Petrogenetic grid for siliceous dolomites extended to mantle peridotite compositions and to conditions for magma generation

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Abstract

Decarbonation reactions in the system $CaO\text{-}MgO\text{-}SiO_2\text{-}CO_2$ involve calcite, dolomite, magnesite, and quartz, and the products enstatite, forsterite, diopside, and wollastonite, among others. Each decarbonation reaction terminates at an invariant point involving a liquid, CO_2 vapor, carbonate minerals, and one or more of the silicate minerals. Fusion curves for mantle mineral assemblages involving forsterite, orthopyroxene, and clinopyroxene in the presence of CO_2, extending from higher temperature regions, terminate at these same invariant points. The points are connected by a series of liquidus reactions involving the carbonates and mantle silicates, at temperatures generally lower than the silicate-CO_2 melting reactions. Experimental data and theoretical analysis permit construction of a series of partly schematic phase diagrams. Petrological and geophysical conclusions include the following: (1) Free CO_2 cannot exist in the mantle; it is stored as carbonate. (2) CO_2 appears to be as effective as H_2O in causing incipient melting of mantle peridotite, and this remains our preferred explanation for the seismic low-velocity zone. (3) At depths greater than about 80 km, mantle peridotite with CO_2 (as carbonate) yields carbonatitic magmas with about 40 percent CO_2 and 10 percent silicates in solution; with progressive fusion the liquid becomes kimberlitic. (4) Primary carbonatite or kimberlite magmas rising from the asthenosphere must evolve CO_2 near 80 km depth, which would contribute to their explosive eruption. (5) Through a wide pressure range, SiO_2-undersaturated basic magmas with CO_2 in solution can yield residual kimberlitic or carbonatitic magmas. (6) Deep mantle magmas may include the carbonated alkali ultrabasic magmas that have been proposed as the parents from which continental associations of highly alkalic rocks are derived.

Introduction

Bowen's (1940) petrogenetic grid was based initially on decarbonation reactions in the system $CaO\text{-}MgO\text{-}SiO_2\text{-}CO_2$ with starting assemblages involving calcite, dolomite, magnesite, and quartz. Bowen compared the theoretical sequence of reactions with those deduced from the progressive metamorphism of siliceous dolomites. The reactions introduce silicate minerals including enstatite, forsterite, diopside, and wollastonite, and addition of water introduces tremolite (see Turner, 1968, p. 131–151; Skippen, 1974; Kerrick, 1974). Wyllie and Huang (1976) extended some of the decarbonation

reactions to high pressures and temperatures equivalent to those in the upper mantle. Each reaction terminates at an invariant point where the temperature becomes high enough to generate a liquid phase, and these points are connected by a series of univariant melting reactions involving carbonates and silicates. Of particular interest are the reactions involving forsterite, orthopyroxene, and clinopyroxene, the minerals dominant in mantle peridotite. In this paper, we present the partly schematic framework for decarbonation and melting reactions at upper mantle pressures. This provides constraints leading to petrological and geophysical conclusions that must remain

valid, even if continued experimentation indicates changes in the detailed phase relationships.

Mantle volatiles and magma genesis

There is now considerable support for the opinion that both H_2O and CO_2 exist in the mantle, and experimental exploration has indicated that these volatile components would exert significant influence on magmatic processes in and above the seismic low-velocity zone. In the quadrennial *U. S. National Report to the International Union of Geodesy and Geophysics,* Boettcher (1975) reviewed recent experimental efforts to evaluate their influence on upper mantle processes.

Experimental approaches to problems of magma genesis include (1) determination of the melting relationships of whole rocks, including source rocks such as peridotite–H_2O–CO_2 (Mysen and Boettcher, 1975a, 1975b) and possible derivative magma compositions such as olivine melilitite–H_2O–CO_2 (Brey and Green, 1975); (2) determination of the melting relationships of mineral assemblages representing rock systems, such as forsterite–enstatite–diopside–CO_2 (Eggler, 1974) or forsterite–enstatite–CO_2–H_2O (Eggler, 1975); (3) determination of melting relationships in simple systems that include the rock-forming minerals, such as CaO–MgO–SiO_2–CO_2 (Huang and Wyllie, 1974a, 1974b; Wyllie and Huang, 1976).

A dominant role for CO_2 is evident in the genesis of and relationships between kimberlite and carbonatite, according to many papers in the proceedings of the First International Kimberlite Conference (Ahrens *et al.,* 1975). Petrological studies confirm that crystallization of kimberlite magmas can produce residual carbonatite (*e.g.* Watson, 1955; Dawson and Hawthorne, 1973). Our interest in these problems (Franz, 1965; Wyllie, 1966; Franz and Wyllie, 1967; Wyllie and Haas, 1966) led us to investigation of the melting relationships between carbonates and silicates in parts of the system CaO–MgO–Al_2O_3–SiO_2–CO_2–H_2O at high pressures, which provides a magnified view of the influence of small proportions of CO_2 on mantle peridotite (Boettcher and Wyllie, 1969; Huang and Wyllie, 1974a, 1974b, 1975, 1976; Huang, Wyllie and Nehru, in preparation, CaO–SiO_2–CO_2; Irving and Wyllie, 1973, 1975; Maaløe and Wyllie, 1975; Maaløe and Wyllie, in preparation, pyrope–magnesite; Wyllie and Boettcher, 1969; Wyllie and Huang, 1976). Other experimental data have been incorporated into the analysis of phase relations (Eggler, 1973, 1975; Eggler *et al.,* 1974; Newton and Sharp, 1975; Yoder, 1975).

Decarbonation reactions in the system CaO–MgO–SiO_2–CO_2

Table 1 lists the reactions illustrated in the figures, identifies them by number increasing in the direction of increasing temperature (or decreasing pressure), and explains the abbreviations used in the figures. Figure 1 shows the measured or estimated positions of most of the decarbonation reactions. Binary and ternary reactions are terminated at invariant points where the subsolidus phase assemblage is joined by a liquid phase, and these are connected by ternary melting reactions.

The quaternary decarbonation reactions are distinguished by heavy lines extending into the region be-

TABLE 1. Univariant decarbonation reactions in the system CaO–MgO–SiO_2–CO_2

Reaction Number	System and reaction
	CaO–MgO–CO_2
10.	MC $=$ Pe + V
11.	Cm $=$ Cd + Pe + V
12.	Cd $=$ Cc + Pe + V
14.	CC $=$ C + V
	CaO–SiO_2–CO_2
7.	CC + Qz $=$ Wo + V
13.	CC + Wo $=$ Sp + V
	MgO–SiO_2–CO_2
1.	MC + Qz $=$ En + V
3.	MC + En $=$ Fo + V
	CaO–MgO–SiO_2–CO_2
2.	Cm + Qz $=$ En + V
4.	Cm + Opx $=$ Fo + Cd + V
5.	Cd + Opx + Qz $=$ Cpx + V
6.	Cd + Opx $=$ Cpx + Fo + V
8.	Cc + Qz $=$ Wo_{ss} + V
9.	Cd + Cpx $=$ Fo^{ss} + Cc + V

Abbreviations: V = CO_2, CC = calcite, MC = magnesite, Pe = periclase, C = lime, Qz = quartz, Wo = wollastonite, Sp = spurrite, En = enstatite, Fo = forsterite, Opx = orthopyroxene, Cpx = clinopyroxene, ss = solid solution; Cc, Cd, and Cm = carbonate solid solutions with composition related to calcite, dolomite, or magnesite, respectively, at lower temperature or pressure; Ccd or Cdm intermediate solid solutions. Other abbreviations used in figures: Ar = aragonite, 2L = immiscible liquids, Ca = lime, La = polymorphs of dicalcium silicate, Ph = phlogopite.
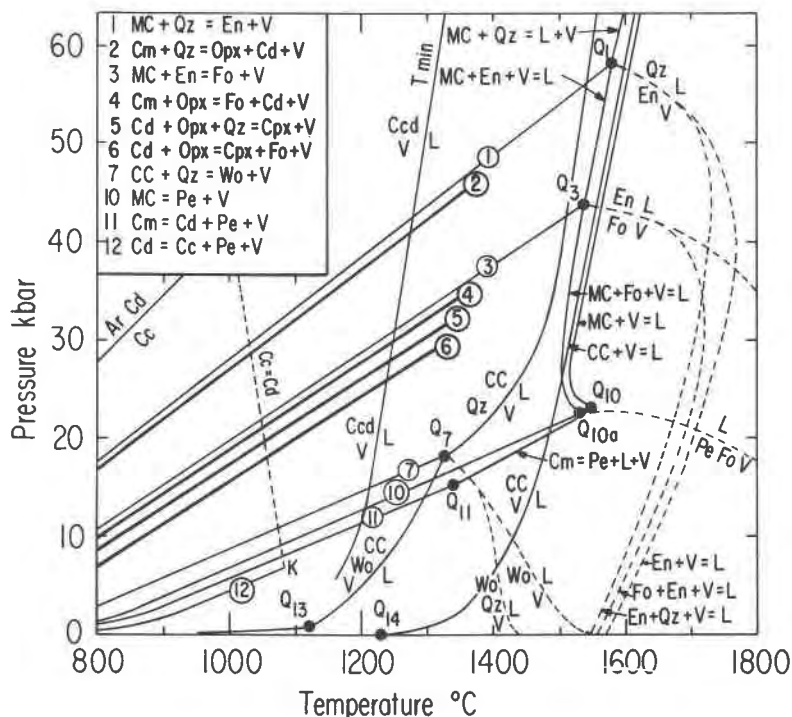
FIG. 1. Decarbonation reactions in the system $CaO-MgO-SiO_2-CO_2$, partly schematic and extrapolated. For sources of data see text. See Table 1 for reactions and abbreviations. Binary and ternary reactions terminate at invariant points involving liquids. The quaternary reactions (heavy lines) extend into the melting region between the ternary silicate–carbonate–CO_2 liquidus reactions and the liquidus minimum in the system $CaO-MgO-CO_2$. The dashed lines show the effect of CO_2 under pressure on the melting temperatures of silicates (Wyllie and Huang, 1976).

tween the silicate-carbonate melting reactions in the systems $CaO-SiO_2-CO_2$ and $MgO-SiO_2-CO_2$, and the estimated liquidus temperature minimum in the system $CaO-MgO-CO_2$. A glance ahead to Figure 2 shows that these reactions also terminate at invariant points involving liquids. Low-pressure reactions involving monticellite, akermanite, and spurrite have been omitted for simplicity. They are not involved at mantle pressures (Kushiro and Yoder, 1964; Yoder, 1968, 1975; Huang, Wyllie and Nehru, in preparation).

The group of reactions (3), (4), (5), and (6) involve two or more of the mantle minerals Fo, Opx, and Cpx, together with a carbonate and CO_2 as vapor. Reaction (3) in the system $MgO-SiO_2-CO_2$ was measured by Newton and Sharp (1975) to 40 kbar. We have confirmed their results and located the position of reaction (6) with reversed brackets. It passes through 15 kbar-960°C with slope 45 bar/°C, within 75°C and 3 kbar of reaction (3). Reactions (4) and (5) must lie between these two.

The compositions of coexisting carbonates and pyroxenes in these reactions are given by the solvus data of Davis and Boyd (1966), Nehru and Wyllie (1974), and Irving and Wyllie (1975). For the mantle silicate assemblage Fo+Opx+Cpx of reaction (6), CO_2 vapor can exist only on the high temperature (or low pressure) side, and this reacts with the silicates to yield the carbonate Cd on the low temperature (or high pressure) side. The carbonate Cd is a calcic dolomite, with Ca/Mg near 70/30, varying with pressure and temperature.

Melting reactions in the system $CaO-MgO-SiO_2-CO_2$

The quaternary decarbonation reactions from Figure 1 plus reaction (8) from Table 1 are shown in Figure 2 terminating at six-phase invariant points where the subsolidus assemblages are joined by a liquid phase. The invariant points occur at temperatures below the melting reactions for the ternary systems $CaO-SiO_2-CO_2$ and $MgO-SiO_2-CO_2$, the un-
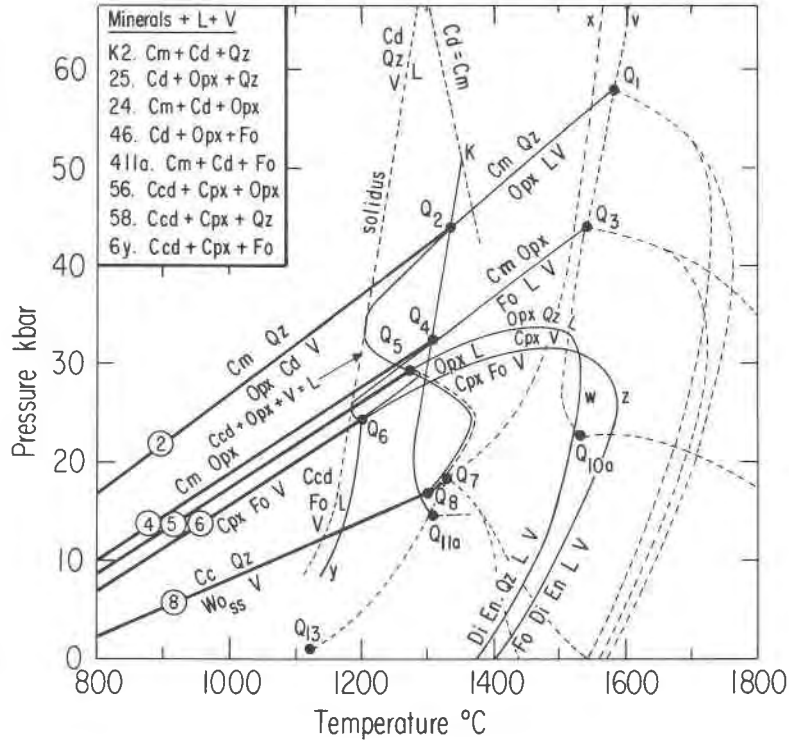
FIG. 2. Decarbonation and melting reactions in the system CaO–MgO–SiO$_2$–CO$_2$, partly schematic. Quaternary decarbonation reactions and ternary melting reactions transferred from Fig. 1 For sources of data see text. See Table 1 for abbreviations. Quanternary 5-phase liquidus reactions emanate from the invariant points reaction K2 connects points K and Q_2; reaction 25 connects Q_2 and Q_5, etc. (Wyllie and Huang, 1976).

labeled dashed lines transferred from Figure 1, and above the estimated quaternary solidus curve, which is placed about 50°C below the liquidus minimum for carbonates shown in Figure 1. The solidus is shown as a dashed line where it corresponds to a thermal minimum on the liquidus surface, with short intervals as a solid line where it is represented by a eutectic reaction.

From each invariant point there extends a series of additional univariant curves involving a liquid, and the arrangement of these quaternary CO$_2$-saturated melting reactions connecting the invariant points is shown. Reactions without vapor are omitted for clarity.

Construction of Figure 2 began with the application of Schreinemakers' (1916) rules and continued with a series of trial assumptions about the compositions of liquids added to each subsolidus five-phase tie-figure (decarbonation assemblage), followed by construction of the CO$_2$-saturated liquidus surfaces corresponding to Figure 3 at different pressures. The

final result is not a unique solution, but it is internally consistent, and consistent with changes on the CO$_2$-saturated liquidus surface through a range of pressures. See Wyllie and Huang (1976) for details.

Eggler (1974) studied the effect of CO$_2$ on the melting of Fo+En+Di, with results shown in Figure 2. The measurements of Eggler et al. (1974) suggest that the solubility of CO$_2$ in this liquid is about 5 weight percent at 30 kbar, which causes depression of the melting temperature by about 75°C. Eggler (1974) reported that the melting reaction was incongruent at 30 kbar and 1565°C. This curve is continuous with reaction 6z, and because Q$_6$ is located at about 24 kbar, the reaction must pass through a pressure maximum which is estimated to be near 31 kbar. Based on this information, reaction 5w was drawn with similar shape. There are other quaternary melting reactions merging with curves 6z and 5w at singular points, but these have been omitted for clarity.

The phase relationships depicted on the CO$_2$-satu-

rated liquidus surface at 25 kbar in Figure 3 are based on limited experimental data and detailed analysis of the univariant CO_2-saturated liquidus reactions plotted in Figure 2. Note the boundary separating fields for the primary crystallization of silicates from those of carbonates. The lowest temperature on the liquidus surface is on this field boundary at the eutectic 46 for the reaction:

$$Fo + Opx + Ccd + CO_2 = L.$$

Figure 3 shows that for compositions in the area SiO_2–$CaSiO_3$–$MgSiO_3$ at 25 kbar the CO_2 solubility remains low, but for compositions ranging from the pyroxene join to the carbonate join, the CO_2 content of liquids increases to more than 45 weight percent in the system CaO–MgO–CO_2 (Huang and Wyllie, 1974b, 1976). The dashed lines on the liquidus surface show the intersections of the joins Wo–En–CO_2 and Fo–Di–CO_2. At low pressures, the liquid 6z lies within the dashed triangle, but Eggler (1974) showed that somewhere between 15 kbar and 30 kbar it crossed the join Fo–Di to become larnite-normative, as in Figure 4.

The reaction 6z in Figure 2 is intersected twice at 25 kbar, and this requires that the primary fields for Fo, Opx, and Cpx meet at a second point 6z in Figure 3, at a temperature almost 400°C lower than the peritectic point determined by Eggler (1974). This requirement is satisfied by the second field for primary Opx shown between the fields for primary carbonates and other silicates. With decreasing pressure, this field decreases in area until it disappears at the pressure of Q_6 (Figure 2) as the three points 6z, 56, and 46 in Figure 3 become coincident. Note that the liquid at Q_6 contains about 40 weight percent dissolved CO_2. With increasing pressure, the two points 6z in Figure 3 approach each other, becoming coincident at the pressure maximum in Figure 2. At higher pressures, the CO_2-saturated liquidus fields for forsterite and clinopyroxene are separated by the field for orthopyroxene, and CO_2-saturated liquids cannot exist in equilibrium with the assemblage Fo+Opx+Cpx (see Wyllie and Huang, 1976, for details).

Application of Schreinemakers' (1916) rules to the invariant assemblage at Q_6 confirms the existence of a vapor-absent melting reaction involving the phases Fo+Opx+Cpx+Cd, in addition to the five reactions shown in Figure 2. This is shown rising to higher pressures from Q_6 in Figure 4 (estimated slope). The first liquid produced from this assemblage would contain about 40 percent dissolved CO_2, similar to
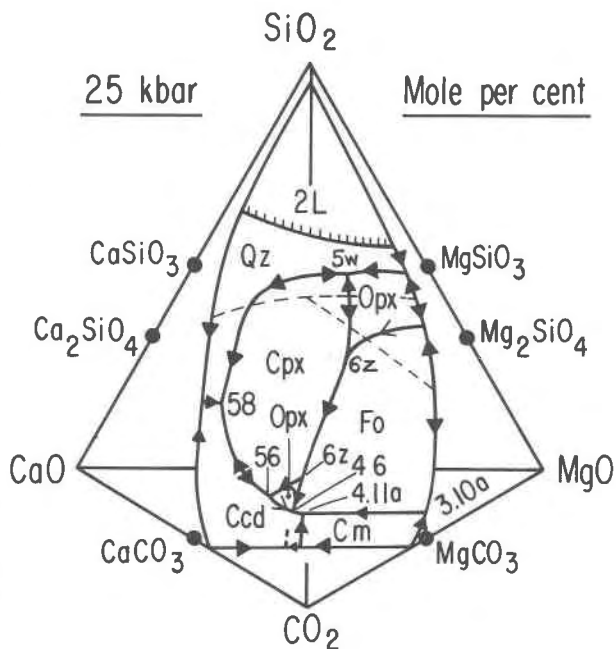

FIG. 3. The CO_2-saturated liquidus surface in CaO–MgO–SiO_2–CO_2 at 25 kbar, partly schematic. For sources of data see text. See Table 1 for abbreviations. Liquid compositions coexisting with three minerals and CO_2 vapor are identified by numbers corresponding to the univariant reactions listed in the key to Fig. 3. (Wyllie and Huang, 1976).

the liquid at Q_6. With increasing temperature and progressive melting, the CO_2 content of the liquid, behind the CO_2-saturated liquidus surface in Figure 3, would decrease as the liquid composition changed along a field boundary between liquidus volumes for Fo, Opx, and Cpx.

Petrological and geophysical applications

Figure 4 summarizes phase relationships for the mineral assemblage Fo+Opx+Cpx, which will be referred to as mantle peridotite, with the full realization that this is an oversimplification. The melting temperatures of natural peridotites with additional components FeO, Al_2O_3, alkalies, H_2O, and others would be lower (Wyllie, 1973, Figure 2; Mysen and Boettcher, 1975a, 1975b), but we do not believe that this would invalidate the processes discussed below. The addition of alkalis could introduce other processes, however, such as liquid immiscibility (Koster van Groos and Wyllie, 1973; Koster van Groos, 1975).

The ocean and shield geotherms shown in Figure 4 are those calculated by Clark and Ringwood (1964) and subsequently modified by Ringwood (1966). According to these geotherms, and the phase relation-
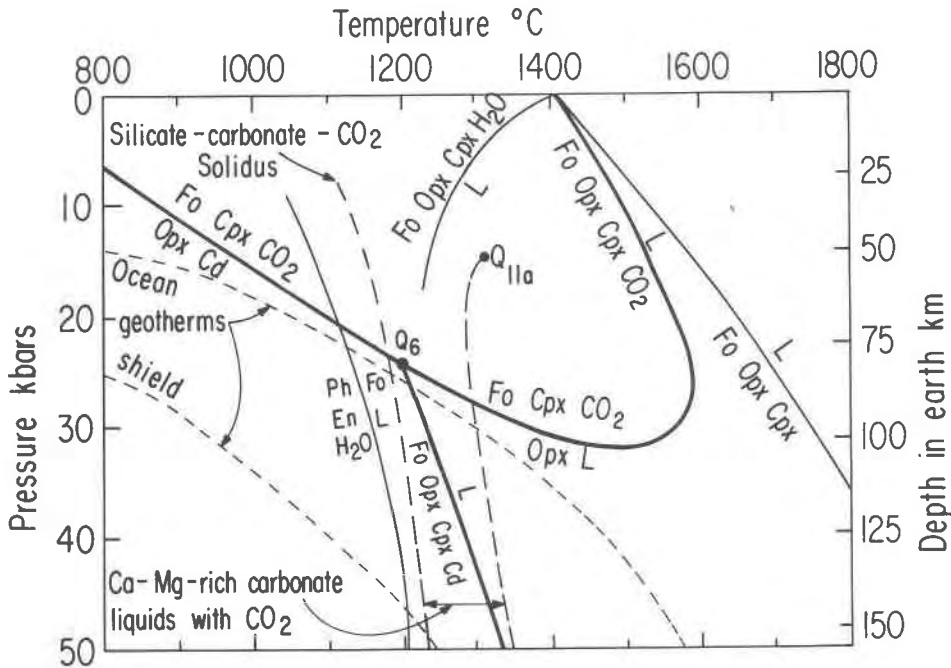
Fig. 4. The melting curve for model mantle peridotite assemblage Fo+Opx+Cpx, compared with reactions in the presence of H_2O (Kushiro, 1972), and with a small proportion of CO_2, either as vapor phase at lower pressures (Eggler, 1974), or as crystalline carbonate at higher pressures. See Fig. 2. The melting curve for phlogopite in the presence of Fo+En with excess H_2O (Modreski and Boettcher, 1973) is given for comparison. See Table 1 for abbreviations. See text for other data sources (Wyllie and Huang, 1975).

ships in Figures 2 through 4, we reach the following conclusions.

(1) Irving and Wyllie (1973, 1975) reviewed the possible sites for storage of CO_2 in the upper mantle, in crystals, liquids, or vapors. Figure 4 shows that CO_2 would normally be stored as carbonate, Cd, with composition between dolomite and calcite. This confirms the conclusion of Newton and Sharp (1975) from their study of reaction (3) in Figure 1, and of Koster van Groos (1975).

(2) There is no possibility for the presence of free CO_2 vapor in the crystalline upper mantle, with normal temperature distributions. In the presence of CO_2–H_2O mixtures, the univariant carbonation reaction becomes a divariant surface extending to lower temperatures, and this would permit the coexistence of carbonated mantle peridotite with diluted CO_2-bearing vapor.

(3) Free CO_2 cannot be the explosive agent blasting kimberlites to the surface from a position on the subsolidus shield geotherm, as proposed by Kennedy and Nordlie (1968).

(4) The CO_2 bubbles present in many mantle peridotite xenoliths (Roedder, 1965; Green and Rad-

cliffe, 1975) must be associated with diapiric uprise of solid mantle peridotite at relatively low temperatures (below Q_6) or with magmatic processes where crystallization at relatively high temperatures could lead to CO_2 evolution and entrapment in growing minerals.

(5) In the depth range of the asthenosphere, CO_2 appears to be as effective as H_2O in causing incipient melting of mantle peridotite (see Hill and Boettcher, 1970). Therefore, the low-velocity zone can not be caused by interstitial CO_2 in dry crystalline peridotite, as proposed by Green (1972). Incipient melting of the mantle remains our preferred interpretation, either due to the presence of traces of H_2O (Lambert and Wyllie, 1968, 1970) or to the presence of traces of CO_2 in the form of carbonate (Figure 4).

(6) Magmas generated from mantle peridotite in the presence of CO_2 at depths to about 80 km are SiO_2-undersaturated, with less than 5 weight percent dissolved CO_2 (Eggler, 1973; Eggler et al., 1974). In the presence of H_2O, in contrast, the liquids are relatively enriched in SiO_2 (Kushiro, 1972).

(7) Magmas from mantle peridotite in the presence of CO_2 at depths greater than 80 km are generated at temperatures about 400°C lower. The first

liquids are essentially carbonatites, with about 40 percent dissolved CO_2, and about 10 percent silicates. With increasing temperature the CO_2 content decreases, the silicate content increases, and the liquids become kimberlitic. Only at much higher temperatures do the liquids approach more normal basic magmas.

(8) Carbonatitic or kimberlitic magmas rising from the asthenosphere must pass through a reaction evolving CO_2 at depths between 100 and 80 km. This would certainly contribute to their explosive eruption from the region of the asthenosphere-lithosphere boundary.

(9) At low pressure, basic magmas with dissolved CO_2 crystallize to yield silicates with evolution of CO_2. No carbonates or CO_2-rich residual liquids are produced by fractional processes.

(10) Above a certain pressure, value not yet determined, the crystallization of basic magmas with dissolved CO_2 can yield residual kimberlitic and carbonatitic liquids.

(11) At depths greater than 80–100 km, CO_2-rich, SiO_2-poor liquids in small amounts can coexist with mantle peridotite through a wide temperature range. These liquids are possible sources of primary kimberlites and carbonatites, if conditions are suitable for their local concentration. The liquids may also include the primary, carbonated alkali ultrabasic magmas that have been cited by many petrologists as the parent from which the continental associations of highly alkalic rocks, volcanic and plutonic, have been derived (*e.g.* King, 1965).

Note added in proof

Eggler (1974, Figure 7) published a diagram showing the coexistence of $Fo+En+Di+L+Co_2$ at 30 kbar and 1565°C. Our adoption of this point forced reaction 6z to pass through a pressure maximum in Figures 2 and 4. In more recent versions of this reaction, Eggler (1976) either neglected or reinterpreted his previous results, stating that the pressure maximum on the solidus curve "is not observed according to the data in Figure 3a." Therefore, the pressure maximum on solidus can be removed from Figures 2 and 4. This produces a single continuous field for liquidus Opx in Figure 3, and for all pressures Q_6, instead of two fields each terminating at a separate point 6z.

Removal of this pressure maximum does not change our conclusion that near-solidus liquids at pressures greater than Q_6 are carbonatitic, with compositions near points 56 and 46 in Figure 3. In fact, although this does require reexamination of some of the schematic phase relationships (Wyllie and Huang, 1976),

it makes no difference to any of our petrological or geophysical conclusions.

Acknowledgments

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