

## Melting phase relations of natural peridotite + CO<sub>2</sub> as a function of degree of partial melting at 15 and 30 kbar

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### Abstract

Phase relations of peridotite + CO<sub>2</sub> have been determined at 15 and 30 kbar using <sup>185</sup>W to monitor the degree of melting. At 15 kbar the initial <5 percent melting interval is affected by the presence of H<sub>2</sub>O formed by the reaction of some H<sub>2</sub> (diffused through the capsule wall) with CO<sub>2</sub> to form H<sub>2</sub>O + CO. This effect becomes insignificant with ≥5 percent melt (~1400°C), where the melting (to ~20 percent melt) is nearly invariant. In this latter melting interval, the melt coexisting with olivine, orthopyroxene, clinopyroxene, and vapor is tholeiitic.

Melting commences more than 200°C lower at 30 kbar than at 15 kbar for both CO<sub>2</sub>-saturated and CO<sub>2</sub>-undersaturated conditions. Again, the exact nature of the melting interval from the solidus to about 5 percent melting is uncertain because of the presence of small amounts of H<sub>2</sub>O in the experimental charges. Dolomite is a solidus phase together with olivine, orthopyroxene, and garnet, and the initial melt is carbonatitic, as evidenced by quenching of the melt to carbonate. With increasing degree of partial melting the melt compositions become richer in silicate components, as evidenced by quenching of the melt to mixtures of silicate glass and carbonate minerals.

These results indicate that the principal phase relations in simple systems such as CaO–MgO–SiO<sub>2</sub>–CO<sub>2</sub> apply to melting of natural peridotite. Published experimental results in this system show a great depression of the solidus temperature (~150°C) as the pressure is raised above that of the carbonation reaction,



At the same time, the liquid composition changes from haplobasalt to haplocarbonatite and therefore serves as a suitable model for liquids produced in the system peridotite + CO<sub>2</sub>.

### Introduction

Investigations in the system CaO–MgO–SiO<sub>2</sub>–CO<sub>2</sub> have emphasized the potential importance of CO<sub>2</sub> and carbonates in the genesis of magmas at pressures corresponding to those of the upper mantle (Eggler, 1975, 1976, 1977, 1978; Wyllie and Huang, 1975a,b). Figure 1 shows the most important melting reactions in a pressure–temperature projection for this system. At pressures below approximately 25 kbar, the solubility of CO<sub>2</sub> in the liquid generated by the melting of diopside + enstatite + forsterite + CO<sub>2</sub> is small (tholeiitic melts contain less than 2 percent CO<sub>2</sub>; Mysen *et al.*, 1975), and the CO<sub>2</sub>-saturated solidus

occurs at only slightly lower temperatures than the volatile-absent solidus. At pressures greater than 25 kbar, the solubility of CO<sub>2</sub> in the initial melt is greater than 20 percent (Holloway *et al.*, 1976), and a great decrease in the solidus temperature occurs over a small (less than 5 kbar) pressure interval. At a pressure between 25 and 30 kbar, at approximately 1200°C, an invariant point, *I*<sub>1</sub>, occurs where the CO<sub>2</sub>-saturated solidus intersects the decarbonation reaction for the assemblage enstatite + dolomite. This point marks the appearance of dolomite as a solidus phase. Melting of the assemblage dolomite + enstatite (both with and without CO<sub>2</sub> vapor present) at higher pressures than *I*<sub>1</sub> results in liquids that have been termed haplocarbonatitic (Eggler, 1976; Wyllie and Huang, 1975a). It is not clear, however, why the

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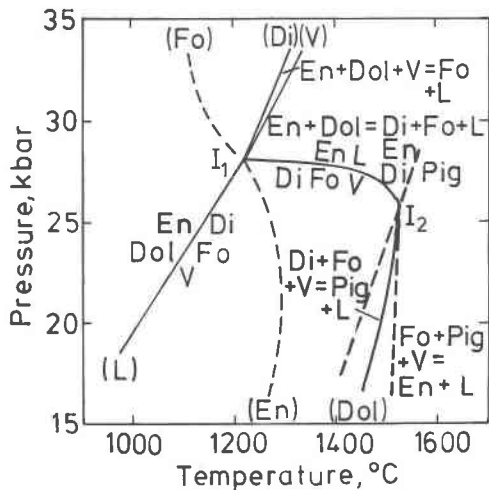


Fig. 1. Melting reactions in the system  $\text{CaO-MgO-SiO}_2\text{-CO}_2$ . Reactions presented in solid lines are applicable to an upper-mantle mineralogy (lherzolite) +  $\text{CO}_2$ . Dashed-line reactions are unimportant because of compositional restrictions. The univariant reactions are labeled by phase-absent notation (in parentheses). Abbreviations: Fo, forsterite; Di, diopside; En, enstatite; Dol, dolomite; L, liquid; V,  $\text{CO}_2$  vapor (data from Eggler, 1976, 1977).

phase relations in this system change so dramatically as the pressure and temperature are changed from those corresponding to  $I_2$  to those corresponding to  $I_1$ .

Although the system  $\text{CaO-MgO-SiO}_2\text{-CO}_2$  is a convenient analogue of a mantle peridotite containing forsterite, enstatite, and clinopyroxene, its applicability to processes of partial melting in the upper mantle is limited by its compositional simplicity. The purpose of the present study was to test whether melting in natural systems can be effectively modeled on the basis of simple systems. The phase relations of a natural garnet lherzolite have been determined at two pressures, one above and the other below the invariant point as determined in the system  $\text{CaO-MgO-SiO}_2\text{-CO}_2$ , to assess whether the melt compositions and solidus temperatures change as indicated by the data in the model system.

#### Experimental details

The starting material was a sheared garnet lherzolite nodule, PHN 1611, described by Nixon and Boyd (1973). The composition of this nodule is considered representative of undepleted peridotite in the upper mantle, and its melting relations as a function of degree of partial melting at 20 and 35 kbar for volatile-absent and water-undersaturated conditions were published by Mysen and Kushiro (1977).

In the present study, a powdered sample of the nodule (approximately -200 mesh) was dried at  $600^\circ\text{C}$  in air for 20 hours to decompose secondary hydrous minerals. About 15 ppb radioactive  $^{185}\text{W}$  (kindly supplied by Dr. George Cowan of the Los Alamos Scientific Laboratory) was added to the powder. The liquid-crystal and liquid-vapor partition coefficients for this isotope have been determined to be in excess of 50; hence, practically all of it enters the melt relative to crystals and vapor. The degree of melting of the rock can be determined by relating the  $^{185}\text{W}$  concentration in a partially melted sample to that in a completely melted sample. The beta activities of both standard and unknowns were recorded on Ilford K-5 nuclear emulsions using the technique of Mysen and Seitz (1975) as adapted to this type of problem by Mysen and Kushiro (1977).

The experiments were conducted in a solid-media, high-pressure apparatus (Boyd and England, 1960) using a piston-out technique with no pressure correction for friction. Pressures are precise to  $\pm 0.5$  kbar and accurate to  $\pm 1.5$  kbar (Eggler, 1977). Temperatures were measured with Pt-Pt90Rh10 thermocouples and automatically controlled to  $\pm 1^\circ\text{C}$  (Hadiadacos, 1972). Temperatures were not corrected for the effect of pressure on the electromotive force of the thermocouple, and are accurate to  $\pm 5^\circ\text{C}$  or better. The latter accuracy is determined by monitoring the electromotive force of the thermocouples as a function of pressure.

The starting materials were contained in sealed 2 mm Pt95Au5 capsules. Carbon dioxide was added as silver oxalate (Boettcher *et al.*, 1973). Talc-Pyrex furnace assemblies were employed for all the experiments. The Pyrex sleeve inhibits migration of water from the breakdown of talc into the sample region, thus decreasing hydrogen diffusion into the capsule. Low hydrogen fugacity retards iron loss to the capsule container and also prevents reduction of  $\text{CO}_2$  and concomitant formation of  $\text{H}_2\text{O}$ .

Even with these precautions, iron loss is substantial. Mysen and Kushiro (1977) reported a 20 percent iron loss from PHN 1611 at 20 kbar and approximately  $1550^\circ\text{C}$  in runs of 60-minute duration. In the present investigation, experiments at low pressures and temperatures generating small amounts of relatively iron-rich melts were occasionally marked by capsule failure due to Fe-Pt alloying. Run durations had to be minimized (to approximately 90 minutes at  $1400^\circ\text{C}$ ) to maintain a coherent capsule. The problem is less serious, however, both at higher temperatures (because the iron content of the melt is

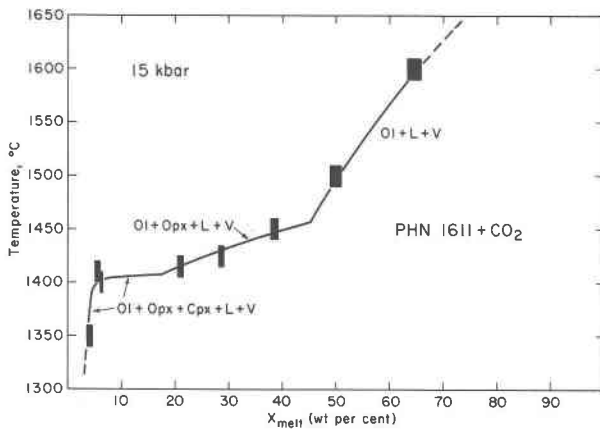


Fig. 2. Melting curve of PHN 1611 + CO<sub>2</sub> at 15 kbar. Size of symbols incorporates uncertainties in temperature ( $\pm 10^\circ\text{C}$ ) and determination of percentage of liquid ( $\pm 1\sigma$ ). Abbreviations: Ol, olivine; Opx, orthopyroxene; Cpx, clinopyroxene; L, liquid; V, vapor.

then substantially diluted) and at higher pressures (at which the melt is carbonatitic).

The presence of trace amounts of water in the charges is suspected on the basis of the observed melting relations at temperatures immediately above

the solidus at both 15 and 30 kbar (see below). The source of this water may be attributed to absorbed H<sub>2</sub>O on the silver oxalate or, more likely, to the *in situ* generation of H<sub>2</sub>O by diffusion of hydrogen from the breakdown of talc into the charge (Eggler *et al.*, 1974).

### Phase relations

The 15 kbar, CO<sub>2</sub>-saturated melting relations of nodule PHN 1611 are shown in Figure 2 as a function of  $X_{\text{melt}}$  (weight percent partial melting). Details of the experiments are given in Table 1. Three phase assemblages were observed: olivine + orthopyroxene + clinopyroxene + liquid + vapor, olivine + orthopyroxene + liquid + vapor, and olivine + liquid + vapor. These phase fields are distinguished by the changes in the slope of the melting curve (Fig. 2). Similar relations for volatile-absent conditions were proposed by Kushiro and Yoder (1974) and by O'Hara (1968) in the system CaO-Al<sub>2</sub>O<sub>3</sub>-MgO-SiO<sub>2</sub> and were observed for natural peridotite by Mysen and Kushiro (1977). Additionally, many simplified phase diagrams show similar changes in slope. The

Table 1. Experimental data

Run no.	P, kbar	T, °C	CO <sub>2</sub> , wt %	Duration, min.	Assemblage*	X <sub>melt</sub> , wt %
538	15	1350	5.95	105	Ol,Opx,Cpx,L,V	4.9 ± 0.1
453	15	1400	8.30	90	Ol,Opx,Cpx,L,V	6.1 ± 0.2
462	15	1410	5.25	75	Ol,Opx,Cpx,L,V	5.3 ± 0.2
482	15	1415	3.75	75	Ol,Opx,L,V	21.1 ± 0.7
461	15	1425	5.10	75	Ol,Opx,L,V	28.6 ± 0.9
456	15	1450	4.75	75	Ol,Opx,L,V	38.4 ± 0.8
451	15	1500	7.70	60	Ol,L,V	49.7 ± 1.0
452	15	1600	10.0	30	Ol,L,V	64.8 ± 1.5
516	30	1150	5.14	180	Ol,Opx,Ga,Carb,L	1.09 ± 0.10
504	30	1200	5.16	120	Ol,Opx,Ga,Carb,L	5.5 ± 0.2
488	30	1225	5.15	120	Ol,Opx,Ga,Carb,L	8.6 ± 0.1
471	30	1250	5.26	90	Ol,Opx,Ga,Carb,L	11.8 ± 0.4
463	30	1300	5.41	120	Ol,Opx,Sp,L	18.4 ± 0.3
475	30	1350	5.19	75	Ol,Opx,L	39.5 ± 0.7
464	30	1400	5.45	75	Ol,Opx,L	43.5 ± 1.0
473	30	1450	5.16	60	Ol,Opx,L	56.7 ± 1.4
465	30	1500	5.35	60	Ol,Opx,L	62.1 ± 1.4
466	30	1600	4.27	30	Ol,L	66.0 ± 1.2
517	30	1100	19.0	270	Ol,Opx,Ga,Carb,L,V	1.14 ± 0.04
509	30	1150	19.2	180	Ol,Opx,Ga,Carb,L,V	3.5 ± 0.1
505	30	1200	15.8	165	Ol,Opx,Ga,Carb,L,V	6.5 ± 0.3
511	30	1300	19.0	120	Ol,Opx,Sp,L,V	40 ± 2
508	30	1400	18.1	60	Ol,Opx,L,V	55.3 ± 2.0
510	30	1500	19.6	30	Ol,Opx,L,V	65.5 ± 2.5

\*Abbreviations: Ol, olivine; Opx, orthopyroxene; Cpx, clinopyroxene; Ga, garnet; Sp, spinel; Carb, carbonate solid solution (dolomite); L, liquid; V, vapor.

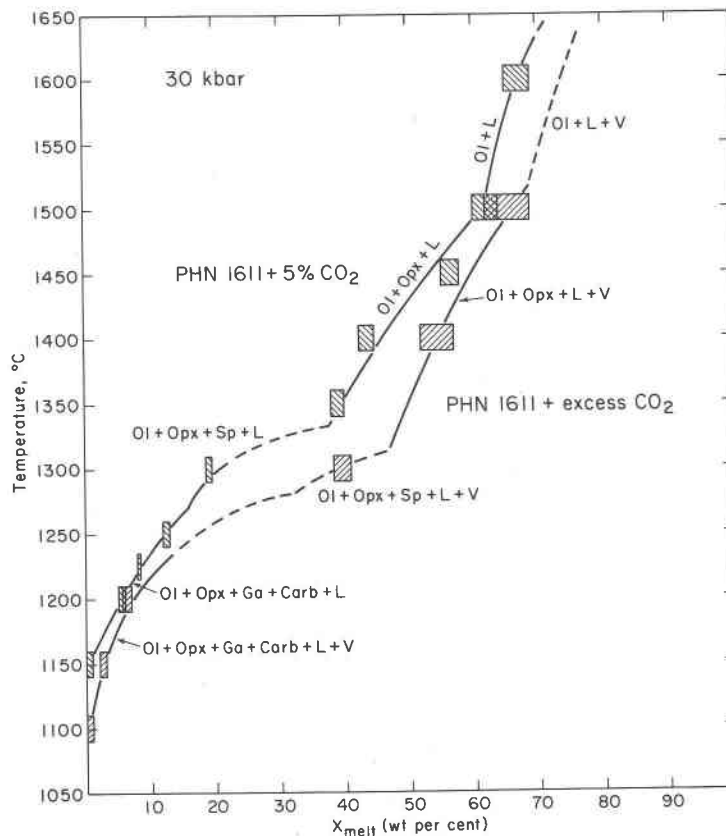
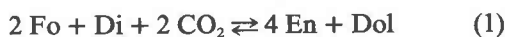


Fig. 3. Melting curves of PHN 1611 + 5 percent  $\text{CO}_2$  (wt) and PHN 1611 + excess  $\text{CO}_2$  at 30 kbar. Size of symbols as defined in Fig. 2. Dashed lines are inferred. Abbreviations as in Fig. 2 and Ga, garnet; Sp, spinel; Carb, carbonate solid solution (dolomite).

solidus temperature of PHN 1611 +  $\text{CO}_2$  at 15 kbar is approximately  $1400^\circ\text{C}$ ; the depression of the melting curve to lower temperatures may be attributed to the presence of approximately 0.2–0.3 percent water if it is assumed that the melt is entirely due to  $\text{H}_2\text{O}$  generated by reaction between  $\text{CO}_2$  and  $\text{H}_2$  and that >99 mole percent of the vapor remains  $\text{CO}_2$  after an experiment (Eggler *et al.*, 1974).

In Figure 3 the 30 kbar melting relations for PHN 1611 +  $\text{CO}_2$  are presented as a function of  $X_{\text{melt}}$ . Two isobars have been determined, the first for  $\text{CO}_2$ -saturated conditions and the second for a total  $\text{CO}_2$  content of 5 weight percent ( $\text{CO}_2$ -undersaturated). In the latter case, the amount of  $\text{CO}_2$  is slightly less than is required to carbonate completely the bulk composition by the reaction



Consequently, a  $\text{CO}_2$  vapor phase is not present during melting.

Major mineralogical differences occur in the phase relations between 15 and 30 kbar, including the ap-

pearance of carbonate and a highly aluminous phase, garnet or spinel, and the disappearance of clinopyroxene. At 30 kbar two major changes have occurred relative to the results at 15 kbar. First, the solidus temperature is lowered by at least  $200^\circ\text{C}$ . Second, dolomite and garnet occur on the solidus.

For conditions of excess  $\text{CO}_2$  at 30 kbar, three phase assemblages were observed: olivine + orthopyroxene + dolomite + garnet + liquid + vapor, olivine + orthopyroxene + spinel + liquid + vapor, and olivine + orthopyroxene + liquid + vapor. The maximum stability ranges of garnet and carbonate were not closely determined; hence they are shown to have the same limits. The solidus temperature is approximately  $1100^\circ\text{C}$  at 30 kbar. This temperature may be too low, however, because some  $\text{H}_2\text{O}$  may have been formed by reaction between  $\text{CO}_2$  in the capsule and  $\text{H}_2$  diffusing through the capsule wall (see above).

Dolomite occurs as discrete stable grains and as quenched intergranular carbonatitic melt to at least  $1200^\circ\text{C}$ . At  $1300^\circ\text{C}$  the quenched liquid contains approximately equal proportions of carbonate and sili-

cate components that are believed to have exsolved during the quench. Spinel is observed at 1300°C and 40 percent melt, and probably represents an incongruent melting product of garnet. At temperatures above 1300°C, forsterite + orthopyroxene + liquid + vapor coexist over a broad temperature and  $X_{\text{melt}}$  range. Relative to the 15-kbar results, the stability of orthopyroxene above the solidus is expanded.

In the presence of 5 percent  $\text{CO}_2$  at 30 kbar, the phase assemblages are olivine + orthopyroxene + dolomite + garnet + liquid, olivine + orthopyroxene + spinel + liquid, olivine + orthopyroxene + liquid, and olivine + liquid. Because there is insufficient  $\text{CO}_2$  to react all the clinopyroxene by equation 1, a small (though undetected) interval of olivine + orthopyroxene + clinopyroxene + dolomite + garnet + liquid must exist near the solidus. Garnet and dolo-

Table 2. Melt compositions at 15 kbar

	Melt temperature			
	1415°C*	1425°C**	1500°C†	1600°C†
$\text{SiO}_2$	51.49	50.11	48.99	45.69
$\text{TiO}_2$	0.75	0.79	0.50	0.38
$\text{Al}_2\text{O}_3$	10.47	10.79	5.56	4.27
$\text{Fe}_2\text{O}_3$	n.d.	n.d.	2.80	2.14
$\text{FeO}$	9.87††	10.75††	14.01	11.94
$\text{MnO}$	0.24	0.24	0.18	0.15
$\text{MgO}$	9.08	9.13	20.47	29.28
$\text{CaO}$	9.26	9.11	6.58	5.02
$\text{Na}_2\text{O}$	0.53	0.67	0.68	0.52
$\text{K}_2\text{O}$	0.37	0.42	0.28	0.21
$\text{NiO}$	<0.05	<0.05	n.d.	n.d.
$\text{Cr}_2\text{O}_3$	0.48	0.49	0.46	0.38
Totals	92.54	92.49	100.00	100.00

\*Run no. 482; four analyses.

\*\*Run no. 461; eight analyses.

†Calculated using known proportions of melt and olivine compositions.

††All iron determined as  $\text{FeO}$ .

mite disappear at approximately 1275°C, and spinel is then observed in a small melting interval.

As in the presence of excess  $\text{CO}_2$  vapor, dolomite occurs both as discrete, stable grains and as melt quench to approximately 1300°C (20 percent melt). Carbonate quench minerals from the liquid are observed at 1350°C (40 percent melt) but are accompanied by approximately equal amounts of quenched silicate glass that unmixed on the quench. Olivine is the liquidus phase at temperatures in excess of 1500°C.

The melting curve in the presence of a  $\text{CO}_2$ -rich vapor phase occurs at lower temperatures than under  $\text{CO}_2$ -undersaturated conditions. At 1300°C there is a difference of about 30 percent melt between the two isobars; this difference decreases with increasing temperature. The close proximity of the two curves at lower temperatures may be due to the similar  $\text{CO}_2$  contents of both melts under these conditions.

### Compositional relations

In Figure 4 the observed variation of  $\text{Mg}/(\text{Mg} + \Sigma\text{Fe})$  with melting for olivine at 15 and 30 kbar and for orthopyroxene at 30 kbar is illustrated. As a rule, this ratio correlates with the phase relations; it varies only slightly in the intervals of constant mineralogy, but where inflections occur in the melting curve, inflections in the  $\text{Mg}/(\text{Mg} + \Sigma\text{Fe})$  as a function of  $X_{\text{melt}}$  are also observed. In the higher-temperature melting intervals, where fewer phases are present (higher  $X_{\text{melt}}$ ), the  $\text{Mg}/(\text{Mg} + \Sigma\text{Fe})$  tends to increase more continuously with increasing degree of melting.

In Table 2, melt compositions at 15 kbar are tabulated. The totals of the analyses are less than 100 percent because of dissolved  $\text{CO}_2$  and possibly  $\text{H}_2\text{O}$ . Because of difficulties in quenching the higher-

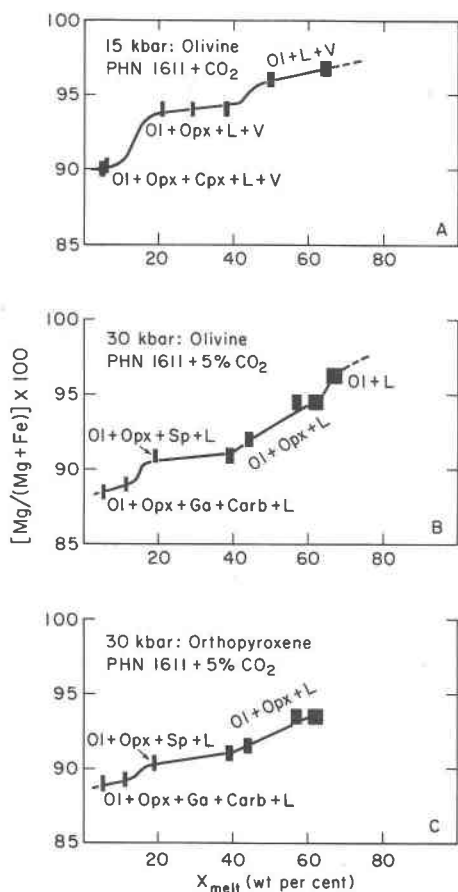


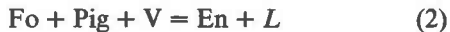
Fig. 4.  $\text{Mg}/(\text{Mg} + \text{Fe})$  compositional data as a function of  $X_{\text{melt}}$  (A) for olivines at 15 kbar, (B) for olivines at 30 kbar, and (C) for orthopyroxenes at 30 kbar. Size of symbols incorporates uncertainties in electron microprobe analyses and percentage of liquid ( $\pm 1\sigma$ ). Abbreviations as in Figs. 2 and 3.

temperature liquids, their compositions are calculated. Melt compositions are approximately tholeiitic at temperatures near the solidus and become picritic at temperatures approaching 1600°C. The melts at 30 kbar could not be analyzed, but they are carbonatitic to at least 20 percent melt, as evidenced by the presence of only quench carbonate in place of melt.

### Discussion

The topology of the melting curve of peridotite + CO<sub>2</sub> resembles that determined in the simple system CaO–MgO–SiO<sub>2</sub>–CO<sub>2</sub> (Fig. 1). In this simple system, at pressures below that of the appearance of carbonate on the solidus, the melting relations in the vapor-absent system are similar to those in the presence of CO<sub>2</sub>. The solidus temperature of natural peridotite + CO<sub>2</sub> at 15 kbar is near 1400°C. Extrapolation of the solidus temperatures of nodule PHN 1611 from the pressures studied by Mysen and Kushiro (1977) indicates that the vapor-absent solidus of nodule PHN 1611 would also be near 1400°C. The insignificant difference between the two temperatures is in agreement with observations in the system CaO–MgO–SiO<sub>2</sub>–CO<sub>2</sub> (Eggler, 1975), and is also expected because the solubility of CO<sub>2</sub> in tholeiitic melts at this pressure and temperature (1 weight percent) is so low that no significant lowering of the temperature of the solidus is anticipated.

The phase relations of natural peridotite + CO<sub>2</sub> in the melting interval also resemble those in the CO<sub>2</sub>-free system, at least for pressures below the appearance of carbonate as a solidus phase. Eggler (1978) suggested that in the system CaO–MgO–SiO<sub>2</sub>–CO<sub>2</sub> the equation



describes the melting. In the CO<sub>2</sub>-free systems, CaO–MgO–SiO<sub>2</sub> and CaO–MgO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>, and nodule PHN 1611, the vapor-absent form of this equation has been shown to describe the melting behavior at pressures of 15–20 kbar (Kushiro, 1969; Kushiro and Yoder, 1974; Mysen and Kushiro, 1977). A similar reaction may take place in peridotite + CO<sub>2</sub> at 15 kbar:



It is notable that Al<sub>2</sub>O<sub>3</sub> is not considered a significant component in any of these melting reactions. Because the pigeonite (see Eggler, 1978, and Mysen and Kushiro, 1977, for discussions of the appearance of pigeonite in these systems) contains about the same amount of alumina as the melt, it does not sig-

nificantly affect the phase relations. In natural peridotite + CO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, FeO, and alkalis occur in solid solution. The Al<sub>2</sub>O<sub>3</sub> was accounted for above. It appears that the small amounts of alkali and iron in solid solution result in only a small temperature change (15°–20°C) of the first melting interval (excluding the portion where H<sub>2</sub>O apparently affects the phase relations) as seen in Figure 2. The slope of the melting curve at higher degrees of freedom (after clinopyroxene has melted out) steepens, as would be expected.

We conclude, therefore, that the melting relations of peridotite and peridotite + CO<sub>2</sub> are for all practical purposes similar at pressures below that corresponding to the intersection of the peridotite solidus and the first carbonation reaction.

From the petrologist's point of view, perhaps the most important observation in the studies in the system CaO–MgO–SiO<sub>2</sub>–CO<sub>2</sub> is the large depression of the solidus in the pressure interval between invariant points *I*<sub>1</sub> and *I*<sub>2</sub> (Fig. 1). The melt at pressures corresponding to perhaps 100 km in the mantle has a haplocarbonatitic composition. The solidus temperature of natural garnet peridotite + CO<sub>2</sub> (Fig. 3) is at least 200°C (perhaps as much as 300°C) lower than that at 15 kbar, and the liquid is carbonatite. In both these respects, the results agree with those obtained in the system CaO–MgO–SiO<sub>2</sub>–CO<sub>2</sub> (Eggler, 1975, 1976, 1978; Wyllie and Huang, 1975a,b, 1976). The presence of H<sub>2</sub> in the CO<sub>2</sub>-undersaturated experiments will result in a small amount of vapor through reaction with carbonate; thus, the solidus of CO<sub>2</sub>-undersaturated peridotite PHN 1611 + CO<sub>2</sub> will be at a slightly higher temperature than 1150°C at 30 kbar (see Fig. 3).

The presence of garnet on the solidus of peridotite + CO<sub>2</sub> at 30 kbar shows that the phase equilibria of garnet peridotite + CO<sub>2</sub> cannot be modeled accurately by the simple system CaO–MgO–SiO<sub>2</sub>–CO<sub>2</sub>. Although no detailed phase-equilibrium data are available for the system CaO–MgO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>–CO<sub>2</sub> at pressures corresponding to those of the experimental results, a few generalized comments can be made. In the case of CO<sub>2</sub>-undersaturated melting, a small amount (1–2 percent) of clinopyroxene should be present on the solidus. An isobarically invariant mineral assemblage, Ol + Opx + Cpx + Ga + Dol + L, with a liquid of carbonatitic composition, must exist near the solidus. This melting interval is undetectable experimentally, probably because the amount of quench carbonate tends to obliterate the experimental charges, making detection of small amounts of

any phase difficult. After the clinopyroxene is melted out, the melting interval involving Ol + Opx + Ga + Dol + L (Fig. 3) is reached, and the melt becomes increasingly depleted in carbonate component as the degree of melting (and temperature) is increased. The width of both these first melting intervals will be a function of the amount of CO<sub>2</sub> in the rock.

Melting of peridotite with CO<sub>2</sub> in excess of that needed to convert the diopside component to carbonate (CO<sub>2</sub>-oversaturated) differs from CO<sub>2</sub>-undersaturated melting in that the clinopyroxene is absent in the melting interval and the melt is always CO<sub>2</sub>-saturated. The latter feature accounts for the lower temperatures of the melting interval of the Ol + Opx + Ga + Dol + L + V compared with that of Ol + Opx + Ga + Dol + L. The former mineral assemblage is isobarically invariant in the system CaO–MgO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>–CO<sub>2</sub>. The significant deviations from constant temperature of this melting interval (Fig. 3) are inferred to be caused by small amounts of H<sub>2</sub>O in the charge, although the possibility that the deviations are related to the presence of small amounts of other components cannot be ruled out entirely. The observations of Egger *et al.* (1974) indicate that as much as 0.4–0.5 weight percent H<sub>2</sub>O may have been generated by the reaction of CO<sub>2</sub> with H<sub>2</sub> (about 15 weight percent CO<sub>2</sub> was added to the charges and about 1 mole percent CO<sub>2</sub> has been reduced to form H<sub>2</sub>O and CO).

### Petrological applications

Oceanic tholeiite characteristically contains CO<sub>2</sub> as the major volatile component (Delaney *et al.*, 1978). Despite this observation, it has been suggested that the formation of primary abyssal tholeiite beneath oceanic ridges reflects melting of volatile-free peridotite mantle. This suggestion is based on the close similarity between bulk compositions of oceanic tholeiites and the composition of the partial melts from the near-invariant melting interval of peridotite in the absence of volatiles at pressures corresponding to depths of 25 to 30 km in the oceanic mantle (Kushiro, 1973; Hodges and Bender, 1976; Fujii and Kushiro, 1977; Mysen and Kushiro, 1977; Presnall *et al.*, 1979). Our phase equilibrium data on peridotite + CO<sub>2</sub> at 15 kbar may be used to reconcile the apparent discrepancy between observations from rocks and suggestions based on phase equilibrium data. According to these data, the melting behavior of peridotite with CO<sub>2</sub> is essentially identical with invariant-like melting, resulting in tholeiitic liquid at least in the 5–20 percent melting interval. It is concluded,

therefore, that abyssal tholeiite may have formed by partial melting with carbon dioxide.

Carbonatites in stable continental shields such as that of southern Africa commonly contain garnet peridotite nodules (*e.g.*, Ridley and Dawson, 1975), testifying to their depth of origin. On the basis of his data on the system CaO–MgO–SiO<sub>2</sub>–CO<sub>2</sub>, Egger (1975) first suggested that peridotite + CO<sub>2</sub> at pressures above 25 kbar may form melts that contain several tens of weight percent CO<sub>2</sub> and have kimberlitic affinities. This suggestion was subsequently slightly modified to one indicating that the partial melt probably is carbonatitic (Egger, 1976; Wyllie and Huang, 1976). The present data show that even a natural carbonated peridotite containing garnet, two pyroxenes, and olivine in addition to carbonate will produce carbonatitic liquids upon partial melting at depths of 90–100 km in the mantle. In fact, as was also the case for the simple system (Egger, 1976), pressures corresponding to such depths are necessary to produce carbonatitic partial melts. It should also be mentioned that Mysen and Boettcher (1975) noted quench carbonate in their experiments with peridotite in equilibrium with a vapor with CO<sub>2</sub>/(CO<sub>2</sub> + H<sub>2</sub>O) ≥ 0.75 at 25 kbar and with that volatile ratio equal to 0.5 at 30 kbar. They suggested that this carbonate represented quench material from the vapor. In the light of our data and the physical appearance of those quench carbonate minerals, their products may well have included quench phases from partial melts, not vapor. In that case, it seems that even if the vapor is diluted by as much as 50 mole percent H<sub>2</sub>O, the partial melt at 30 kbar will have carbonatitic affinities.

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### References

- Boettcher, A. L., B. O. Mysen and J. C. Allen (1973) Techniques for the control of water fugacity and oxygen fugacity for experimentation in solid-media, high-pressure apparatus. *J. Geophys. Res.*, 78, 5898–5901.
- Boyd, F. R. and J. L. England (1960) Apparatus for phase-equilibrium measurements at pressures up to 50 kilobars and temperatures up to 1750°C. *J. Geophys. Res.*, 65, 741–748.
- Delaney, J. R., D. W. Muenow and D. G. Graham (1978) Abundance and distribution of water, carbon and sulfur in glassy rims of submarine pillow basalts. *Geochim. Cosmochim. Acta*, 42, 581–594.
- Egger, D. H. (1975) Peridotite–carbonate relations in the system CaO–MgO–SiO<sub>2</sub>–CO<sub>2</sub>. *Carnegie Inst. Wash. Year Book*, 74, 468–474.

- (1976) Does CO<sub>2</sub> cause partial melting in the low-velocity layer of the mantle? *Geology*, 4, 69–72.
- (1977) The principle of the zone of invariant vapor composition: an example in the system CaO–MgO–SiO<sub>2</sub>–H<sub>2</sub>O and implications for the mantle solidus. *Carnegie Inst. Wash. Year Book*, 76, 428–435.
- (1978) The effect of CO<sub>2</sub> upon partial melting of peridotite in the system Na<sub>2</sub>O–CaO–Al<sub>2</sub>O<sub>3</sub>–MgO–SiO<sub>2</sub>–CO<sub>2</sub> to 35 kb, with an analysis of melting in a peridotite–H<sub>2</sub>O–CO<sub>2</sub> system. *Am. J. Sci.*, 278, 305–343.
- , B. O. Mysen and T. C. Hoering (1974) Gas species in sealed capsules in solid-media, high-pressure apparatus. *Carnegie Inst. Wash. Year Book*, 73, 228–232.
- Fujii, T. and I. Kushiro (1977) Melting relations and viscosity of an abyssal tholeiite. *Carnegie Inst. Wash. Year Book*, 76, 461–465.
- Hadidiacos, C. (1972) Temperature controller for high-pressure apparatus. *Carnegie Inst. Wash. Year Book*, 71, 620–622.
- Hodges, F. N. and J. F. Bender (1976) Petrogenesis of basalt glass from project FAMOUS: experimental study from 1 atm to 15 kbar (abstr.). *Geol. Soc. Am. Abstracts with Programs*, 8, 920.
- Holloway, J. R., B. O. Mysen and D. H. Eggler (1976) The solubility of CO<sub>2</sub> in liquids on the join CaO–MgO–SiO<sub>2</sub>–CO<sub>2</sub>. *Carnegie Inst. Wash. Year Book*, 75, 626–631.
- Kushiro, I. (1969) The system forsterite–diopside–silica with and without water at high pressures. *Am. J. Sci.*, 267A, 269–294.
- (1973) Origin of some magmas in oceanic and circum-oceanic regions. *Tectonophysics*, 17, 211–222.
- and H. S. Yoder, Jr. (1974) Formation of eclogite from garnet lherzolite: liquidus relations in a portion of the system MgSiO<sub>3</sub>–CaSiO<sub>3</sub>–Al<sub>2</sub>O<sub>3</sub> at high pressure. *Carnegie Inst. Wash. Year Book*, 73, 266–269.
- Mysen, B. O. and A. L. Boettcher (1975) Melting of a hydrous mantle. I. Phase relations of a natural peridotite at high pressures and temperatures with controlled activities of water, carbon dioxide and hydrogen. *J. Petrol.*, 16, 520–548.
- and I. Kushiro (1977) Compositional variations of coexisting phases with degree of melting of peridotite in the upper mantle. *Am. Mineral.*, 62, 843–865.
- and M. G. Seitz (1975) Trace element partitioning determined by beta-track mapping—an experimental study using carbon and samarium as examples. *J. Geophys. Res.*, 80, 2627–2635.
- , R. J. Arculus and D. H. Eggler (1975) Solubility of carbon dioxide in melts of andesite, tholeiite and olivine nephelinite composition to 30 kbar pressure. *Contrib. Mineral. Petrol.*, 53, 227–239.
- Nixon, P. H. and F. R. Boyd (1973) Petrogenesis of the granular and sheared ultrabasic nodule suite in kimberlites. In P. H. Nixon, Ed., *Lesotho Kimberlites*, p. 48–56. Lesotho National Development Corporation, Maseru, Lesotho.
- O'Hara, M. J. (1968) The bearing of phase equilibria studies in synthetic and natural systems on the origin and evolution of basic and ultrabasic rocks. *Earth Sci. Rev.*, 4, 69–133.
- Presnall, D. C., J. R. Dixon, T. H. O'Donnell and S. A. Dixon (1979) Generation of mid-ocean ridge tholeiites. *J. Petrol.*, 20, 3–35.
- Ridley, W. I. and J. B. Dawson (1975) Lithophile trace element data bearing on the origin of peridotite xenoliths, ankaramite and carbonatite from Lashaine volcano, N. Tanzania. *Phys. Chem. Earth*, 9, 559–571.
- Wyllie, P. J. and W. L. Huang (1975a) Influence of mantle CO<sub>2</sub> in the generation of carbonatites and kimberlites. *Nature*, 257, 297–299.
- and ——— (1975b) Peridotite, kimberlite, and carbonatite explained in the system CaO–MgO–SiO<sub>2</sub>–CO<sub>2</sub>. *Geology*, 3, 621–624.
- and ——— (1976) Carbonation and melting reactions in the system CaO–MgO–SiO<sub>2</sub>–CO<sub>2</sub> at mantle pressures with geophysical and petrological applications. *Contrib. Mineral. Petrol.*, 54, 79–107.

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