets the liquidus at points corresponding to the temperature maxima on isoobaric forsterite–enstatite–vapor liquidus field boundaries.

At low pressures the congruent melting of forsterite, Fo + V → L, is represented by the crest of a thermal ridge on the liquidus surface, extending continuously from H$_2$O to CO$_2$. At pressures approaching the stabilization of magnesite at the solidus, the lowering of liquidus temperatures by CO$_2$ depresses...
the thermal ridge, causing it to shrink and migrate away from the CO$_2$ side, with the result that the crest of the ridge has a temperature maximum for some intermediate vapor composition, as shown in Figure 6C.

The field boundary for Fo + En + V → L is a simple valley on the vapor-saturated liquidus surface at low pressures (Figs. 4A and 5A), but with its migration towards MgCO$_3$ (Figs. 4B and 5B), it approaches the thermal ridge associated with the congruent melting of forsterite plus vapor. The crest of this ridge falls away towards the CO$_2$ side (Fig. 6C), and as the forsterite-enstatite-vapor field boundary approaches, it traverses the flank of the ridge obliquely, passing over a temperature maximum before it can fall off to the lower temperatures required by the migrating position of its CO$_2$-rich end. This produces the temperature maximum shown in Figure 6C. At somewhat higher pressure, at the singular point near 40 kbar in Figure 1, the field boundary reaches the forsterite–CO$_2$ joint as described by Wyllie and Huang (1976). At higher pressures the field boundary crosses the forsterite–vapor ridge on its low-temperature CO$_2$ side and extends down towards the liquidus field for primary magnesite (see Figs. 5A, B, C, and D). The temperature maximum on the field boundary does not coincide precisely with the forsterite–vapor ridge crest, but is situated at a point within the volume forsterite-enstatite–vapor (as required by chemographic relationships), which is the highest point crossed as the field boundary traverses the flank of the forsterite–vapor ridge before crossing the ridge crest itself—the crest being at lower temperatures at points closer to the CO$_2$ side.

With increasing pressure, the forsterite–vapor ridge contracts further away from the CO$_2$ side, and the forsterite–enstatite field boundary moves progressively down towards MgCO$_3$. The vapor present at the temperature maximum consequently becomes richer in H$_2$O (Fig. 5) as does the coexisting vapor, as shown in Figures 3C and 6.

At pressures up to at least 20 kbar, H$_2$O/CO$_2$ is higher in liquid than in vapor for melting reactions involving forsterite plus enstatite (Eggler, 1975; Mysen and Boettcher, 1975a,b). At the temperature maximum on the field boundary, the chemographic relationships require that H$_2$O/CO$_2$ is the same in coexisting liquid and vapor; the dashed line in Figure 3C is the locus for this equality. On the carbonate side of the temperature maximum, therefore, H$_2$O/CO$_2$ is higher in vapor than in liquid. This is consistent with phase relationships in the system MgO–CO$_2$–H$_2$O (Ellis and Wyllie, 1979a). This condition exists for the portion of the surface in Figure 3C between the dashed line and the solid line for the buffered melting of partly carbonated forsterite–enstatite assemblage.

**Phase relationships from (Pe,Br,Q) at 42 kbar to (En,Q,Fo,MC) at 58 kbar**

In the pressure interval from 42 to 58 kbar, changes in melting relationships are due to two factors, as shown in Figure 1. Brucite becomes stable in
the presence of vapor-saturated liquids, and as pressure increases the assemblage stable at the CO₂-saturated solidus changes from forsterite plus magnesite plus CO₂ to enstatite plus magnesite plus CO₂ to quartz plus magnesite plus CO₂.

Brucite first becomes stable in the presence of liquid at 44 kbar at the invariant point (En, Q) as shown schematically in Figure 7A, where a eutectic between forsterite, magnesite, brucite, and vapor replaces the eutectic stable at lower pressures between forsterite, magnesite, periclase, and vapor. Figure 5C illustrates how a crystallization volume for brucite has appeared and begun to cut off the periclase crystallization volume from the vapor-saturated liquidus. At 45 kbar the reaction MC + En → Fo + V has intersected the solidus, and the enstatite volume has begun to cut the forsterite volume off from coexisting with vapor. The thermal maximum on the reaction Fo + En + V → L moves to more H₂O-rich compositions for the same reason. The movement of the thermal maximum to more H₂O-rich compositions also shows in Figure 5C, D, and E, as well as the fact that the enstatite volume is cutting off the forsterite area on the vapor-saturated liquidus with increasing pressure.

At the invariant point (En, Q, Fo) shown in Figures 1 and 7A, brucite becomes stable in the system MgO-H₂O-CO₂. Schematic phase relations at 50 kbar are shown in Figures 5D and 6D. Figure 5D shows that, due to the expansion of the brucite crystallization volume, the peritectic reaction between periclase, magnesite, and vapor has been replaced by two new peritectics: between periclase, brucite, and vapor and between brucite, magnesite, and vapor. This change is reflected in the schematic T-Xco₂ section, Figure 6D, by the reactions Fo + Pe + V → L and Pe + V → L being replaced at isobaric invariant points by the reactions Fo + Br + V → L and Pe + V → Br + L. Figure 5E at 55 kbar illustrates how the periclase area on the vapor-saturated liquidus continues to contract as pressure increases until it is covered completely by brucite at the invariant point (En, Q, Fo, MC).

Phase relationships from (En, Q, Fo, MC) at 58 kbar to (Pe, Q) at 80 kbar

The invariant points (En, Q, Fo, MC) and (Pe, Br, Fo) lie at nearly the same pressure, about 58 kbar. Above that pressure periclase is not stable with vapor-saturated liquids, and quartz is the solidus silicate in the presence of pure CO₂. A T-Xco₂ diagram at 60 kbar, Figure 6E, shows that a second thermal maximum must be present at the reaction En + Q + V → L. This develops because that melting reaction crosses the enstatite–vapor thermal ridge at pressures above 40 kbar in the same way that the reaction Fo + En + V → L crosses the forsterite–vapor ridge at pressures above 35 kbar.

Ellis and Wyllie (1979b) demonstrated that the hydrous melting of forsterite must become incongruent between 50 and 90 kbar and arbitrarily placed that singular point at about 65 kbar. At pressures above that singular point, the reactions Fo + V → L and Br + Fo + V → L are stable only in the presence of mixed H₂O-CO₂ vapor. Figures 4C, 5F, and 6F show phase relations at pressures above the singular point at 65 kbar.

Comparison of the isobaric liquidus diagrams for 50 and 70 kbar (Figs. 4B and 4C, respectively) shows that by 70 kbar the crystallization volumes for quartz and enstatite have expanded to greater volatile and lower SiO₂ contents and that near the CO₂ corner of the tetrahedron they have begun to move away from the vapor-saturated liquidus surface across the top of the brucite–magnesite “prism.”

The vapor-saturated liquidus surface shown in Figure 5F demonstrates more simply how much the crystallization volume of quartz has expanded relative to forsterite and enstatite. Comparison of Figure 6E and 6F shows that the range of Xco₂ over which forsterite melts congruently steadily decreases with increasing pressure.

Phase relationships from (Pe, Q) at 80 kbar to (Pe, MC, Q) at 90+ kbar

The topology of invariant points in the pressure range from 80 to 90+ kbar is shown in Figure 1 and in enlarged and detailed form in Figure 7B. At pressures greater than 80 kbar, forsterite may no longer coexist with vapor rich enough in CO₂ to stabilize magnesite. Figure 8A shows the water-rich part of the T-Xco₂ diagram at 85 kbar. The subsolidus reaction Br + En → Fo + V meets the solidus at the peritectic reaction between brucite, enstatite, forsterite, and vapor which is shown in Figure 8B. The small forsterite area on the vapor-saturated liquidus still stretches across both the forsterite–vapor and enstatite–vapor joins.

At the point (Pe, Q, MC) at 90 kbar, forsterite becomes unstable in the presence of pure H₂O, though for a narrow interval at slightly higher pressures it is stable with mixed H₂O-CO₂ vapor. At the point (Pe, Q, MC), the reactions En + Br → Fo + V, En + V → Fo + L, and Fo + V → Br + L meet at the H₂O
sideline of the $T-X_{CO_2}$ diagram. As pressure increases, this peritectic reaction migrates toward more CO$_2$-rich vapor compositions, generating the topologies seen in Figures 8C and 8D at ~91 kbar.

When in Figure 8D the brucite-enstatite boundary migrates across the enstatite-vapor join, several things happen. The melting reaction immediately becomes congruent, a thermal maximum on the field boundary is soon created, and the boundary then terminates at a eutectic between forsterite, brucite, enstatite, and vapor. The field of forsterite on the vapor-saturated liquidus has been reduced to a tiny patch.

The $T-X_{CO_2}$ topology at ~91 kbar is given in Figure 8C and shows that in a limited pressure interval temperature maxima exist on three melting reactions. The subsolidus reaction $En + Br \rightarrow Fo + V$ is terminated at both ends by invariant points involving the reactions $En + Br \rightarrow Fo + L$ and $Br + En + V \rightarrow L$. Note, however, that one invariant point is a peritectic and the other is a eutectic. The fields for all assemblages and reactions containing forsterite plus vapor
Phase relations at pressures >95 kbar

At pressures greater than the invariant points (Pe,Q) and (Pe,Q,MC), phase relationships are considerably simpler. Schematic phase relationships at 95 kbar are shown in Figures 1, 4D, 5H, 6G, and 7B. Figure 7B shows that forsterite and vapor are never stable together at very high pressures. Enstatite takes the place of forsterite in vapor-present melting reactions, and forsterite is found only in vapor-absent assemblages. This is also illustrated in the 95-kbar isobaric liquidus diagrams, Figures 4D and 5H, which show that the volumes of forsterite and vapor do not meet at any point.

Figure 6G schematically shows the vapor-present subsolidus and melting relations at 95 kbar. Thermal maxima still exist in two reactions: En + Br + V → L and En + Q + V → L. Eutectics exist between brucite, magnesite, enstatite, and vapor and between brucite, magnesite, and vapor.

Estimates of liquid compositions

The compositions of liquids present at the solidus for bulk compositions of forsterite plus enstatite plus a small proportion of volatiles may be estimated from experimental evidence at low pressures in combination with isobaric liquidus diagrams, such as Figures 4A, B, C, and D. Estimates have been made at pressures of 20, 50, and 90 kbar for a bulk composition containing H₂O and CO₂ in a 3:1 mole ratio. The estimates are given in Table 1.

The experiments of Eggler (1975) demonstrate that at 20 kbar H₂O is partitioned toward the liquid phase. The experiments shown in his Figure 2 indicate that at 1450°C the H₂O/(H₂O + CO₂) mole ratio in liquid coexisting with enstatite is about 0.77, while the vapor phase has an H₂O/(H₂O + CO₂) mole ratio of 0.38. The results of Mysen and Boettcher (1975a,b) on the solidus in peridotite-H₂O-CO₂ are adopted for the slope of the divarant forsterite-enstatite-vapor melting surface: about 20°C per 0.1 increase in X₃CO₂, of the vapor. These two pieces of information may be used in combination to estimate that the liquid coexisting with forsterite plus enstatite plus vapor, whose X₃CO₂ = 0.25 at 20 kbar and about 1380°C, has an H₂O/(H₂O + CO₂) mole ratio of 0.08. Given this estimate, one may calculate geometrically from the isobaric liquidus diagram, Figure 4A, the first liquid composition given in Table 1. This composition is SiO₂-saturated, in agreement with the conclusions of Eggler (1975) and Mysen and Boettcher (1975a,b). The high water content is due to the fact that the measured H₂O solubility in forsterite at 20 kbar is 65 mole percent (Hodges, 1973).

The estimate at 50 kbar is less constrained. The subsolidus reaction MC + En → Fo + V buffers the vapor phase to an X₃CO₂ of 0.11 where its reaction intersects the buffered melting reaction at about 1400°C and 50 kbar. In order to estimate the liquid composition, we assumed that the slope of the melting reaction MC + Fo → L is similar to that of the reaction MC → L in the system Mg(OH)₂-MgCO₃. Using the P-T net given in Figure 2, one may then estimate that the H₂O/(H₂O + CO₂) mole ratio of the liquid at 1400°C is roughly 0.4. This may be regarded as the maximum for the H₂O content of the liquid, because the slope of the vapor-present melting reaction would be expected to be shallower than that of the vapor-absent melting reaction. The estimated liquid composition given in Table 1 is therefore the most SiO₂-rich estimate possible. Even so, it is very low in SiO₂ and has large amounts of both H₂O and CO₂.

In the estimate of composition made at 90 kbar, the position of the Mg(OH)₂-MgCO₃ eutectic, calculated by Ellis and Wyllie (1979a), fixes the H₂O/(H₂O + CO₂) mole ratio of the vapor-absent melt at 0.27. From that, geometric estimation of the liquid composition is straightforward. The composition of the liquid formed at high pressure has an intermediate SiO₂/MgO ratio. It has normative forsterite and enstatite and is high in volatiles. The quaternary eutectic between magnesite, enstatite, brucite, and forsterite would be expected to move farther from the vapor-saturated surface as pressure increases. There-

Table 1. Geometrically estimated compositions of first liquids coexisting with forsterite plus enstatite in a bulk composition with an H₂O/CO₂ ratio of 3/1

<table>
<thead>
<tr>
<th>Pressure</th>
<th>H₂O Mole %</th>
<th>SiO₂ Mole %</th>
<th>H₂O Weight %</th>
<th>SiO₂ Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 kbar</td>
<td>12</td>
<td>17</td>
<td>18</td>
<td>37</td>
</tr>
<tr>
<td>50 kbar</td>
<td>34</td>
<td>10</td>
<td>36</td>
<td>17</td>
</tr>
<tr>
<td>90 kbar</td>
<td>32</td>
<td>18</td>
<td>36</td>
<td>31</td>
</tr>
</tbody>
</table>
fore, liquids formed at higher pressures should be slightly higher in MgO and lower in volatiles.

The estimated compositions of first liquids change rapidly near 50 kbar, where the subsolidus reaction \( MC + En \rightarrow Fo + V \) intersects the solidus. A bulk composition that produces an H₂O-rich, SiO₂-saturated first liquid at lower pressures produces a CO₂-rich, low SiO₂ liquid near 50 kbar and a liquid of intermediate SiO₂ content with H₂O > CO₂ at higher pressures. These same trends of melt composition

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**Fig. 9.** Partial \( P-T \) net for the system MgO-SiO₂-H₂O-CO₂. Only reactions involving the assemblage forsterite plus enstatite are shown. Forsterite and vapor may coexist only in the \( P-T \) region enclosed by the heavy lines. The heavy dashed line shows the position of the thermal maximum on the reaction \( Fo + En + V \rightarrow L \).
with increasing pressure should also occur in the mantle system, although certainly at lower pressure, as shown by Wyllie (1978) and Eggler (1978). The data for the system MgO-SiO$_2$-H$_2$O-CO$_2$ suggest that the liquid present in the upper part of the low-velocity zone is likely to be carbonatitic, whereas that in the lower part of the low-velocity zone should be kimberlitic in composition.

**Discussion**

The model proposed for the system MgO-SiO$_2$-H$_2$O-CO$_2$ gives an internally consistent explanation for both the experimentally observed subsolidus and melting reactions and the effects of mixed H$_2$O-CO$_2$ vapor on those reactions. The model allows prediction of phase relations at pressures up to 100 kbar, where detailed experimental work is not presently feasible. The system contains the assemblage forsterite plus enstatite; H$_2$O and CO$_2$; a hydrate, brucite; and a carbonate, magnesite. Although many compositions in the system MgO-SiO$_2$-H$_2$O-CO$_2$ are far removed from those of the upper mantle, the relationships among these phases indicate the general features of phase relationships between those types of compounds in the upper mantle.

Figures 9 and 10 show respectively the reactions and mineral assemblages containing both forsterite and enstatite as a function of temperature and pressure. They show clearly that the stability of forsterite plus vapor is restricted by reactions producing enstatite plus a hydrate, a carbonate, or both. Forsterite and vapor do not coexist at pressures greater than that of the invariant point (Pe,MC,Q) at about 90 kbar. The low P-T field within which forsterite and vapor coexist is circumscribed by a heavy line in Figure 9. The processes of vapor-present melting and mantle metasomatism can occur only at pressures and temperatures within this field and are therefore restricted to depths less than 270 km. In the more complex system CaO-MgO-Al$_2$O$_3$-SiO$_2$-H$_2$O-CO$_2$, the region of vapor-present forsterite reactions may be restricted to a smaller pressure interval, due to the fact that reactions involving diopside occur at lower pressures than analogous reactions involving enstatite.

The model developed for the system MgO-SiO$_2$-H$_2$O-CO$_2$ requires that, in successively higher pressure ranges, three different types of melting processes characterize the melting of forsterite plus enstatite in the presence of H$_2$O-CO$_2$ vapor.

1. At low pressures, the melting reaction is either enstatite + vapor → forsterite + liquid at low $X_{CO_2}$, or forsterite + enstatite + vapor → liquid at high $X_{CO_2}$. The composition of the liquids produced varies from quartz-normative in the presence of H$_2$O to forsterite-normative in the presence of CO$_2$. This agrees with the conclusions of Eggler (1975) and Mysen and Boettcher (1975a,b). At 20 kbar H$_2$O is partitioned toward silicate liquids, and CO$_2$ is partitioned toward the coexisting vapor.

2. At pressures between 42 and 80 kbar, the important melting reaction is Fo + MC + V → En + L. The composition of the vapor phase taking part in this reaction is buffered by the subsolidus reaction En + MC → Fo + V. At temperatures above the solidus for the assemblage forsterite plus enstatite, a thermal maximum exists on the reaction forsterite + enstatite + vapor → liquid. The $X_{CO_2}$ of the vapor at this thermal maximum rapidly becomes smaller as pressure increases.

3. At pressures above 90 kbar, forsterite plus enstatite melts at a quaternary eutectic with brucite and magnesite with no vapor present. H$_2$O/CO$_2$ mole ratio of the liquid is fixed at about 3/1 by the eutectic between Mg(OH)$_2$ and MgCO$_3$.

The composition of the first liquid formed in bulk compositions of forsterite plus enstatite and a small amount of volatiles with 3/1 H$_2$O/CO$_2$ ratio changes
from quartz-normative to periclase-forsterite-normative to enstatite-forsterite-normative as pressure increases.

These three kinds of melting reactions must also occur in peridotite, where \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) are present as vapor or are stored in amphibole, phlogopite, and carbonate. The distribution of \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) among liquid, crystals, and vapor in the simple system \( \text{MgO}-\text{SiO}_2-\text{H}_2\text{O}-\text{SiO}_2 \) provides a guide for interpretation of the phase relationships in the complex peridotite-\( \text{H}_2\text{O}-\text{CO}_2 \) system (Wyllie, 1978).

Two sorts of incongruent melting of silicate minerals occur in the system \( \text{MgO}-\text{SiO}_2-\text{H}_2\text{O}-\text{CO}_2 \) at high pressure. In the presence of \( \text{H}_2\text{O} \)-rich vapor, melts richer in \( \text{SiO}_2 \) than the mineral are produced; however, in the presence of \( \text{CO}_2 \)-rich vapor, the silicates melt incongruently to give a liquid poorer in \( \text{SiO}_2 \) than the mineral. The \( T-X_{\text{CO}_2} \) diagrams in Figure 6 show that the incongruent melting reactions originate at invariant points where related congruent melting reactions terminate. For example, in Figure 6F, the incongruent melting reactions \( \text{Fo} + \text{V} \rightarrow \text{En} + \text{L} \) and \( \text{Fo} + \text{V} \rightarrow \text{En} + \text{L} \) both originate at invariant points where the congruent melting reaction \( \text{Fo} + \text{En} + \text{V} \rightarrow \text{L} \) terminates. Figures 1 and 6 show that as pressure increases the \( X_{\text{CO}_2} \) range over which the melting of forsterite plus enstatite is congruent decreases until congruent melting disappears at the pressure at which the thermal maximum disappears. The \( T-X_{\text{CO}_2} \) diagrams in Figure 6 also show that all reactions with the thermal maxima terminate at invariant points involving incongruent melting reactions.

The existence of a thermal maximum on the reaction \( \text{Fo} + \text{En} + \text{V} \rightarrow \text{L} \) has important consequences. The thermal maximum is required at pressures above 35 kbar, as demonstrated earlier. It always occurs at a vapor composition richer in \( \text{H}_2\text{O} \) than the vapor at the intersection of the reactions \( \text{Fo} + \text{En} + \text{V} \rightarrow \text{L} \) and \( \text{MC} + \text{En} \rightarrow \text{Fo} + \text{V} \). This requires the thermal maximum to move to \( \text{H}_2\text{O} \)-rich vapor compositions within a small pressure interval after it appears. The size of the maximum is postulated to decrease as it moves to more water-rich compositions. The thermal maximum occurs where the \( \text{H}_2\text{O}/\text{CO}_2 \) ratios in the liquid and vapor are equal. Such a thermal maximum presumably exists also in the complex mantle system, as discussed by Wyllie (1978).

Thermal maxima could be responsible for the rapid eruption of kimberlites from the upper mantle. The fact that melts present in the earth’s upper mantle at pressures greater than 25 kbar are kimberlitic or carbonatitic has been postulated by Wyllie (1978) on the basis of experimental evidence. If a parcel of mantle whose temperature was just above its solidus were rising and encountered a thermal maximum on its solidus, all melt would crystallize and dissolved gases would be exsolved. If the parcel of mantle continued to rise and also retained its volatiles, it would recross its solidus and would partially melt. However, the composition of the partial melt would be different. The data of Bultitude and Green (1971) and of Brey and Green (1975) indicate that the liquid formed by remelting would be an olivine melilitite rather than a carbonatite.

A more likely series of events would have a fracture initiated due to the increased volume of the exsolved gases when the thermal maximum is first crossed. Once initiated, such a fracture could propagate very rapidly (Anderson, 1977). The fact that carbonatitic and kimberlitic liquids are extremely fluid would allow them to migrate easily to the fracture to continue its propagation. The rapid influx of melt and upward propagation of a fracture would make possible quick transportation of xenoliths and magma to a shallow depth, where wholesale exsolution of volatiles from the magma could initiate the violent surface eruption characteristics of kimberlites.

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