

Carbonation, hydration, and melting relations in the system MgO–H₂O–CO₂ at pressures up to 100 kbar

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Abstract

A model has been derived for the subsolidus and melting relationships in the system MgO–H₂O–CO₂ for pressures up to 100 kbar. Using both low- and high-pressure experimental data, the ΔH° and ΔS° for the subsolidus reactions $\text{Mg}(\text{OH})_2 \rightarrow \text{MgO} + \text{H}_2\text{O}$, $\text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2$, and $\text{MgCO}_3 + \text{H}_2\text{O} \rightarrow \text{Mg}(\text{OH})_2 + \text{CO}_2$ are estimated to be respectively: $\Delta H^\circ = 18400$ cal/mol and $\Delta S^\circ = 33.16$ cal/°mol, $\Delta H^\circ = 20140$ cal/mol and $\Delta S^\circ = 34.87$ cal/°mol and $\Delta H^\circ = 1740$ cal/mol and $\Delta S^\circ = 1.71$ cal/°mol. In the presence of MgCO₃, vapor is buffered to high values of H₂O/CO₂ except for a narrow pressure interval just above the reaction $\text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2$. As pressure is increased the vapor coexisting with an MgCO₃-bearing assemblage becomes richer in H₂O. MgCO₃ first melts at an invariant point located at 23 kbar and 1550°C. Mg(OH)₂ melts at an invariant point estimated to be near 58 kbar and 1310°C. Mg(OH)₂ + MgCO₃ + vapor melt together at a eutectic at pressures greater than or equal to that of an invariant point located near 46 kbar and 1210°C. The composition of the eutectic liquid on the join Mg(OH)₂–MgCO₃ is estimated to be 73 mole percent Mg(OH)₂ plus 27 mole percent MgCO₃. The system MgO–H₂O–CO₂ provides the thermodynamic basis for estimating the distribution of H₂O and CO₂ between coexisting liquids and vapors in the presence of hydrates and carbonates, and is an essential first step leading to the interpretation of similar phase relationships in the model mantle system CaO–MgO–Al₂O₃–SiO₂–H₂O–CO₂.

Introduction

The most abundant volatile compounds in the earth's crust are H₂O and CO₂. Dehydration and decarbonation reactions which take place in the presence of pure or mixed volatile phases are typical of progressive regional metamorphism. The thermodynamic basis for interpreting dissociation reactions taking place in the presence of a mixed volatile phase has been discussed by Greenwood (1962, 1967), and its application to complex systems has been reviewed by Kerrick (1974) and by Kerrick and Slaughter (1976). The theoretical treatments show that the composition of a vapor phase present in a closed system may be buffered either by the dissociation of hydrates or carbonates, or by exchange reactions involving both hydrates and carbonates.

It is now apparent that H₂O and CO₂ are also capable of playing important roles in mantle processes, although under normal conditions their abundances in the mantle would be much lower than in

crustal rocks. Vapor-phase compositions in the mantle are probably buffered by subsolidus reactions involving small amounts of hydrates and carbonates, as reviewed by Wyllie (1977). In some circumstances all H₂O and CO₂ may be stored as hydrates and carbonates, yielding a vapor-absent mantle (Holloway and Eggler, 1976). The effects of H₂O, CO₂, and H₂O–CO₂ mixtures on the phase relations of mantle peridotite or on simple model systems have been explored in several laboratories, with emphasis on the melting relationships in those systems at pressures up to 35 kbar (Brey and Green, 1975, 1976; Eggler, 1974, 1976a; Mysen and Boettcher, 1975a, 1975b; Wyllie and Huang, 1975, 1976). Differences in experimental results and interpretations have been extensively discussed (Eggler, 1976b; Green, 1976; Mysen and Boettcher, 1975a, 1975b; Nehru and Wyllie, 1975; Wyllie, 1977; Wyllie and Huang, 1975, 1976). We have adopted the method of calculating subsolidus and melting relationships where possible in simple systems as a guide for the interpretation of experimental data in more complex systems, and as a guide for the modelling of phase relationships at pressures

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up to 100 kbar. Errors in the calculated positions of curves and surfaces could be evaluated at low pressures, but the uncertainties involved at 100 kbar are such that error analyses would not be very informative. The purpose of this paper is to construct the topology of reactions involving hydrates, carbonates, and mixed vapors, and to examine the types of reactions occurring among these phases and liquids. The conclusions reached are not likely to be affected if refinements in thermodynamic parameters require changes in precise P - T values of the calculated reactions.

MgO-H₂O-CO₂ is a simple system with composition clearly far removed from that of mantle peridotite. However, it provides the thermodynamic basis for estimating the distribution of H₂O and CO₂ between coexisting liquids and vapors in the presence of hydrates and carbonates. This is an essential first step leading to the interpretation of similar phase relationships in the model mantle system CaO-MgO-Al₂O₃-SiO₂-H₂O-CO₂.

Throughout this paper compounds in the system MgO-H₂O-CO₂ will be referred to using the names of corresponding minerals. The following abbreviations for these mineral names have been used to write reactions and to label all figures: periclase (MgO) = Pe, magnesite (MgCO₃) = MC, brucite [Mg(OH)₂] = Br, liquid = L, pure H₂O vapor = H₂O, pure CO₂ vapor = CO₂, and mixed H₂O-CO₂ vapor = V.

The system C-O-H

Phase relations in the system C-O-H in the presence of crystalline carbon have been described by Ohmoto and Kerrick (1977) at pressures up to 10 kbar. As pressure increases, H₂O and CO₂ form a greater proportion of the vapor phase coexisting with carbon. We may therefore assume, without being far from the truth, that the vapor present in the system MgO-H₂O-CO₂ at high pressures will be a binary mixture of H₂O and CO₂.

Holloway (1976, 1977) has shown that the fugacities of H₂O and CO₂ can be accurately predicted at pressures up to 40 kbar and temperatures up to 1800°C by the modified Redlich-Kwong equation, referred to as the MRK equation, proposed by DeSantis *et al.* (1974). Haselton *et al.* (1977) showed from experimental studies on decarbonation reactions that CO₂ fugacities predicted by the MRK equation are reasonably accurate at pressures as high as 50 kbar. All MRK calculations in this paper used

the values for a° , b , $a(T)$, and $\ln K$ given by Holloway (1977).

The system MgO-H₂O

Studies of phase relations in the system MgO-H₂O have been limited to determination of the P - T path of the reaction Br → Pe + H₂O. Barnes and Ernst (1963) located this reaction at pressures up to 2 kbar, and reviewed earlier experimental work. Yamoaka *et al.* (1970) studied the reaction at pressures up to 40 kbar. They reported that it reached a maximum temperature at 32 kbar and 1000°C. Irving *et al.* (1977) determined the path of the reaction at pressures from 17 to 33 kbar and found no evidence for the temperature maximum reported by Yamoaka *et al.*

The experimental data on the dehydration of brucite given by Walter *et al.* (1962), by Barnes and Ernst (1963), and by Irving *et al.* (1977) were used to derive thermodynamic data for the dehydration reaction. Following the method of Orville and Greenwood (1965), ΔH and ΔS were derived from a plot of $\ln f_{\text{H}_2\text{O}}$ vs. $1/T$, shown in Figure 1. The volume of reaction was estimated from the tables of Robie and Waldbaum (1968). For the reaction Br → Pe + H₂O, $\Delta H^\circ = 18,400$ cal/mol, $\Delta S^\circ = 33.16$ cal/mol, and $\Delta V^\circ = -13.18$ cm³/mol.

The P - T path of the dehydration reaction may be predicted using the relation

$$\ln K = -\Delta H^\circ/RT - \Delta V^\circ(P-1)/RT + \Delta S^\circ/R \\ = \ln f(\text{H}_2\text{O})$$

which becomes $\ln f(\text{H}_2\text{O}) = -9270/T + 0.161(P-1)/T + 16.69$ when the derived values for ΔH° , ΔS° , and ΔV° are substituted, in combination with the fugacities predicted by the MRK equation. When the H₂O fugacity predicted by the equation is equal to that predicted by the MRK equation, Br, Pe, and H₂O should coexist. The P - T path predicted, shown in Figure 4, is very close to the path published by Irving *et al.* (1977). No temperature maximum is predicted between 0 and 100 kbar.

Because the reaction Br → Pe + H₂O maintains a positive P - T slope, and the reaction Pe + H₂O → L must have a negative P - T slope due to increasing solubility of H₂O in the liquid with increasing pressure, we anticipate that the two curves will meet, as do the corresponding curves in the system MgO-CO₂ (Huang and Wyllie, 1975). Brucite would then melt at pressures and temperatures greater or equal to those of the invariant point. There are no constraints on the location of this invariant point except the data of Irving *et al.* (1977), which show that it is at a pressure

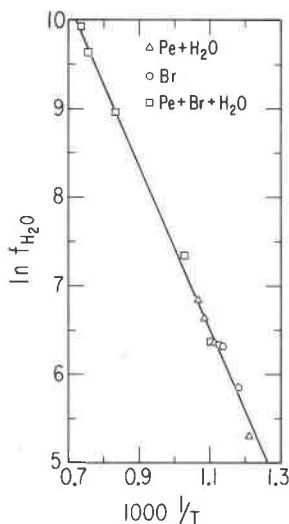


Fig. 1. Plot of $\ln f(\text{H}_2\text{O})$ vs. $1/T$ for the reaction $\text{Mg}(\text{OH})_2 \rightarrow \text{MgO} + \text{H}_2\text{O}$. All data recalculated to a pressure of one bar. The slope of the line equals the enthalpy of reaction, and the intercept where $1/T$ equals zero is the entropy of reaction. Data sources used are Walter *et al.* (1962), Barnes and Ernst (1963), and Irving *et al.* (1977). Abbreviation used in figures: Pe = MgO, Br = $\text{Mg}(\text{OH})_2$, MC = MgCO_3 , L = liquid, V = mixed H_2O - CO_2 vapor, H_2O = pure H_2O vapor, CO_2 = pure CO_2 vapor, $X(\text{CO}_2)$ = mole fraction CO_2 in vapor phase.

greater than 33 kbar. The position of the invariant point has been arbitrarily located at 58 kbar and 1310°C in order to be at a temperature higher than the forsterite-plus-water melting curve in the system MgO - SiO_2 - H_2O .

The four univariant reactions for the system MgO - H_2O meet at the invariant point labeled (MC) in

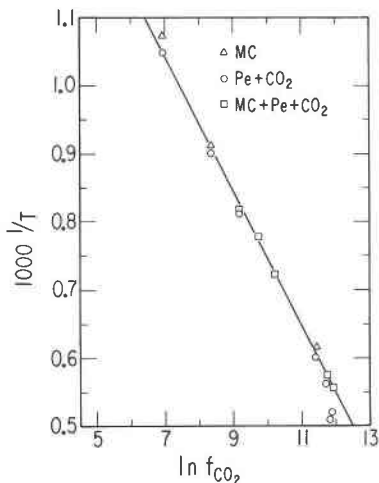


Fig. 2. Plot of $\ln f(\text{CO}_2)$ vs. $1/T$ for the reaction $\text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2$. All data recalculated to a pressure of one bar. Data sources used are the closed system experiments of Goldsmith and Heard (1960) and Irving and Wyllie (1975).

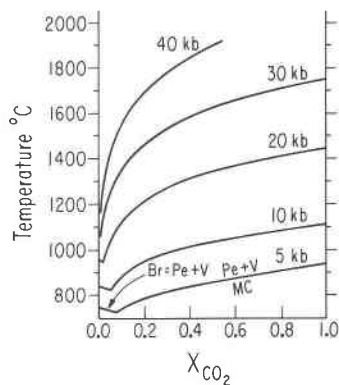


Fig. 3. Isobaric T - $X(\text{CO}_2)$ sections showing subsolidus reactions in the system MgO - H_2O - CO_2 at pressures of 5, 10, 20, 30, and 40 kbar. Positions of the reactions were calculated using the H_2O and CO_2 fugacities predicted by the MRK equation and the thermodynamic data derived from Figs. 1 and 2.

Figure 4. The brucite dissociation curve is derived from Figure 1. The arrangement of curves around the invariant point must be similar to that determined by Huang and Wyllie (1975) for MgO - CO_2 , except that the temperature of the reaction $\text{Br} + \text{H}_2\text{O} \rightarrow \text{L}$ is shown to decrease with increasing pressure by analogy with available experimental data on hydrous solidus curves. The melting curve $\text{Pe} + \text{H}_2\text{O} \rightarrow \text{L}$ extends to the triple point of periclase, near 2800°C at a pressure well below 1 bar.

The system MgO - CO_2

The system MgO - CO_2 has been studied at pressures up to 32 kbar. Goldsmith and Heard (1960) determined the decarbonation temperature of magnesite up to 10 kbar. Their experiments were conducted with the system either open or closed to CO_2 . The open-system experiments have a higher temperature for the decarbonation of magnesite by 50 - 150°C , depending upon pressure. We have used the closed-system experimental data, because both the results and the experimental method are more consistent with the work of Huang and Wyllie (1975) and of Irving and Wyllie (1975) at higher pressures. Walter *et al.* (1962) determined the decarbonation temperature of magnesite at 1000 bars. Their temperature of reaction was between that determined by the open- and closed-system experiments of Goldsmith and Heard (1960). Huang and Wyllie (1976) and Irving and Wyllie (1975) extended the experimental studies to 32 kbar, and found that magnesite melts at an invariant point at 23 kbar and 1550°C .

The enthalpy and entropy of reaction for $\text{MC} \rightarrow \text{Pe} + \text{CO}_2$ were derived from the plot of $\ln f(\text{CO}_2)$ vs. $1/T$ shown in Figure 2. We estimate that $\Delta H^0 = 20140$

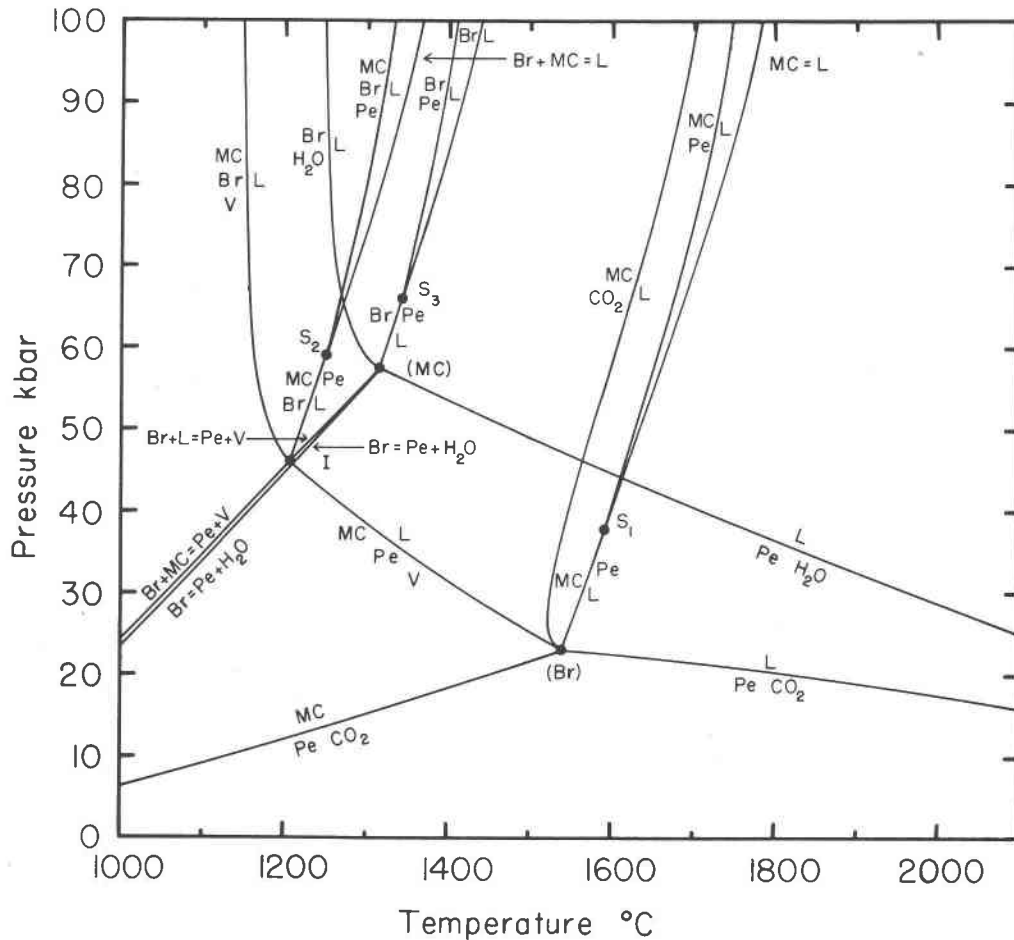


Fig. 4. Univariant reactions in the system MgO-H₂O-CO₂. Constructed as discussed in text. Partly schematic.

cal/mol and that $\Delta S^0 = 34.87$ cal/mol. The volume of reaction estimated from the tables of Robie and Waldbaum (1968) is $\Delta V^0 = -17.77$ cm³/mol. The equilibrium equation for the decarbonation of magnesite is therefore

$$\ln f(\text{CO}_2) = -10130/T + 0.202(P-1) + 17.55$$

The four univariant reactions for the system MgO-CO₂ meet at the invariant point labeled (Br) in Figure 4. This is based on experimental data to 32 kbar presented and compiled by Huang and Wyllie (1976) and by Irving and Wyllie (1975). The melting curves are extrapolated to 100 kbar with little change in slope. The melting curve $\text{Pe} + \text{CO}_2 \rightarrow \text{L}$ extends to the triple point of periclase near 2800°C at low pressure.

Subsolidus phase relations in the system MgO-H₂O-CO₂

Walter *et al.* (1962) investigated reactions in the system MgO-H₂O-CO₂ at pressures up to 4 kbar.

They showed that no melting occurred at moderate temperatures within this pressure range, and that the vapor coexisting with brucite plus magnesite becomes richer in H₂O as pressure increases.

There are three subsolidus reactions in the system MgO-H₂O-CO₂. The binary univariant reactions $\text{Br} \rightarrow \text{Pe} + \text{H}_2\text{O}$ and $\text{MC} \rightarrow \text{Pe} + \text{CO}_2$ each become divariant in the presence of mixed H₂O-CO₂ vapor. They are shown in Figure 3 as a series of isobaric univariant lines extending to lower temperatures from the isobaric univariant temperatures for pure H₂O and CO₂ respectively. At a given pressure the two dissociation reactions meet at an isobaric invariant point. The third univariant reaction, $\text{MC} + \text{H}_2\text{O} \rightarrow \text{Br} + \text{CO}_2$, extends from that isobaric invariant point to lower temperatures without much change in the composition of the vapor phase, as shown by Walter *et al.* (1962).

Thermodynamic data for the reaction $\text{MC} + \text{H}_2\text{O} \rightarrow \text{Br} + \text{CO}_2$ may be derived from an integral combination of the thermodynamic data for the other two

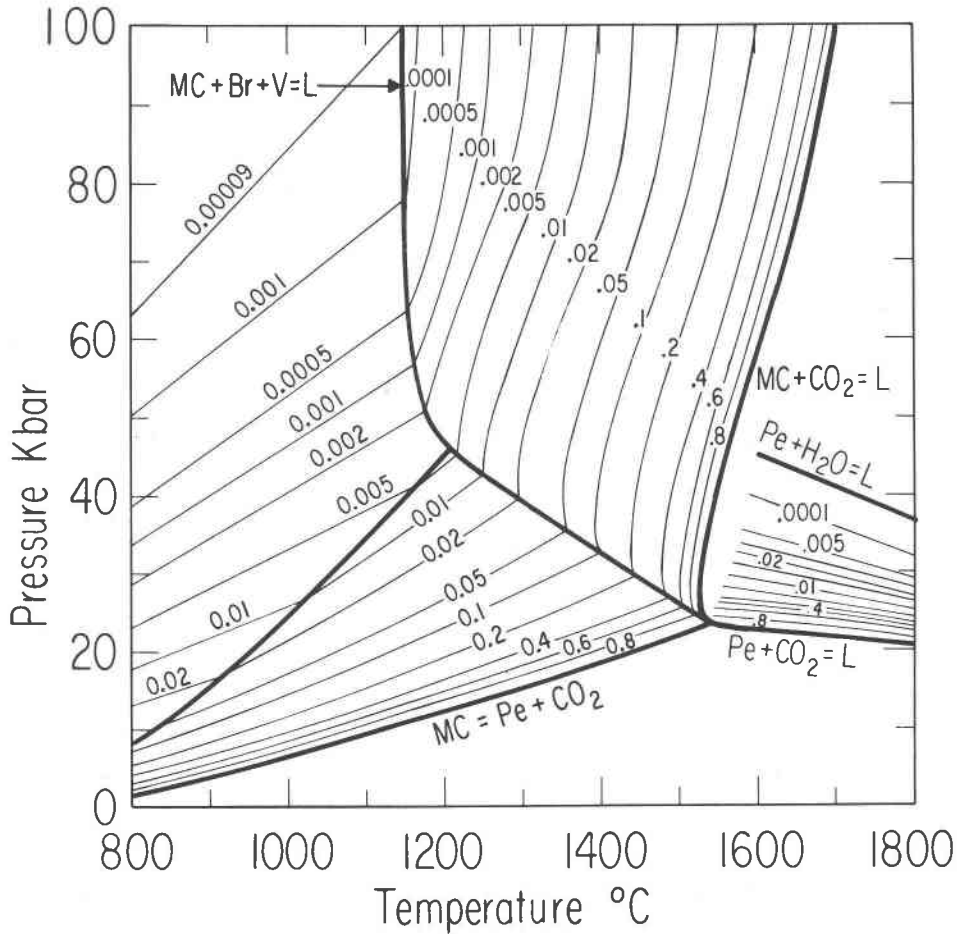


Fig. 5. Contours of constant $X(CO_2)$ in the vapor phase coexisting with selected assemblages. At low pressures and low temperatures the calculated compositions of the vapor coexisting with the assemblages $MgCO_3 + MgO$ and $Mg(OH)_2 + MgCO_3$ are illustrated. At high temperatures the composition of vapor coexisting with the assemblages MgO plus liquid and $MgCO_3$ plus liquid is shown. Partly schematic.

reactions which it meets at the isobaric invariant point, just as its stoichiometry may be derived from their stoichiometries. By that method one obtains $\Delta H^\circ = 1740$ cal/mol, $\Delta S^\circ = 1.71$ cal/mol, and $\Delta V^\circ = 3.38$ cm³/mol, so that the equilibrium expression becomes $\ln K = [\ln f(CO_2)] - [\ln f(H_2O)] = -874/T + 0.041(P-1)/T + 0.86$. Walter *et al.* (1962) estimated from the geometry of phase relations that the compositions of vapor present at the isobaric invariant point at 1 and 4 kbar were 2.5 and 1.75 mole percent CO_2 respectively. These values are considerably lower than the 7.5 mole percent CO_2 shown in Figure 3 for the isobaric invariant point at 5 kbar. However, the effect of increasing pressure as determined by the experiments is the same as that determined by calculation. The isobaric invariant point is located at increasingly H_2O -rich compositions as pressure increases.

In the subsolidus region magnesite can coexist with vapor of a very wide range of compositions, while brucite may coexist only with H_2O -rich vapor (see Fig. 3). Only a very small amount of CO_2 is required in the vapor phase to produce magnesite from brucite. The presence of both brucite and magnesite buffers the composition of the vapor phase to high values of H_2O-CO_2 . With increasing temperature at constant pressure the buffered vapor phase composition becomes richer in CO_2 , while at constant temperature the composition of the buffered vapor phase becomes much richer in H_2O as pressure increases. Partial dissociation of either brucite or magnesite to form periclase plus vapor produces an assemblage which is capable of buffering the composition of the vapor phase at lower pressures than the assemblage brucite plus magnesite. The way in which these two kinds of assemblages buffer the compositions of the

vapor phase is shown in Figure 3 and in Figure 5, which shows contours of constant vapor composition on several of the divariant subsolidus surfaces.

With increasing pressure the field for the assemblage periclase plus vapor progressively decreases in size. The reactions delineating the subsolidus stability field for periclase plus vapor intersect at invariant points labeled (Br), I, and (MC) in Figure 4. At pressures above the reaction Br + MC → Pe + V, periclase may exist only in bulk compositions containing too little volatiles to react it completely to brucite and magnesite. Even in bulk compositions which do not contain a vapor phase, the presence of brucite plus magnesite fixes the activities and therefore the fugacities of H₂O and CO₂. Because of the high H₂O/CO₂ ratios fixed by the three-phase assemblage brucite plus magnesite plus periclase, most volatile-rich bulk compositions would lie in the divariant field between magnesite and vapor.

Melting relations in the system MgO-H₂O-CO₂

We have considered five phases in the system MgO-H₂O-CO₂: brucite, magnesite, periclase, vapor, and liquid. In a ternary system there is only one point where all five phases coexist. In this system it must happen where the subsolidus reaction Br + MC → Pe + V intersects the solidus. The *P-T* net for the ternary system is shown in Figure 4, where the ternary invariant point is labeled I.

From each of the binary invariant points, (Br) and (MC), shown in Figure 4 a ternary univariant line extends to lower temperatures. These lines meet at the ternary invariant point I at a pressure intermediate between (Br) and (MC). The position of I has been estimated by tracing the path of the reaction MC + Pe + V → L. Because this reaction is a line passing through *P-T-X*(CO₂) space, contours of constant *X*(CO₂) on the divariant surfaces for the reactions MC → Pe + V and MC + Pe + V → L must meet along the line. The *T-X*(CO₂) relations of magnesite with periclase below the solidus have already been discussed, and the contours of constant *X*(CO₂) shown in Figure 5 may be derived easily from the *T-X*(CO₂) sections illustrated in Figure 3. There is no information on vapor-liquid relations in this system. If one assumes that the relations between the compositions of liquid and vapor are analogous to those in the system CaO-H₂O-CO₂, described by Wyllie and Tuttle (1960, Figure 10, curve AF), the contours of constant *X*(CO₂) shown in Figure 5 may be derived. The line along which the two sets of *X*(CO₂) contours intersect is the path of the reaction MC + Pe + V →

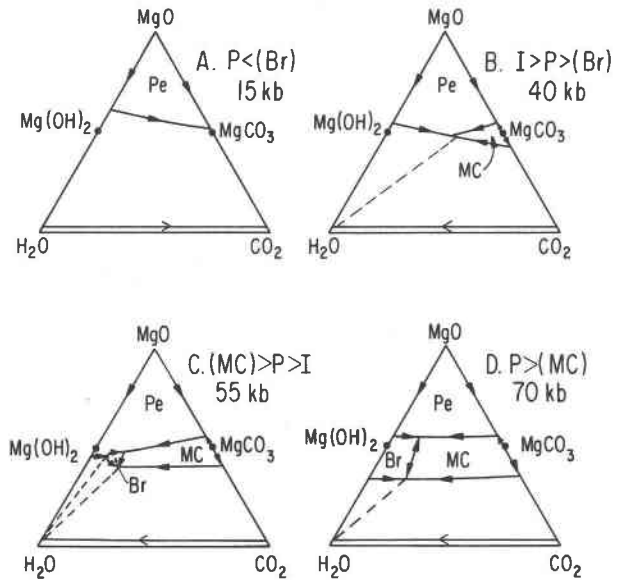


Fig. 6. Schematic isobaric liquidus diagrams for the system MgO-H₂O-CO₂ at various pressures. These diagrams are derived from information in Figs. 3, 4, and 7.

L shown in Figure 4. The ternary invariant point I is located near 46 kbar and 1210°C.

Three reactions originating at the invariant point I trend toward higher pressures: MC + Br + V → L, MC + Br → Pe + L, and Br + L → Pe + V. The slope of the vapor-absent reaction is assumed to be similar to other vapor-absent reactions at the same temperature and pressure, about 5°C per kbar (Huang and Wyllie, 1975). By analogy to the system CaO-H₂O-CO₂ we conclude that the Pe-absent reaction will have a slight negative slope. The MC-absent reaction must be essentially parallel to the reaction Br → Pe + H₂O, because it meets the latter reaction at the invariant point (MC) and originates at I, which is only a few degrees lower in temperature than the brucite dehydration reaction. The changes in melting relations from low to high pressures may be illustrated by reference to the series of schematic isobaric liquidus diagrams shown in Figure 6, which is derived from the *P-T* net given in Figure 4. At pressures below the invariant point (Br) melting begins according to the reaction Pe + V → L, as shown in Figure 6A. The temperature of the first melting varies according to the composition of the vapor, as shown in Figure 5. As increasing pressure causes the solubility of H₂O and CO₂ in the liquid to increase, the solidus temperature is lowered, until at invariant point (Br) the reaction Pe + V → L meets the subsolidus reaction for the decarbonation of magnesite. Melting relations

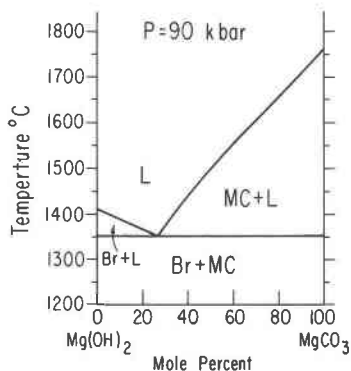


Fig. 7. Calculated phase relations in the binary system $Mg(OH)_2$ - $MgCO_3$. Calculations were made following the method developed by Bradley (1962) for the system $Ca(OH)_2$ - $CaCO_3$. The eutectic composition is 73 mole percent $Mg(OH)_2$ plus 27 mole percent $MgCO_3$.

at pressures between (Br) and I are illustrated in Figure 6B. Magnesite first appears from the MgO - CO_2 sideline of the diagram, and its field of primary crystallization expands toward lower temperatures and more H_2O -rich bulk compositions as pressure increases. The composition of the vapor phase coexisting with periclase and magnesite on the solidus is buffered by the subsolidus decarbonation reaction to high values of H_2O/CO_2 except at pressures just above that of invariant point (Br). The vapor phase is therefore enriched in H_2O with respect to the liquid.

Brucite first appears on the solidus at invariant point I. At pressures above that of I, the solidus is a eutectic reaction between brucite, magnesite, and vapor. As shown in Figures 3 and 5, the composition of the vapor is buffered to very high ratios of H_2O/CO_2 by the subsolidus reaction $MC + H_2O \rightarrow Br + CO_2$. Between invariant points I and (MC) there are also the peritectic reactions $Br + Pe + V \rightarrow L$ and $Br + MC \rightarrow Pe + L$. The first reaction terminates at (MC), because the field for brucite shown in Figure 6C reaches the MgO - H_2O sidelines at the pressure of (MC). The second reaction becomes congruent at the singular point labeled S_2 in Figure 4, changing to the ternary eutectic reaction $Br + MC + Pe \rightarrow L$. At pressures above singular point S_2 there are the two ternary eutectics shown in Figure 6D: between brucite, magnesite, and vapor, and between brucite, magnesite and periclase.

The composition of the eutectic on the join brucite-magnesite has been estimated by the method developed by Bradley (1962) for the system CaO - H_2O - CO_2 . In that system the enthalpies of melting of portlandite and calcite are nearly the same, and the liquid behaves as if it is an ideal solution of portland-

ite and calcite. Assuming that the enthalpies of brucite and magnesite are also equal and using the temperatures of melting given in Figure 4, the binary eutectic shown in Figure 7 may be calculated. The composition of the eutectic liquid is 73 mole percent brucite plus 27 mole percent magnesite. The calculated eutectic composition does not change as pressure is varied.

Figure 6 shows that brucite and magnesite appear in different ways. Magnesite first appears at the MgO - CO_2 sideline and expands across the liquidus surface to isobarically lower temperatures. Brucite first appears at the eutectic on the liquidus surface. Its primary field of crystallization then expands outward to reach the MgO - H_2O sideline at isobarically higher temperatures.

The effect of pressure on the compositions of coexisting liquid and vapor is illustrated in Figure 8, a P - $X(CO_2)$ projection of liquid and vapor compositions along the solidus. A logarithmic scale has been used to plot the compositions because the vapor is very low in CO_2 at high pressures. The labeled points I and (Br) are identical to points with the same labels shown in Figure 4. The heavy line from (Br) to I_1 shows the $H_2O/(H_2O+CO_2)$ ratio of liquids produced by the melting reaction $MC + Pe + V \rightarrow L$, while the light line from (Br) to I_2 shows the $H_2O/(H_2O+CO_2)$ ratio of the coexisting vapor. The com-

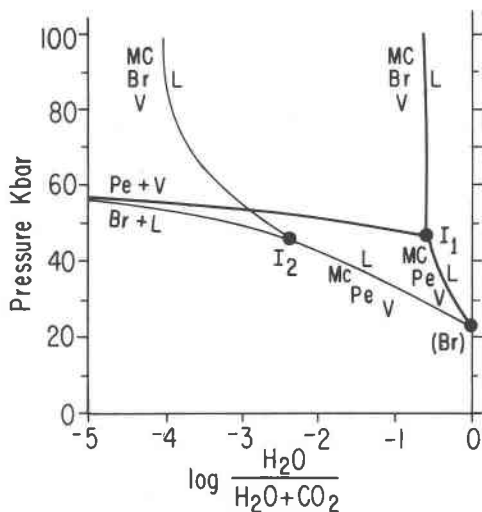


Fig. 8. P - $X(CO_2)$ projection showing the $H_2O/(H_2O+CO_2)$ ratios of coexisting liquid and vapor along the solidus in the system MgO - H_2O - CO_2 . Lines illustrating the composition of vapor are light, and lines illustrating the composition of liquid are heavy. Points I_1 and I_2 show respectively the compositions of liquid and vapor at the invariant point I shown in Fig. 4. Reactions are identified as in Fig. 4.

position of vapor at the solidus at pressures below I is fixed by the intersection of the subsolidus reaction $MC \rightarrow Pe + V$ with the solidus. The points I₁ and I₂ show the H₂O/(H₂O+CO₂) ratios of the coexisting liquid and vapor at invariant point I. The H₂O/(H₂O+CO₂) ratio of liquids coexisting with magnesite does not change significantly at pressures greater than that of the point I. However, the H₂O/(H₂O+CO₂) ratio of the vapor decreases because it is buffered by the intersection of the subsolidus reaction $MC + H_2O \rightarrow Br + CO_2$ with the solidus, till at pressures near 100 kbar there is very little CO₂ in the coexisting vapor. The compositions of liquid and vapor participating in the reaction $Br + L \rightarrow Pe + V$ are also shown in Figure 8. This reaction terminates at the invariant point (MC). That point cannot be shown on the $P-X(CO_2)$ section because it occurs at minus infinity on the logarithmic scale used.

Discussion

There are three kinds of subsolidus reactions in this system which involve vapor: hydration, carbonation, and exchange of H₂O and CO₂. The most significant of these three kinds of reactions for the mantle and for metamorphic rocks is the carbonation of periclase with increasing pressure, and the decarbonation of magnesite with increasing temperature. Only a small amount of CO₂ is required to stabilize magnesite at any pressure above 46 kbar. In the presence of either periclase or brucite, magnesite buffers the composition of the coexisting vapor to high H₂O/CO₂ ratios, except for a narrow pressure interval just above the carbonation reaction which stabilizes magnesite. These same assemblages also buffer the composition of vapor coexisting with liquid at the solidus.

There are three kinds of melting reactions with increasing pressure. (1) At pressures below invariant point (Br), 23 kbar, the melting takes place without either hydrates or carbonates. The melting temperature is controlled by the composition of the vapor phase, which is unbuffered. CO₂ is preferentially partitioned into the liquid. (2) Between the pressures of invariant points (Br) and I, 23 to 46 kbar, magnesite is stable on the solidus in all compositions except for a limited range with extremely high H₂O contents. The solidus is a eutectic reaction between magnesite, periclase, and vapor. The composition of the vapor at that eutectic is buffered by the subsolidus reaction $MC \rightarrow Pe + V$. The composition of the vapor phase is buffered to increasingly higher H₂O/CO₂ ratio as pressure increases through the interval 23 to 46 kbar. Although the H₂O content of the liquid increases

with pressure through this interval, H₂O is strongly partitioned into the vapor and CO₂ into the liquid and carbonate. (3) At pressures above that of invariant point I, 46 kbar, the solidus is a eutectic between brucite, magnesite, and vapor. The H₂O/CO₂ ratio of the liquid probably changes little as pressure increases, and the coexisting vapor is buffered to more H₂O-rich compositions by the subsolidus reaction $MC + H_2O \rightarrow Br + CO_2$. In the high-pressure range there is another eutectic melting reaction for bulk compositions with too few volatiles to react completely with periclase. It is $Br + MC + Pe \rightarrow L$. The liquid formed has an H₂O/CO₂ ratio similar to that of the liquid formed at the eutectic with vapor.

The same sorts of subsolidus hydration, carbonation, and exchange reactions which buffer the composition of coexisting vapor, as well as buffered melting reactions that occur in this system, also occur in more complex systems such as MgO-SiO₂-H₂O-CO₂ (Ellis and Wyllie, in preparation). The presence of a carbonate in these systems at high pressures will control the H₂O/CO₂ ratio of both the near-solidus liquid and the coexisting vapor phase.

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References

- Barnes, H. L. and W. G. Ernst (1963) Ideality and ionization in hydrothermal fluids: the system MgO-H₂O-NaOH. *Am. J. Sci.*, 261, 129-150.
- Bradley, R. S. (1962) Thermodynamic calculations on phase equilibria involving fused salts. Part I. General theory and application to equilibria involving calcium carbonate at high pressure. *Am. J. Sci.*, 260, 374-382.
- Brey, G. and D. H. Green (1975) The role of CO₂ in the genesis of olivine melilitite. *Contrib. Mineral. Petrol.*, 49, 93-103.
- and — (1976) Solubility of CO₂ in olivine melilitite at high pressures and role of CO₂ in the earth's upper mantle. *Contrib. Mineral. Petrol.*, 55, 217-230.
- DeSantis, R., G. J. F. Breedveld and J. M. Prausnitz (1974) Thermodynamic properties of aqueous gas mixtures at advanced pressures. *Ind. Eng. Chem., Process Des. Develop.*, 13, 374-377.
- Eggler, D. H. (1974) Effect of CO₂ on the melting of peridotite. *Carnegie Inst. Wash. Year Book*, 73, 215-224.
- (1976a) Does CO₂ cause partial melting in the low-velocity layer of the mantle? *Geology*, 4, 69-72.
- (1976b) Composition of the partial melt of carbonated peridotite in the system CaO-MgO-SiO₂-CO₂. *Carnegie Inst. Wash. Year Book*, 75, 623-626.
- Goldsmith, J. R. and H. C. Heard (1961) Subsolidus phase relations in the system CaCO₃-MgCO₃. *J. Geol.*, 69, 45-74.
- Green, D. H. (1976) Experimental testing of "equilibrium" partial melting of peridotite under water-saturated high-pressure conditions. *Can. Mineral.*, 14, 255-268.

- Greenwood, H. J. (1962) Metamorphic reactions involving two volatile components. *Carnegie Inst. Wash. Year Book*, 61, 82-85.
- (1967) Mineral equilibria in the system MgO-SiO₂-H₂O-CO₂. In P. H. Abelson, Ed., *Researches in Geochemistry*, v. 2, p. 910-944. Wiley, New York.
- Haselton, H. T., Jr., W. E. Sharp and R. C. Newton (1977) Decarbonation reactions and derived CO₂ fugacities at high pressures and temperatures (abstr.). *EOS (Am. Geophys. Union Trans.)*, 58, 1243.
- Holloway, J. R. (1976) Fugacity and activity coefficients of molecular species in fluids at high pressures and temperatures. *Carnegie Inst. Wash. Year Book*, 75, 771-775.
- (1977) Fugacity and activity of molecular species in supercritical fluids. In D. G. Fraser, Ed., *Thermodynamics in Geology*, p. 161-181. Reidel, Dordrecht, Holland.
- and D. H. Eggler (1976) Fluid-absent melting of peridotite containing phlogopite and dolomite. *Carnegie Inst. Wash. Year Book*, 75, 636-639.
- Huang, W. L. and P. J. Wyllie (1975) Melting and subsolidus phase relationships for CaSiO₃ to 35 kilobars pressure. *Am. Mineral.*, 60, 213-217.
- and ——— (1976) Melting relationships in the systems CaO-CO₂ and MgO-CO₂ to 33 kilobars. *Geochim. Cosmochim. Acta*, 40, 129-132.
- Irving, A. J., W. L. Huang and P. J. Wyllie (1977) Phase relations of portlandite, Ca(OH)₂, and brucite, Mg(OH)₂, to 33 kilobars. *Am. J. Sci.*, 277, 313-321.
- and P. J. Wyllie (1975) Subsidiary and melting relationships for calcite, magnesite and the join CaCO₃-MgCO₃ to 36 kilobars. *Geochim. Cosmochim. Acta*, 39, 35-53.
- Kerrick, D. M. (1974) Review of metamorphic mixed volatile (H₂O-CO₂) equilibria. *Am. Mineral.*, 59, 729-762.
- and J. Slaughter (1976) Comparison of methods for calculating and extrapolating equilibria in P-T-X_{CO₂} space. *Am. J. Sci.*, 276, 883-916.
- Mysen, B. O. and A. L. Boettcher (1975a) Melting of a hydrous mantle. I. Phase relations of natural peridotite at high pressures and temperatures with controlled activities of water, carbon dioxide, and hydrogen. *J. Petrol.*, 16, 520-548.
- and ——— (1975b) Melting of a hydrous mantle. II. Geochemistry of crystals and liquids formed by anatexis of mantle peridotite at high pressures and temperatures as a function of controlled activities of water, hydrogen, and carbon dioxide. *J. Petrol.*, 16, 549-592.
- Nehru, C. E. and P. J. Wyllie (1975) Compositions of glasses from St. Paul's peridotite partially melted at 20 kilobars. *J. Geol.*, 83, 455-471.
- Ohmoto, H. and D. Kerrick (1977) Devolatilization equilibria in graphitic systems. *Am. J. Sci.*, 277, 1013-1044.
- Orville, P. M. and H. J. Greenwood (1965) Determination of ΔH of reaction from experimental pressure-temperature curves. *Am. J. Sci.*, 263, 678-683.
- Robie, R. A. and D. R. Waldbaum (1968) Thermodynamic properties of minerals and related substances at 298.15°K (25.0°C) and one atmosphere (1.013 bars) pressure and at higher temperatures. *U. S. Geol. Surv. Bull.* 1259.
- Walter, L. S., P. J. Wyllie and O. F. Tuttle (1962) The system MgO-CO₂-H₂O at high pressures and temperatures. *J. Petrol.*, 3, 49-64.
- Wyllie, P. J. (1977) Mantle fluid compositions buffered by carbonates in peridotite-CO₂-H₂O. *J. Geol.*, 85, 187-207.
- and W. L. Huang (1975) High CO₂ solubilities in mantle magmas. *Geology*, 4, 21-24.
- and ——— (1976) Carbonation and melting reactions in the system CaO-MgO-SiO₂-CO₂ at mantle pressures with geophysical and petrological applications. *Contrib. Mineral. Petrol.*, 54, 79-107.
- and O. F. Tuttle (1960) The system CaO-CO₂-H₂O and the origin of carbonatites. *J. Petrol.*, 1, 1-46.
- Yamaoka, S., O. Fukunaga and S. Saito (1970) Phase equilibrium in the system MgO-H₂O at high temperatures and very high pressures. *J. Am. Ceram. Soc.*, 53, 179-181.

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