Carbon and carbonates in the mantle

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Abstract—Carbon may be present in the mantle as a fluid, as diamond or graphite, as carbonate, or as a dissolved component in a silicate-rich or carbonate-rich melt. Which of these hosts are stable depends on pressure, temperature, and composition, including the abundance of volatile constituents and the oxidation state of the region of the mantle under consideration. Because thermal regimes are laterally variable in the mantle - a geotherm under an craton assembled in the Archean is cooler than that in convecting mantle, for example, and because of variations in composition, both large- and small-scale, there is not likely to be a unique answer to how carbon is hosted in the mantle. Some constraints may be placed, however, on the possibilities appropriate for different thermal regimes and lithologies in the mantle.

The basic premise of this chapter is that the hosts for carbon will change systematically with depth. This model has been proposed by a number of workers in various guises and permutations (*e.g.,* GREEN *et al.,* 1987; WOOD *et al.,* 1990; O'NEILL *et al.,* 1993a, b; WOOD *et al.,* 1996). At shallow depth (< 2 GPa), CO_2-bearing fluids host carbon. Between ~ 2 and ~ 5 GPa, carbon would be present as carbonate-bearing peridotite (in sub-continental lithospheric mantle) and in carbonated melts (in convecting mantle). At greater depths in the asthenosphere, carbon would be present as carbonated peridotite. With increasing depth, the carbonate in this peridotite will be progressively reduced to carbon, until at the transition zone, the assemblage of diamond + garnet + wadsleyite overlies diamond + garnet + silicate spinel in "normal" mantle. In more oxygen-rich regions, carbonate may coexist with these assemblages. Below the spinel $\rightarrow$ perovskite + magnesiowüstite reaction at 670 km depth, the stable assemblage will be perovskite + magnesiowüstite + diamond, with carbonate stable in addition only in oxygen-rich regions. The net effect of this stratification is that there is a shallow veneer of oxidized carbon in the Earth, underlain by a much larger volume in which carbon is present dominantly, or exclusively, as elemental carbon. The "excess" oxygen released by the reduction of carbonate with depth oxidizes Fe^{2+} to Fe^{3+} in the coexisting silicates. If subduction introduces oxygen-rich altered oceanic crust and sediments into the mantle, the volume of the mantle in which oxidized carbon is stable will increase over time.

Based on this framework, recent ideas about the oxidation state of the mantle, and how - and why - it may change with depth will be reviewed. Following that will be an examination of the evidence, from both natural samples and experiments, for the stability of different hosts for carbon, starting at shallow depths (and higher degrees of confidence) and progressing to greater depths and uncertainties.

THE OXIDATION STATE OF THE MANTLE

THE OXIDATION state of the mantle has attracted considerable interest and debate, mostly because of the strong influence that it could exert on the composition and speciation of fluids, and thereby on the melting behavior of the mantle. A complication in constraining the oxidation state of the mantle is that samples are limited, being available only from the upper mantle as xenoliths transported by alkali basalts and kimberlites and as abyssal peridotites and peridotite massifs. This intrinsically limits attempts to assess lateral variations in mantle oxidation state. Another limitation is the limited depth of sampling by xenoliths, which hinders attempts to constrain depth profiles of oxidation state.

Controls on oxidation state

A major unresolved question in discussions of the oxidation state of the mantle is what controls it - is it intrinsic to the sample or extrinsic, imposed by some external agent, such as a fluid or melt? Duhem's Law dictates that the oxidation state, and hence the oxygen fugacity (fO_2), which is used as a monitor of the oxidation state, is completely determined by the bulk composition of a closed system at a given pressure and temperature. If the sample can be considered a closed system, the fO_2 it records is an intrinsic value. But is the fO_2 dominated by the Fe^{2+}/Fe^{3+} equilibrium between minerals, by equilibria involving C-bearing phases, such as carbonate or diamond or graphite, by equilibria involving a sulfur-bearing phase (presumably liquid at the P, T of the mantle - see O'NEILL, 1991), or by equilibria involving H-bearing phases (either fluid or solid)? If, on the other hand, the system was not closed, in that it interacted with an externally-derived fluid or melt, are there any constraints we can place on the process? For example, can we say anything about the length and time scale of this interaction?

Based on a closed-system approach, O'NEILL *et al.* (1993a) explored the consequences of an isochemical

mantle on fO_2. They estimated the $Fe^{3+}/\Sigma Fe$ of the upper mantle by measuring the modal abundance and $Fe^{3+}/\Sigma Fe$ of minerals present in mantle-derived xenoliths. They then explored the consequences on the relative oxidation state of the mineralogical changes that an isochemical mantle would undergo as a function of depth. This model was developed further by O'NEILL *et al.* (1993b) and CANIL *et al.* (1994). This approach is appealing in that it makes explicit the requirement of providing sources or sinks for oxygen - other than the "free oxygen" often (erroneously) taken for granted in discussions of fO_2 (see discussion by FROST, 1991).

To evaluate the effect of different equilibria on the oxidation state of a "closed-system" packet of mantle, we need to look at the "buffering" capabilities of the different equilibria, which can be represented by the amount of "excess" oxygen the different equilibria have to offer. CANIL *et al.* (1994) give an estimate of total Fe_2O_3 of ~0.3 ± 0.2 wt. % in mantle-derived lherzolites, with sub equal contributions from orthopyroxene (lowest $Fe^{3+}/\Sigma Fe$, greatest modal abundance), clinopyroxene (intermediate $Fe^{3+}/\Sigma Fe$ and modal abundance), and spinel (highest $Fe^{3+}/\Sigma Fe$, lowest modal abundance). Reduction of this Fe_2O_3 to FeO would liberate 300 ± 200 ppm O_2. To put this amount into context, 113 ± 75 ppm C could be oxidized to form 413 ± 275 ppm CO_2 or 793 ± 526 ppm $MgCO_3$.

In a detailed study of a variety of mantle-derived rock types from geographically diverse locales, CANIL and O'NEILL (1996) found Fe_2O_3 (total) of 0.14–0.39 wt. % for garnet lherzolites, 0.30–0.77 wt.% Fe_2O_3 for garnet websterite, and 0.09–0.16 wt.% Fe_2O_3 for garnet harzburgites (Fig. 1). They also measured Fe^{3+}/Fe^{2+} for garnets from Siberian garnet dunites. Combined with the estimate of ≤5% modal garnet in these samples (POKHILENKO *et al.*), the bulk Fe_2O_3 of these dunites would be ≤ 0.02 wt.% (Fig. 1). Clearly, the oxidative capacity represented by the "excess" oxygen tied up with Fe^{3+} varies with rock type in the mantle.

To compare this to the redox capability of C in the mantle requires some estimate of the average concentration of C in the mantle, as well as the variability in concentration. The available estimates are based on a number of lines of evidence, including direct measurements of C concentrations in mantle-derived xenoliths and in mantle-derived basalts (combined with estimates of the degree of melting required to produce the basalt), and correlations of C with ^3He in mantle-derived samples. The estimates for "average" mantle range from 80 ppm in primitive mantle, respectively (cf. discussion in CANIL *et al.* 1994), through 50–250 ppm (TRULL *et al.*, 1993), to 400 ppm (JAVOY, 1997).
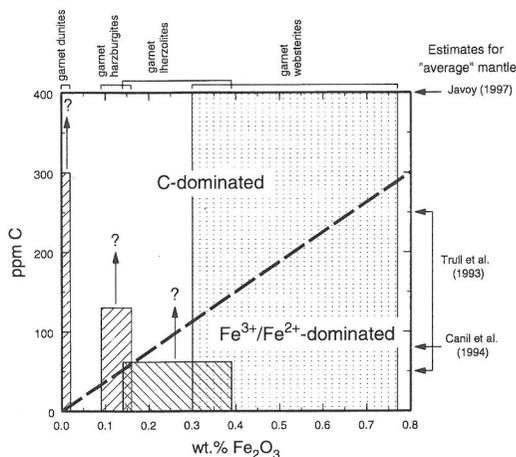

FIG. 1. Ferric iron contents of different mantle-derived samples, plotted as wt.% Fe_2O_3 in the whole rock (CANIL and O'NEILL, 1996), compared to carbon contents in ppm. The heavy dashed line defines stoichiometric amounts of carbon and Fe_2O_3 for the oxygen-conserving reaction 2 Fe_2O_3 + C = 4 FeO + CO_2. Samples plotting above this line would be dominated by carbonate-graphite/diamond-(silicate)-(fluid) equilibria if the carbon was present originally in oxidized form; samples below this line would be dominated by Fe^{2+}/Fe^{3+} equilibria. Carbon estimates for garnet harzburgites and lherzolites from HELMSTAEDT'S (1992) summary of data for diamondiferous peridotites. See text for estimates of the carbon contents for garnet dunite and garnet websterites.

The degree of variability in the concentration of C, and the mechanisms by which C is redistributed in the mantle, are poorly defined. One constraint on this variability is given by the concentration of carbon-bearing phases in xenoliths and other mantle-derived samples, although modal estimates of C in mantle-derived xenoliths are scarce. Diamondiferous garnet lherzolites and garnet harzburgites have been reported with the equivalent of 1–62 and 0.1–130 ppm C, respectively (cf. summary in HELMSTAEDT, 1992). The garnet dunites from Yakutia may have higher abundances. The author was unable to find any modal data for these dunites, but POKHILENKO *et al.* (1991) report a 2.5 cm^3 xenolith with four diamonds and two cavities that were inferred to have previously hosted additional diamonds. If these diamonds were ~1–2 mm diameter (POKHILENKO *et al.*, 1991., report that the diamonds in their samples range up to 4 mm in size), this abundance of diamond corresponds to ~1,300–10,500 ppm C. Although these values are higher than those for diamondiferous lherzolites and harzburgites, and they have a large uncertainty, they may be realistic, given that these dunites are considered to be the primary diamond-bearing protolith sampled by these kimberlites (SOBOLEV *et al.*, 1984;

PEARSON *et al.*, 1995). High values are found in other mantle-derived samples: diamondiferous eclogites can be carbon-rich (3.4–7400 ppm C; HELMSTAEDT, 1992). DAVIES *et al.* (1993) report pyroxenite layers in the Ronda peridotite massif with >15% graphitized diamond (equivalent to ~110,000 ppm C), and PEARSON *et al.* (1994) describe an orthopyroxenite xenolith with 10–20% graphite (equivalent to 72,000–144,000 ppm C). There is no direct information concerning the carbon content of websterites, but there is an association between websterite and diamond, as evidenced by the websterite-paragenesis suite of diamond inclusions in the Orapa kimberlite (DEINES *et al.*, 1993). From these examples, it is clear that there is a large variability in the concentration of C in various parts of the mantle. Whether the high values are characteristic only of subcontinental lithospheric mantle is not known.

The estimates for carbon contents in peridotites and websterites are summarized in Fig. 1. Below the heavy dashed line, the amount of "excess" O present as Fe_2O_3 is greater than the amount that could react with the C present to form carbonate or CO_2. In samples that plot above the line, C-based equilibria will have a larger buffering capacity than those involving Fe^{2+}/Fe^{3+}.

Very limited data are available to evaluate the potential role of S, because of few constraints on the concentration (and variability thereof) of S in the mantle (*cf.* LORAND, 1990; EGGLER and LORAND, 1993; SZABÓ and BODNAR, 1995). CANIL *et al.* (1994) estimated that S in "average" mantle, with 200 ppm S, represents a potential oxygen reservoir of ~380 ppm O_2, on the same order as the reservoir they estimated to be present from Fe^{3+} in "normal" lherzolite.

Because of the similar "buffering capacity", or rather the amount of O_2 potentially represented by each of these redox reservoirs, most workers have concluded that it is the interplay between these reactions that may control the fO_2 of the mantle, and that the mantle is only weakly buffered with respect to fO_2. Perhaps a better way to view this situation is that the controlling equilibrium is likely to be C-based in mantle containing abundant C relative to Fe_2O_3, such as garnet harzburgites or garnet dunites, Fe-based in mantle where the converse holds, and S-based in S-rich regions.

Estimates of mantle fO_2

In discussions of the oxidation state of the mantle, it is customary to reference values of log fO_2 to a synthetic oxygen buffer, such as the quartz-fayalite-magnetite (QFM) buffer. By doing so, much of the temperature-dependence of the values of fO_2 is removed, because of the similar slopes in T-log fO_2 space of most of the reactions written to infer

fO_2 from silicate-oxide, silicate-silicate, or silicate-carbonate-graphite/diamond equilibria.

Early estimates of the oxidation state of mantle-derived samples were based on "intrinsic" oxygen fugacity measurements of individual minerals, and these measurements led to a view that there was a dichotomy in the redox state of the mantle, even among seemingly similar spinel lherzolite samples, with one group clustering at "oxidized" values near QFM, and another clustering at "reduced" values near IW (iron-wüstite) (*cf.* review by ARCULUS, 1985).

Questions were raised regarding the accuracy of these measurements (*cf.* discussion in WOOD, 1991), which led to efforts to find heterogeneous equilibria that would provide independent, and hopefully more robust, monitors of oxidation state. These efforts have been successful, and the equilibrium between olivine, orthopyroxene, and spinel, first applied to mantle samples by O'NEILL and WALL (1987), has been extensively used in this context. Samples of spinel lherzolites range in oxidation state from ~QFM −2 to ~QFM +1 (*cf.* review by WOOD, 1991). Only in the more reduced part of this range, and then only at temperatures < 1000°C, would graphite be expected to be present (Fig. 2).

Samples from the deeper, garnet lherzolite facies are more problematic, because of uncertainties associated with solution models for garnets (LUTH *et al.*, 1990). Depending on the solution model is used, the
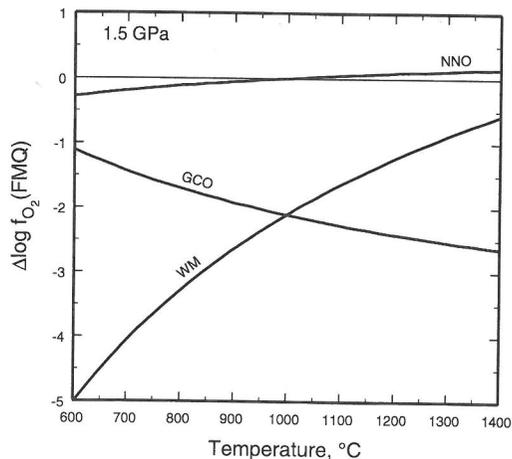

FIG. 2. Calculated location of buffer reactions 2 Ni + O_2 = NiO (NNO), 3 Fe_xO + 2x O_2 = x Fe_3O_4 (WM) and C + O_2 = CO_2 (GCO) at 1.5 GPa, relative to the log fO_2 of the FMQ buffer (3 Fe_2SiO_4 + O_2 = 2 Fe_3O_4 + 3 SiO_2). μlogfO_2 (FMQ) is defined as logfO_2 (sample)- logfO_2 (FMQ) at the same pressure and temperature. Reactions calculated at 1.5 GPa, using data from HOLLAND and POWELL (1990) for NNO, WM, FMQ, and from FROST and WOOD (1997) for GCO.

redox state could be similar to the redox state of spinel lherzolite samples (WOODLAND and O'NEILL, 1993) or significantly more reduced (GUDMUNDSSON and WOOD, 1995). More work, or a new approach, is needed to resolve this question. One possibility would be to apply the olivine-orthopyroxene-spinel oxybarometer to chromite-bearing garnet lherzolites. Such an exercise was attempted by DANIELS and GURNEY (1991), who found quite reduced values of fO_2 (WM- IW) for olivine + spinel ± orthopyroxene assemblages from diamond inclusions, kimberlite mineral concentrates, and spinel-garnet harzburgites. Unfortunately, these authors did not calibrate their microprobe analyses against chromites of known $Fe^{3+}/\Sigma Fe$ and similar composition as their unknowns. Such a calibration has been recognized to be essential in obtaining accurate Fe^{3+} values from stoichiometric calculations (cf. discussion in WOOD, 1991). WOOD (1991) suggests that uncertainties in this situation would be on the order of ±2 log units fO_2, which renders the results of DANIELS and GURNEY (1991) problematic at best.

WOOD et al. (1990) pointed out that the small molar volume of garnet endmembers that contain Fe^{3+} (e.g. $Ca_3Fe_2^{3+}Si_3O_{12}$ or $Fe_3^{2+}Fe_2^{3+}Si_3O_{12}$) requires reduction relative to FMQ if garnet is the dominant host of Fe^{3+}. This idea was extended by BALLHAUS and FROST (1994), who discussed generating "oxidized" magmas from "reduced" source regions, and by BALLHAUS (1995) who suggested that decreasing silica activity with increasing depth would also contribute to decreasing relative fO_2 as a function of depth.

WOOD et al. (1996) developed the molar volume argument further, based on the differences in the volume change of the solids (ΔV_{sol}) in the reaction involving spinel:

$$6\, Fe_2SiO_4 + O_2 = 2\, Fe_3O_4 + 3\, Fe_2Si_2O_6$$
$$(\Delta V_{sol} = +8.6\ cm^3) \quad (1)$$
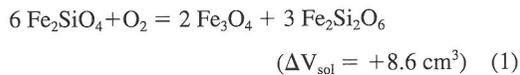
and the reaction involving garnet:

$$4\, Fe_2SiO_4 + Fe_2Si_2O_6 + O_2$$
$$= 2\, Fe_3^{2+}Fe_2^{3+}Si_3O_{12}\ (\Delta V_{sol} = -8.6\ cm^3) \quad (2)$$
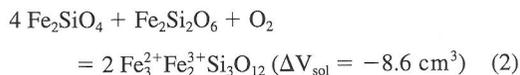
relative to that of the FMQ buffer (ΔV_{sol} = 17.95 cm³; all values of ΔV_{sol} from WOOD et al. 1996). These differences in ΔV_{sol} for these reactions require reduction for both spinel and garnet peridotites relative to FMQ with increasing pressure. The rate of relative reduction would be higher for garnet peridotites, because of the larger difference in ΔV_{sol} for reaction (2) relative to FMQ. This argument presupposes that the Fe redox reactions dom-

inate those of C, and WOOD et al. (1990) argue that this would be the case, based on an assumed carbon concentration of 80 ppm. Given that premise, reduction of oxidized carbon would be inevitable in an isochemical mantle, because the pressure dependencies of the ferric/ferrous reactions force them to more reducing levels relative to reactions governing oxidation/reduction of carbon-bearing species. In the stability field for garnet lherzolite, any oxidized carbon would be present as carbonate, because CO_2 fluids would have reacted with silicates at lower pressures to form carbonate.

The silicate-carbonate-diamond redox equilibrium can be modelled with the Enstatite-Magnesite-Olivine-Diamond (EMOD) reaction (EGGLER and BAKER, 1982):

$$0.5\, Mg_2Si_2O_6 + MgCO_3 = Mg_2SiO_4 + C + O_2$$
$$(\Delta V_{sol} = 4.16\ cm^3). \quad (3)$$
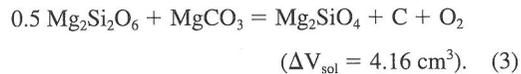
The oxygen liberated by this reaction going to the right would be used to oxidize Fe^{2+} to Fe^{3+} in the silicates. If carbonate is present initially in excess of the amount needed for this oxidation of iron, carbonate and elemental carbon would coexist with silicates, and a carbonate-carbon-silicate reaction such as EMOD would control the oxidation state of this (relatively) carbonate-rich packet of mantle.

WOOD et al. (1996) concluded that carbonate will be reduced to carbon within the upper 200–300 km of the mantle, and carbon will be stored and recycled as diamond, rather than as carbonate. Implicit in this conclusion, again, is the assumption that the amount of carbonate is small, insufficient to completely oxidize the necessary Fe^{2+} to Fe^{3+}.

Their argument may be refined by including the role of pyroxene as a host for Fe^{3+}. No data on molar volumes of Fe^{3+}-bearing orthopyroxene endmembers are available, so no information regarding the pressure dependence of redox equilibria involving these endmembers may be inferred. Data on molar volumes are available, however, for two Fe^{3+}-bearing clinopyroxenes: acmite ($NaFe^{3+}Si_2O_6$) and esseneite ($CaFe^{3+}AlSiO_6$). Redox reactions involving these endmembers have been proposed by LUTH and CANIL (1993):

$$2\, CaAl_2SiO_6 + 2\, CaFeSi_2O_6 + 4\, Fe_2SiO_4 + O_2$$
$$= 4\, CaFeAlSiO_6 + 3\, Fe_2Si_2O_6, \quad (4)$$

$$2\, CaAl_2SiO_6 + 2\, CaMgSi_2O_6 + 2\, Mg_2SiO_4$$
$$+ 2\, Fe_2SiO_4 + O_2 = 4\, CaFeAlSiO_6$$
$$+ 3\, Mg_2Si_2O_6, \quad (5)$$

and

$$4\,NaAlSi_2O_6 + 4\,Fe_2SiO_4 + 2\,CaFeSi_2O_6 + O_2$$
$$= 4\,NaFeSi_2O_6 + 2\,CaAl_2SiO_6 + 3\,Fe_2Si_2O_6. \quad (6)$$
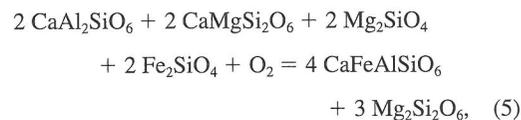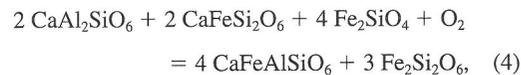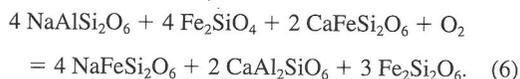
These reactions have values of $\Delta V_{sol} = 28.62, 27.52,$ and $20.54\ cm^3$, respectively (volume data for esseneite from COSCA and PEACOR, 1987; for other phases from HOLLAND and POWELL, 1990). These volume changes are larger than that for FMQ ($\Delta V_{sol} = 17.95$ cm^3), so net *oxidation* relative to FMQ would be expected if pyroxene-based reactions exert a control on fO_2.

The relative importance of pyroxene relative to garnet on controlling fO_2 depends on the partitioning of Fe^{3+} between garnet and clinopyroxene, which may be modelled by the reaction:

$$2\,NaAlSi_2O_6 + Ca_3Fe_2^{3+}Si_3O_{12} = 2\,NaFe^{3+}Si_2O_6$$
$$+ Ca_3Al_2Si_3O_{12}. \quad (7)$$
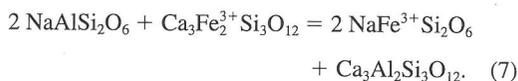
Based on calculations of this equilibrium, the left-hand side of the reaction is favored by increasing pressure (primarily) and decreasing temperature. With increasing pressure, therefore, Fe^{3+} is partitioned preferentially into garnet, which would reinforce the relative reduction with depth advocated by WOOD *et al.* (1990, 1996). Reinforcing this trend at higher pressure is the observation that pyroxene dissolves into majoritic garnet at pressures above ~7 GPa. WOOD *et al.* (1996) point out that once this dissolution occurs, the Fe^{3+} in the garnet will be diluted and relative fO_2 will be reduced.

This reduction in relative fO_2 with depth implies that carbonate will not be stable in the lower part of the upper mantle, unless carbonate is sufficiently abundant that silicate-carbonate-diamond reactions overwhelm the Fe^{3+}/Fe^{2+} equilibria and control the redox state. In low-C mantle, where the Fe^{3+}/Fe^{2+} equilibria dominate, diamond will be the stable host for carbon at these depths. During ascent, for example in the ascending limb of a mantle convection cell, the carbon could react with Fe^{3+}-bearing phases to form carbonate and Fe^{2+}-silicates, as modeled schematically by the reaction:

$$2\,Fe_2O_3\ (silicate) + C = FeCO_3\ (carbonate)$$
$$+ 3\,FeO\ (silicate) \quad (8)$$
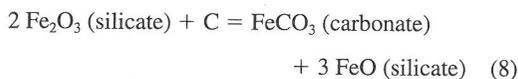
(*e.g.,* WOOD *et al.*, 1996), leading to progressive oxidation upon ascent. This carbonate may be either solid or molten, depending on the temperature in the ascending mantle relative to that of the solidus for carbonated peridotite.

At the depth of the transition zone (400-670 km), there is evidence that depth-sensitive changes in mineralogy lead to relative reduction with depth. O'NEILL *et al.* (1993a,b) synthesized the potential transition-zone minerals (Mg, Fe)SiO_3 (clinopyroxene), (Mg, Fe)SiO_3 (majorite garnet), β- and γ-(Mg, Fe)$_2SiO_4$ (wadsleyite and silicate spinel, respectively) and measured their Fe^{2+}/Fe^{3+} with Mössbauer spectroscopy. They found the garnet, wadsleyite, and silicate spinel had significant $Fe^{3+}/\Sigma Fe$, even when equilibrated with Fe metal. Because the volumetrically-dominant minerals have high $Fe^{3+}/\Sigma Fe$, the oxidation state of the transition zone must therefore be more reduced than the spinel lherzolite portion of an isochemical mantle. This effect is independent of whatever happens in the lower-pressure stability field of garnet lherzolite. In the model of O'NEILL *et al.* (1993a,b), the transition zone forms a reduced shell between the upper and lower mantle. The redox state of the lower mantle was deduced by first assuming that Fe^{3+}/Fe^{2+} in magnesiowüstite and perovskite in the lower mantle were equal. Because of the high $Mg/(Mg + Fe)$ of lower-mantle perovskite, magnesiowüstite would be the dominant host for both total Fe, and Fe^{3+}. They infer that because the bulk of the Fe^{3+} would be concentrated in the modally-minor phase, the lower mantle would be relatively more oxidized than the transition zone, analogous to the situation in the upper mantle.

More recently, McCAMMON (1997) synthesized an aluminous (Mg, Fe)-perovskite with $\sim50\%$ of its Fe as Fe^{3+}, which requires a reappraisal of the issue of the host for Fe^{3+} in the lower mantle. Subsequently, McCAMMON *et al.* (1997) measured the Fe^{3+}/Fe^{2+} of minerals included in diamonds from Brazil with Mössbauer spectroscopy. They found (Mg,Fe)O inclusions with $Fe^{3+}/\Sigma Fe \leq 0.07$ and inclusions of tetragonal almandine-pyrope garnet, inferred to have been stable in the lower mantle, with $Fe^{3+}/\Sigma Fe$ of 0.66- 0.74. Inclusions of (Mg, Fe)-pyroxene composition (inferred to have been (Mg, Fe)-perovskite at conditions of formation) had $Fe^{3+}/\Sigma Fe$ of 0.20– 0.75. The high values of $Fe^{3+}/\Sigma Fe$ in these pyroxenes, if their origin is interpreted correctly, require that (Mg,Fe)-perovskite is the major host of Fe^{3+} in the lower mantle. If the mantle is approximately isochemical, this perovskite is the volumetrically-dominant phase in the lower mantle. Therefore, using the same logic as O'NEILL *et al.* (1993a,b), the sequestration of Fe^{3+} in a volumetrically-dominant phase means that the lower mantle must be reduced (i.e., lower values of relative fO_2) compared to the upper mantle. Even if the lower value of $Fe^{3+}/\Sigma Fe$ in the perovskites measured by McCAMMON *et al.* (1997) is representative of the

lower mantle, there would be at least ~2 wt. % Fe_2O_3 in a lower mantle of pyrolite bulk composition. To oxidize the mantle from the upper-mantle value of 0.3 wt.% Fe_2O_3 to this extent would require addition of 1700 ppm O_2, the amount of O_2 liberated by the reduction of 0.45 wt.% $MgCO_3$.

Conversely, when material is transferred from the lower to the upper mantle, via either single-layer convection or catastrophic overturn, Fe^{3+} in the silicates will be reduced to Fe^{2+}. This liberates 1700 ppm O_2, which could oxidize carbon to carbonate, and perhaps trigger melting, depending on the location of the solidus of the material in the presence of carbonate *compared to that* in the presence of graphite or diamond. This could be considered a form of "redox melting" (GREEN *et al.*, 1987) that does not require a separate fluid phase interacting with the mantle to trigger melting.

POTENTIAL HOSTS FOR CARBON

Now we shall turn to the observational, theoretical, and experimental constraints on the possible hosts for carbon in the mantle. We will start with the role of fluids in the shallow part of the mantle, then looking at the role of graphite, diamond, carbonate, and carbonatitic melts at progressively deeper levels. Because of the limited data available, most of this discussion will be limited to <10 GPa.

C-rich fluids at shallow depths

The ubiquitous presence of CO_2-rich fluid inclusions in minerals in mantle xenoliths hosted in alkali basalts (*e.g.* PASTERIS, 1987; ROSENBAUM *et al.*, 1996) testifies to the presence and hence the stability of a CO_2-rich fluid at some stage in the history of these xenoliths. ROEDDER (1984) discusses at length the difficulty of unambiguously determining "primary" fluid inclusions in xenoliths. Most of these xenoliths are derived from the spinel lherzolite stability field (P~1–3 GPa). CO_2-rich fluids in these rocks would be consistent with their relatively oxidized nature inferred from olivine-orthopyroxene-spinel oxygen barometry (*cf.* discussion above), and with the scarcity of graphite reported in these samples (*cf.* discussion in PEARSON *et al.*, 1994).

Samples of fluids from higher pressure are harder to come by, and most attention has focused on diamond, as the strongest available "container" for such fluids. In this context, SCHRAUDER and NAVON (1993) found solid CO_2 encapsulated in diamond, which they interpret as having been trapped from a CO_2 fluid during crystallization of the diamond. They noted that the fluid must have been trapped from an olivine- and pyroxene-free assemblage, because at the inferred conditions of entrapment (>6 GPa), carbonate, not CO_2 fluid, would have been stable in the presence of these phases. Clearly, such an assemblage would not be characteristic of peridotite or eclogite lithologies, but might represent subducted crust or sediments.

SCHRAUDER and NAVON (1994) found CO_2-H_2O fluids trapped in fluid inclusions in fibrous diamonds from Botswana, and hypothesized that they represented mixtures of hydrous and carbonatitic fluids. They were able to infer endmember compositions, and determined that the hydrous endmember was silica- and alumina-rich, and the carbonatitic endmember was rich in CaO, FeO, MgO, and P_2O_5. These authors suggested that similar fluids are widespread in the subcontinental lithospheric mantle.

Other fluids may be stable in the mantle. In the model of Green and coworkers (*e.g.*, GREEN *et al.*, 1987; TAYLOR and GREEN, 1988; GREEN, 1990), CO_2-H_2O fluids become reduced to CH_4-H_2O with increasing depth concomitant with the depth-dependent reduction in oxidation state they postulate. Upon ascent, these reduced fluids react with the more oxidized upper mantle to form H_2O-rich fluids, which then trigger melting in a process they termed "redox melting". As outlined above, the presence of fluids may not be required to trigger melting during diapiric ascent of relatively reduced mantle. The model of GREEN and coworkers, however, has the appeal that fluids have the potential to rise independently of the silicate matrix, to transport dissolved elements, and to trigger melting at higher levels in the mantle.

In light of this model, the transport capabilities of reduced fluids, as well as the melting behavior of peridotite in the presence of reduced volatiles, need to be understood. No work has been done on the former question. On the latter, TAYLOR and GREEN (1988) demonstrated that CH_4 does not depress the solidus of peridotite to the same extent as does H_2O, so that the temperature of the solidus increases with increasing $X(CH_4)$, at least to 3.5 GPa. Unfortunately, nothing has been done to date at higher pressures to evaluate the effects of reduced, CH_4-rich fluids on mantle geochemistry, mineralogy, or melting behavior.

Elemental Carbon

The potential stability of a C-O fluid in the mantle is constrained by the reduction of CO_2 to elemental C via the reaction:

$$C + O_2 = CO_2 \ (GCO). \qquad (9)$$

Although the GCO reaction occurs at very reducing conditions at atmospheric pressure, it moves to more oxidizing conditions, relative to oxide and silicate oxygen buffers, with increasing pressure because of the higher compressibility of CO_2 relative to solids. There has been considerable effort directed toward calibrating this reaction at high pressures in piston-cylinder and multi-anvil solid-media apparatus (THOMPSON and KUSHIRO, 1972; FEI et al., 1990; ULMER and LUTH, 1991; LA TOURRETTE and HOLLOWAY, 1994; FROST and WOOD, 1995; FROST and WOOD, 1997). The log fO_2 defined by this reaction is given by

$$\log fO_2 = 4.3927$$

$$- \frac{21234 - 117.94P + 0.89112P^2}{T}$$

$$+ 7.679 \times 10^{-3}P + 3.627 \times 10^{-4}P^2$$

(FROST and WOOD, 1997; corrected according to FROST, 1998)

Elemental carbon is stable as graphite at low pressure and as diamond at higher pressure. In addition, there are a number of (metastable) forms of poorly-crystallized elemental carbon found at low pressure (e.g. MATHEZ, 1987; PASTERIS, 1988). The occurrence of both graphite and diamond polymorphs in the mantle is evidenced by their (rare) presence in mantle-derived xenoliths (e.g., VILJOEN et al., 1992; PEARSON et al., 1994; VILJOEN, 1995). In this context, it is worth noting that diamond-bearing rocks are absent from the >80% of the Earth that is not underlain by Precambrian cratons and their lithospheric roots, which are inferred to have been isolated from the convecting asthenosphere for a substantial portion of geologic time. In addition, there are no reported occurrences of macroscopic graphite in xenoliths from off-craton localities (PEARSON et al., 1994).

The other occurrence of graphite in mantle-derived rocks is in some peridotite massifs, such as the graphite pseudomorphs after diamond found in the Beni Bousera and Ronda massifs (PEARSON et al., 1989 and DAVIES et al., 1993, respectively). These massifs are interpreted to be fragments of subcontinental lithosphere, and thus do not provide any support for the presence of graphite or diamond in non-cratonic mantle. There is little direct evidence, therefore, that graphite is present in non-cratonic mantle. This absence in samples from non-cratonic, "normal" mantle is not surprising, however, given the relatively oxidized nature of the upper mantle and the lower-pressure origin of most of the xenoliths that occur in non-cratonic settings. Any carbon present would be expected to be oxidized, and present as carbon dioxide.

Carbonates

Calcite is stable to ~ 3 GPa, and transforms to aragonite, which is stable at higher pressures (BIELLMANN et al., 1993; LIU and LIN, 1995). KUSHIRO et al. (1975) found that calcite reacts with orthopyroxene at 1000°C to form dolomite + clinopyroxene at 2.3–4.5 GPa, and magnesite + clinopyroxene at higher pressures. Therefore, calcite is unlikely to be stable in peridotitic mantle at >2–3 GPa.

Dolomite is stable to ~5 GPa, but decomposes to aragonite + magnesite at higher pressures. This reaction was studied in diamond-anvil experiments at 6–7 GPa at ~1000°C (LIU and LIN, 1995), and at 5 GPa, 600°C in situ in a cubic-anvil apparatus (MARTINEZ et al., 1996). In the presence of orthopyroxene, dolomite is stable between the low-pressure reaction that forms olivine + clinopyroxene + CO_2, and the high-pressure reaction that forms magnesite + clinopyroxene (Fig. 3). In the presence of clinopyroxene, dolomite will not be stable at low pressures, but will react to form calcite + orthopyroxene as found in the experiments of KUSHIRO et al. (1975).

Magnesite has been studied in the presence of $MgSiO_3$ pyroxene by KATSURA and ITO (1990) to 26
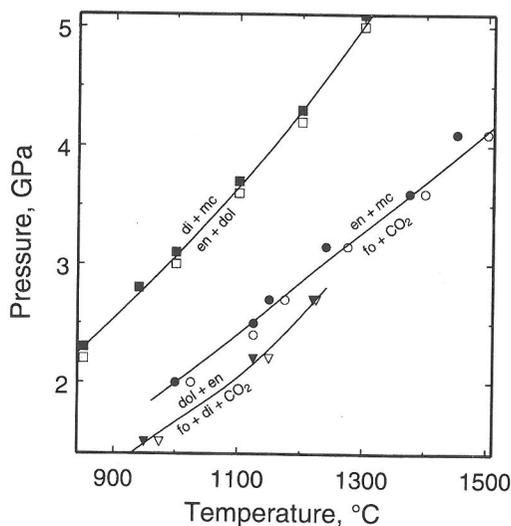
FIG. 3. Experimentally-determined carbonation reactions relevant to peridotites. Squares: from BREY et al. (1983); inverted triangles from WYLLIE et al. (1983), and circles from NEWTON and SHARP (1975) and HASELTON et al. (1978). The lower-pressure data of KOZIOL and NEWTON (1998) on the fo + CO_2 reaction are in excellent agreement with the higher-pressure data shown here.

GPa in a multianvil apparatus. Magnesite coexisted with enstatite at 8 and 15 GPa, and with perovskite at 26 GPa. BIELLMANN *et al.* (1993) studied mixtures of dolomite + enstatite and dolomite + olivine in a laser-heated diamond anvil cell at pressures to 50 GPa and temperatures from 1500–2500 K. They found magnesite to coexist with perovskites (Ca- and Mg-rich) and magnesiowüstite. These authors concluded that magnesite could be stable in the Earth's lower mantle down to at least 1500 km depth.

If carbonate is present in the mantle, why is it so scarce in mantle-derived xenoliths? The simplest explanation for this absence is that carbonate is not present, either because the mantle source is too reducing for carbonate to be stable, or because of a lack of C in any form. From the discussion above, at least parts of the mantle are sufficiently oxidized that carbonate would be the stable form of carbon. In addition, the occurrence of mantle-derived carbonatites argues that oxidized carbon, either as CO_2 or as carbonate, is either present, or can be generated, in the mantle. Therefore, a commonly-invoked explanation for the paucity of carbonate in mantle-derived xenoliths is that the carbonate does not survive the entrainment and transport process but decomposes by reaction with silicates to form CO_2. WYLLIE *et al.* (1983) discussed results of experiments that showed the reaction

$$2\,MgCO_3 + Mg_2Si_2O_6 = 2\,Mg_2SiO_4 + 2\,CO_2 \quad (10)$$
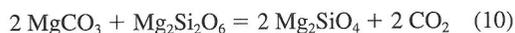
went to completion in <6 min at 850°C. This reaction is relevant for xenoliths derived from the diamond stability field, because magnesite would be the stable carbonate in peridotite at these depths (see discussion below). For xenoliths derived from shallower depths, the decomposition of dolomite is more relevant. CANIL (1990) showed that decomposition by the reaction

$$CaMg(CO_3)_2 + 2\,Mg_2Si_2O_6 = 2\,Mg_2SiO_4$$
$$+ CaMgSi_2O_6 + 2\,CO_2 \quad (11)$$
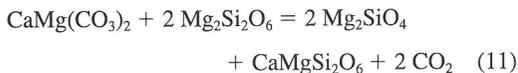
occurs when ascent rates of 45–90 km/h were simulated.

The former presence of carbonate, if this decomposition upon ascent operates, should have several consequences. First, the rapid evolution of CO_2 upon ascent should disaggregate the xenolith, a mechanism used to explain the rarity of some types of xenoliths, such as low-Ca harzburgites, that are purported to be present in greater proportions in xenocryst suites than in xenolith suites (*e.g.,* BOYD and GURNEY, 1982, but see SCHULZE, 1995 for a counter argument). Second, the modal abundance of olivine should increase in the samples that experienced the first decomposition reaction. Without a baseline against which to calibrate such an increase, however, this second consequence would be difficult to test. If the reaction of orthopyroxene and carbonate to form olivine did not generate additional phases to accommodate the minor elements from the orthopyroxene, the product olivine should reflect the chemistry of the orthopyroxene and be richer in TiO_2, Al_2O_3, CaO, and Cr_2O_3, and lower in NiO, than olivine that equilibrated in a peridotite. Whether such effects would be observable in natural samples obviously depends on the amount of carbonate originally present. If the 400 ppm C of JAVOY's (1997) mantle is present as carbonate, the sample would contain 0.15 wt.% carbonate. Decomposition of this amount of carbonate would generate only ~0.25 wt.% "anomalous" olivine- in peridotite with ~60% olivine. P. ULMER (PERS. COMM., 1998) suggested that another possible trace of this reaction could be the common presence of CO_2 inclusions in clinopyroxenes in cryptically-metasomatized xenoliths.

Direct evidence for carbonate in at least some parts of the mantle was provided by WANG *et al.* (1996), who describe a magnesite-containing inclusion in a diamond from the Finsch kimberlite pipe of South Africa. The authors suggested that the carbonate probably survived because of the strength of the diamond "container", and that the included assemblage of olivine + magnesite + diamond + graphite + anatase constrains the ambient oxidation state of the mantle. WANG *et al.* (1996) argued that the EMOD buffer (EGGLER and BAKER, 1982) was appropriate to use in discussing the implications of this inclusion, despite the absence of orthopyroxene. They based this argument on the presence of orthopyroxene in other inclusions in diamonds from Finsch and the improbability of sufficient magnesite present locally to consume all orthopyroxene to form olivine and diamond. The implicit assumption is that equilibration on the (large) grain scale occurs during formation and evolution of these diamonds and their hosts. The forsterite + magnesite + diamond assemblage, in the absence of orthopyroxene, could be stable at oxygen fugacities between EMOD and CCO (*cf.* Fig. 6 of WANG *et al.*, 1996).

Carbonation reactions

Carbon dioxide reacts with peridotitic minerals to form carbonate by a variety of reactions. In the absence of clinopyroxene, the reaction

$$2 Mg_2SiO_4 + 2 CO_2 \rightarrow 2 MgCO_3 + Mg_2Si_2O_6 \quad (12)$$

occurs with increasing pressure (NEWTON and SHARP, 1975; KOZIOL and NEWTON, 1998) (FIG. 3).

If clinopyroxene is present, CO_2 reacts instead via the reaction:

$$2 Mg_2SiO_4 + CaMgSi_2O_6$$
$$+ 2 CO_2 \rightarrow CaMg(CO_3)_2 + 2 Mg_2Si_2O_6 \quad (13)$$
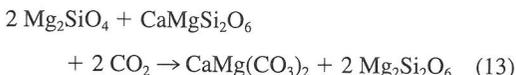
(e.g., WYLLIE et al., 1983).

DALTON and WOOD (1993a) observed magnesian calcite in equilibrium with peridotite at 1050°C and 2 GPa, and inferred a limited stability field for magnesian calcite in peridotite. The revised sequence of carbonation reactions that occur with increasing pressure may be written as:

$$2 Mg_2SiO_4 + 2 CaMgSi_2O_6$$
$$+ 2 CO_2 \rightarrow 2 CaCO_3 + 3 Mg_2Si_2O_6 \quad (14)$$

$$2 CaCO_3 + Mg_2Si_2O_6 \rightarrow CaMg(CO_3)_2$$
$$+ CaMgSi_2O_6. \quad (15)$$
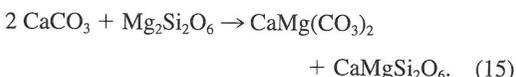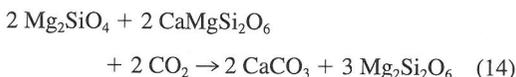
At higher pressures, dolomite is not stable in peridotitic assemblages, and reacts with enstatite:

$$CaMg(CO_3)_2 + Mg_2Si_2O_6 \rightarrow 2 MgCO_3$$
$$+ CaMgSi_2O_6 \quad (16)$$
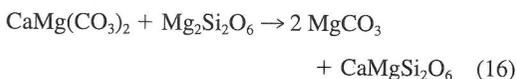
to form magnesite and diopside (Fig. 3) (KUSHIRO et al., 1975; BREY et al., 1983). In both Ca-rich peridotites (lherzolites) and Ca-poor peridotites (harzburgites), the stable carbonate in the stability field of diamond would be magnesite (Fig. 3).

The situation for eclogites of basaltic composition, such as subducted oceanic crust, is less constrained at present. In the absence of olivine, CO_2 could react with either clinopyroxene or garnet, or both, to form carbonates. LUTH (1995) determined the position of the potential carbonation reaction

$$CaMgSi_2O_6 + 2 CO_2 \rightarrow CaMg(CO_3)_2 + 2 SiO_2 \quad (17)$$

to 6 GPa.

KNOCHE et al. (ms. in revision) experimentally constrained the reaction:

$$Mg_3Al_2Si_3O_{12} + 3 CO_2 \rightarrow 3 MgCO_3 + Al_2SiO_5$$
$$+ 2 SiO_2. \quad (18)$$
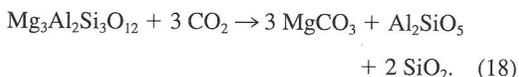
Both of these reactions occur at higher pressures than do the peridotite carbonation reactions (Fig. 4). In the natural system, activities of both diopside and pyrope are expected to be less than unity, so both curves would be displaced to higher pressure at a given
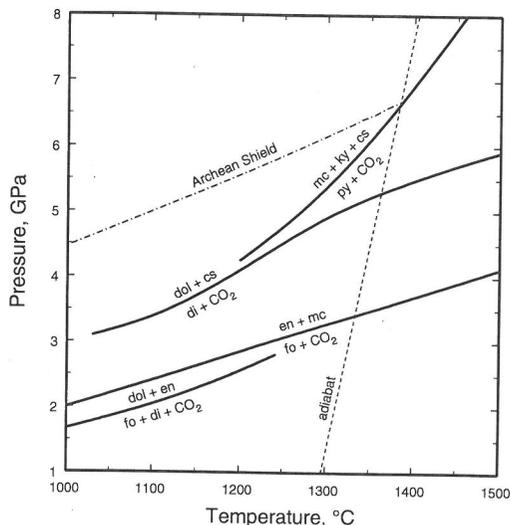

FIG. 4. Location of carbonation reactions relevant to eclogites compared to carbonation reactions for peridotites. Position of dol + cs = di + CO_2 from LUTH (1995); position of mc + ky + cs = py + CO_2 from KNOCHE et al. (in revision). Adiabat and Archean Shield geotherm from MCKENZIE and BICKLE (1988).

temperature from their locations in Fig. 4, which would increase the difference between the carbonation reactions for eclogite and peridotite. This difference would allow for the potential coexistence of eclogite containing CO_2-rich fluid and peridotite containing carbonate over at least a 1–2 GPa pressure interval at temperature conditions of the convecting mantle. The lower temperatures present in subcontinental mantle would stabilize carbonate in both eclogite and peridotite.

The next step is to determine the effect of addition of Ca to the system (LUTH and KNOCHE, 1997). Preliminary results are that Ca-bearing garnet + clinopyroxene + carbonate assemblages melt at significantly lower temperatures than do the garnet + carbonate assemblages in MgO-Al$_2$O$_3$-SiO$_2$-CO$_2$. In the experiments to date, carbonate-bearing melt coexists with silicates, rather than CO_2.

Effects of coexistence of carbonate with elemental carbon and silicates

EGGLER and BAKER (1982) proposed that in a peridotic assemblage, the coexistence of silicates, carbonates, and graphite or diamond define the oxidation state of the assemblage by reaction (3) (EMOD) discussed above. This reaction intersects reactions (9) and (12) in P-fO$_2$ space at an isothermal invariant

point, such that at higher values of fO_2, CO_2 is formed rather than graphite or diamond.

The stability of carbonate at high fO_2 was studied by DALTON and WOOD (1995), who calibrated the reaction

$$6 FeCO_3 + O_2 = 2 Fe_3O_4 + 6 CO_2 \qquad (19)$$
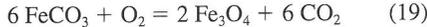
at 2 GPa in olivine-carbonate mixtures compositionally appropriate for the mantle. This reaction constrains the maximum fO_2 at which carbonate would be stable. Based on their results, carbonate would be stable at values of $\Delta log\, fO_2$ between -1.5 and 1.5 (relative to FMQ). The stability of carbonate would be quite sensitive to the composition of the spinel present.

In olivine-free lithologies such as basaltic eclogite or pyroxenite, LUTH (1993) proposed that the reaction

$$CaMg(CO_3)_2 + 2 SiO_2 = CaMgSi_2O_6$$
$$+ 2 C + 2 O_2 \qquad (20)$$
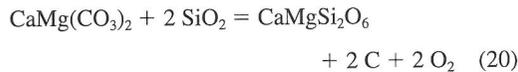
(DCDG/D) describes the coexistence of silicate + carbonate + graphite or diamond in a fashion analogous to EMOG/D.

A useful way in which to view these relationships
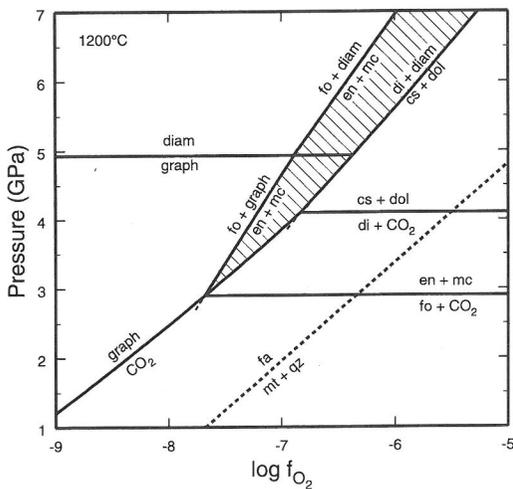
FIG. 5. Pressure- $log\, fO_2$ section at 1200°C. For brevity, O_2 is omitted from the redox reactions. Non-redox reactions illustrated are graphite = diamond, 2 SiO_2 (cs) + $CaMg(CO_3)_2$ (dol) = $CaMgSi_2O_6$ (di) + 2 CO_2, and $Mg_2Si_2O_6$ (en) + 2 $MgCO_3$ (mc) = 2 Mg_2SiO_4 (fo) + 2 CO_2. Redox reactions shown are graphite + O_2 = CO_2, 2 Mg_2SiO_4 (ol) + 2 C (graphite or diamond) + 2 O_2 = 2 $Mg_2Si_2O_6$ (en) + 2 $MgCO_3$ (mc), and $CaMgSi_2O_6$ (di) + 2 C (graphite or diamond) + 2 O_2 = 2 SiO_2 (cs) + $CaMg(CO_3)_2$ (dol). FMQ reaction shown for reference. Curves calculated with HOLLAND and POWELL (1990) Thermocalc and FROST and WOOD (1997) for GCO.
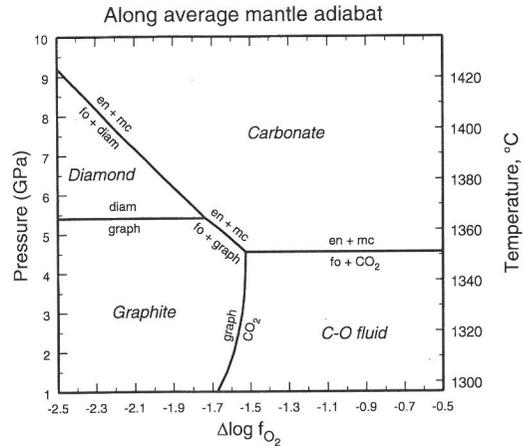

FIG. 6. Phase relationships along the average mantle adiabat shown in Fig. 4, illustrating the stable forms of C-bearing phases (after FROST and WOOD, 1997). Values of $\mu log fO_2$ are calculated relative to the $log fO_2$ of the FMQ reaction at the same pressure and temperature. Curves calculated with Thermocalc (HOLLAND and POWELL, 1990).

is in an isothermal P- $log\, fO_2$ projection (Fig. 5). The horizontal lines on this figure represent the fO_2-independent carbonation reactions, and the polymorphic diamond = graphite reaction. The other curves represent the reactions outlined above that involve O_2 for both the peridotite (EMOG/D) and eclogitic (DCDG/D) lithologies. For reference, the location of the FMQ buffer is given. LUTH (1993) drew attention to the P,T, fO_2 region in which carbonate would be stable in a peridotite but elemental carbon would be stable in a coexisting eclogite. This region corresponds to the wedge-shaped, diagonally-ruled area bounded by the EMOG/D, DCDG/D, and GCO reactions in Fig. 5. If we have a situation where the EMOG/D reaction in peridotite imposes its fO_2 on coexisting eclogite, diamond-bearing eclogite could coexist with peridotite-containing carbonate or both carbonate and diamond. Such a situation may hold in a dominantly peridotite region with subordinate eclogite- as is inferred to exist in many areas of subcratonic mantle from the relative abundances of these lithologies in xenolith suites, and in subcontinental mantle in general, which is pervasively veined with pyroxenites as evidenced by peridotite massifs (see earlier).

Another way to view these relationships that is more directly applicable to the Earth is to consider the stabilities along contrasting thermal regimes, such as an average mantle adiabat (Fig. 6, after FROST and WOOD, 1997) and an Archean Shield geotherm (Fig. 7). In these two figures, $log\, fO_2$ relative to FMQ is plotted on the abscissa, and temperature varies with
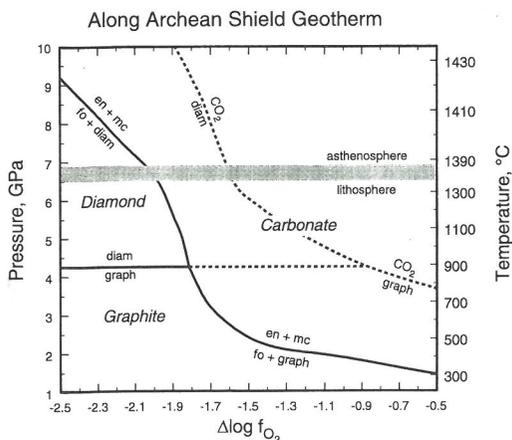
FIG. 7. Phase relationships along the Archean Shield geotherm shown in Fig. 4, illustrating the stable forms of C-bearing phases (after FROST and WOOD, 1997). The metastable curves for the C-O system (dashed lines) are shown for comparison. Values of μlogfO_2 are calculated relative to the logfO_2 of the FMQ reaction at the same pressure and temperature. For reference, the lithosphere- asthenosphere boundary is shown, which corresponds to where the Archean Shield geotherm intersects the average mantle adiabat. Curves calculated with Thermocalc (HOLLAND and POWELL, 1990).

pressure along the ordinate as shown on the righthand axis. Along an average mantle adiabat (Fig. 6), fields for C-O fluid or graphite or diamond exist at low pressure, but a large field for carbonate stability exists at higher pressure along such an adiabat, as was pointed out by FROST and WOOD (1997). For clarity, only the peridotite reactions are shown in Fig. 6; the eclogite reactions (DCDG/D or the carbonation reaction) would be displaced to higher pressures relative to the peridotite reactions. In addition, portions of the fields labeled "C-O fluid" and "carbonate" would be replaced by a field of "carbonate-bearing melt" at pressures to ~6 GPa based on the results on peridotite + CO_2 melting of FALLOON and GREEN (1989) that are discussed below.

Along the geotherm in lithosphere beneath a craton assembled in the Archean (Fig. 7), CO_2 would not be stable at any depth, and carbonate would be the only stable oxidized form of carbon in either peridotite or eclogite lithologies, as may be seen by comparing the geotherm with the appropriate carbonation reactions in P-T space (Fig. 4). As well, melting of peridotite (carbonate-bearing or in the presence of a CO_2 fluid at lower pressure) would not be expected along this cooler geotherm. Graphite is stable to higher values of Δlog fO_2 at lower pressure (<2.5 GPa), than it is in convecting mantle. The stability field of carbonate, however, expands to lower values of Δlog fO_2 at the

expense of graphite/diamond from 2.5 to ~6.5 GPa, at the base of the lithosphere. Graphite or diamond would be expected to be stable to more oxidizing conditions in eclogitic assemblages than in peridotitic assemblages, with the DCDG/D reaction falling between the GCO and EMOG/D reactions in Fig. 7.

Consequences of the presence of carbonate: Partitioning of cations between carbonates and silicates

If carbonate is stable in the mantle, then the effect that this additional phase has on the partitioning of elements needs to be explored. To date, most of the effort has been directed to understanding the partitioning of major elements between carbonate and silicates. Trace-element studies have focussed primarily on carbonate *melt*- silicate partitioning (*e.g.,* BRENAN and WATSON, 1991; GREEN *et al.,* 1992; RYABCHIKOV *et al.,* 1993; KLEMME *et al.,* 1995; SWEENEY *et al.,* 1992, 1995) and will not be discussed here.

DALTON and WOOD (1993a) determined the partitioning behavior of Fe and Mg between olivine and carbonate at 2 and 3.5 GPa, 1000–1100°C. They found that Fe favors olivine relative to magnesite and ordered dolomite, but that there is no preferential partitioning of Fe or Mg between disordered, calcic carbonate and olivine. They derived mixing properties for Fe-Mg carbonates from their data, and calculated that the presence of Fe would expand the stability field of dolomite-bearing peridotite by ~0.3 GPa relative to the Fe-free CaO-MgO-SiO_2-CO_2 system. In studies of carbonate liquid- silicate equilibria, DALTON and WOOD (1993B) found that the partitioning of Mg and Fe between carbonate liquid and olivine is more subdued than between silicate liquid and olivine (i.e., $K_d \gg 0.3$). Additional evidence for this level of partition coefficient comes from the study of RYABCHIKOV *et al.* (1989).

In a phase equilibrium study, YAXLEY and GREEN (1994) obtained data on coexisting clinopyroxene, garnet, and carbonate in basaltic systems. They found that increasing temperature, or decreasing pressure, stabilized a more calcic carbonate coexisting with a more magnesian garnet, and suggested that the reaction

$$Ca_3Al_2Si_3O_{12} + 3\ CaMg(CO_3)_2 = Mg_3Al_2Si_3O_{12}$$
$$+ 6\ CaCO_3 \quad (21)$$
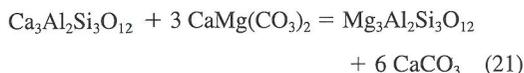
goes to the right with increasing temperature or decreasing pressure.

In more magnesian systems, they found similar behavior, with increasing temperature favoring Mg-rich garnet and Ca-rich carbonate. These inferences

are consistent with the behavior predicted from the equilibrium

$$Ca_3Al_2Si_3O_{12} + 3\,MgCO_3 = Mg_3Al_2Si_3O_{12}$$
$$+ 3\,CaCO_3. \quad (22)$$
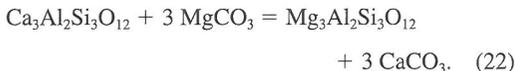
The left-hand side of this reaction is favored by low temperatures at a given pressure, consistent with the findings of YAXLEY and GREEN (1994).

The partitioning of Ca between coexisting garnet and carbonate is of interest because of the observed correlation between Ca-poor garnets and diamonds in kimberlites. Based on their low Ca concentrations, these so-called subcalcic garnets are inferred to have equilibrated last in a clinopyroxene-absent peridotite. These garnets are found both as inclusions in diamonds and in garnet harzburgite xenoliths. BOYD and GURNEY (1982) and BOYD *et al.* (1993) proposed that equilibration of magnesite with garnet, in the absence of clinopyroxene, could partition Ca preferentially into the carbonate, so that the garnet becomes depleted in Ca. In terms of the exchange reaction (22), the right-hand side should be favored. As discussed above, based on YAXLEY and GREEN's (1994) study and calculated equilibria, the right-hand side of this reaction is favored by high temperatures. So one immediate inference is that this mechanism, if it operates at all, will work best at high temperatures. This reaction has the equilibrium constant, K_{eq}, defined by

$$K_{eq} = \frac{(X_{Mg}^{gar})^3(X_{Ca}^{carb})^3(\gamma_{Mg}^{gar})^3(\gamma_{Ca}^{carb})^3}{(X_{Ca}^{gar})^3(X_{Mg}^{carb})^3(\gamma_{Ca}^{gar})^3(\gamma_{Mg}^{carb})^3} = K_D K_\gamma \quad (23)$$

If the hypothesis of BOYD and GURNEY (1982) and BOYD *et al.* (1993) is correct, K_D should be large for the conditions of origin of these low-Ca garnets.

To begin to constrain the partitioning behavior of Ca and Mg between garnet and carbonate, the author conducted reconnaissance experiments on a pyrope + calcite mixture at 5 and 7 GPa at 1000°, 1300°, and 1600°C, and at 11 GPa at 1000° and 1300°C. Run durations in these experiments were 8 hr. In the 1600°C experiments at 5 and 7 GPa, garnet coexists with carbonate-rich interstitial liquid. At lower temperature at all three pressures, the run products contained discrete carbonate grains surrounded by garnet. The garnet contained cores of high-Mg garnet, interpreted as being relic from the pyrope starting material, surrounded by rims (typically 10–20 mm wide) of more calcic garnet. This lack of homogeneity, although not surprising given the low diffusion rates in garnet and its well-known recalcitrance to react in experimentally-reasonable time scales, makes the results somewhat problematic. This
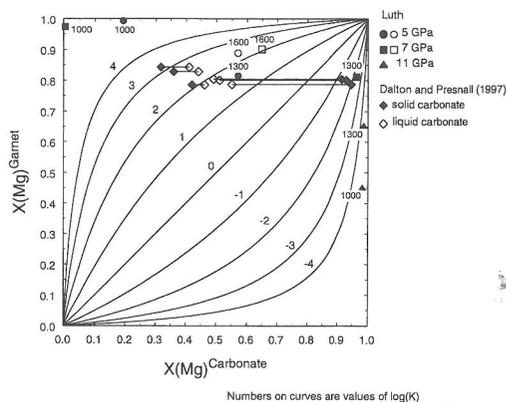
FIG. 8. Compositions of garnet coexisting with solid carbonate (filled symbols) and of garnet coexisting with carbonatitic liquid (open symbols). Data from the author's study of pyrope + calcite starting material shown as circles (5 GPa), squares (7 GPa), and triangles (11 GPa). Numbers next to each datum are temperatures (in °C). Each datum represents the compositions most changed from the starting material, which plots in the upper left-hand corner of the diagram. Data from DALTON and PRESNALL (1998) (diamonds) are compositions of garnet, carbonate, and carbonatitic liquid coexisting with olivine, orthopyroxene, and clinopyroxene in the CMAS-CO_2 system. Tie-lines connect compositions of coexisting carbonate (filled diamonds) and carbonatitic liquid (open diamonds). Reading from left to right [increasing $X(Mg)^{carbonate}$, the data are from 3 GPa, 1245°C; 3.5 GPa, 1270°C; 4 GPa, 1290°C; 5 GPa, 1330°C; 6 GPa, 1380°C; 7 GPa, 1430°C]. Solid lines on diagram are partitioning behavior calculated for values of $\log(K_D)$ given by number on each curve. K_D is the distribution coefficient corresponding to the reaction $Ca_3Al_2Si_3O_{12}$ (gar) + $3\,MgCO_3$ (carb) = $Mg_3Al_2Si_3O_{12}$ (gar) + $3\,CaCO_3$ (carb). Values of $\log(K_D) > 0$ correspond to Ca partitioning into carbonate preferentially to garnet.

is especially true for the 1000°C experiments at 5 and 7 GPa (Fig. 8), which could be interpreted reasonably as showing no reaction, rather than equilibrium compositions, given that the compositions of both phases are very close to those of the starting materials.

In the experiments where some reaction was evident, and garnet coexists with magnesite (7 GPa, 1300°C; 11 GPa, 1000° and 1300°C; see Fig. 8), the values of K_D are < 1, such that Ca favors garnet, rather than carbonate. This result is opposite of that expected if the hypothesis of BOYD and GURNEY (1982) is correct. At 5 GPa and 1300°C, where garnet coexists with an intermediate, "dolomitic" carbonate, $K_D > 1$. At 1600°C at both 5 and 7 GPa, where the coexisting carbonate is quench liquid, $K_D > 1$ as well (Fig. 8).

This last observation raises the interesting possibility that it is interaction of the garnet with a carbonatitic melt, not equilibration with magnesite, that depletes the garnet of Ca. The alternative, that it is

interaction with dolomitic carbonate rather than magnesite, is unlikely to explain low-Ca garnets associated with diamonds because dolomitic carbonate would not be stable at those pressures, having reacted via reaction (16) to form magnesite. Interaction of carbonatitic melts with subcalcic garnets has been proposed on trace element and isotopic grounds by PEARSON et al. (1995), but they did not suggest that the characteristic depletion of the garnet in Ca was a result of this interaction.

Independent substantiating evidence for the potential of this mechanism is provided by the study of DALTON and PRESNALL (1998). They measured the compositions of coexisting olivine, orthopyroxene, clinopyroxene, garnet, solid carbonate, and carbonatitic liquid along the solidus of carbonated lherzolite in the CaO-MgO-Al$_2$O$_3$-SiO$_2$-CO$_2$ system from 3 to 7 GPa. The solid diamonds in Fig. 8 represent partitioning of Ca and Mg between garnet and solid carbonate derived from their compositional data, and the open diamonds represent partitioning between garnet and carbonatitic liquid. The tie lines connect the compositions of the coexisting carbonate and carbonatitic melt at a given pressure and temperature. The X$_{Mg}$ for solid carbonate increases systematically from 3 to 7 GPa, so the data portray a trend of approximately constant garnet composition coupled with progressively more Mg-rich carbonate with increasing pressure (and temperature) along the solidus.

At low pressure (3, 3.5, and 4 GPa), the values of K$_D$ for both solid and liquid carbonate are >1. Once the stable carbonate on the solidus becomes magnesite, however, the K$_D$ for garnet/solid carbonate becomes significantly <1, meaning that Ca favors garnet to solid carbonate. This results from the observation that the Ca/(Ca + Mg) of the liquid did not change abruptly when the composition of the solidus carbonate changed. This conclusion was anticipated by WYLLIE and HUANG (1976), who predicted that the liquid composition will be influenced strongly by the Ca/(Ca + Mg) of the temperature minimum on the liquidus of the CaCO$_3$-MgCO$_3$ system. The composition of the liquid remains "dolomitic", with X$_{Mg}$ ~ 0.5–0.6. The consequence of this is that Ca partitions into the liquid preferentially to the garnet, so that K$_D$ (gar/liquid) > 1 (Fig. 8).

Based on these studies, it is proposed that the low-Ca harzburgites are the result of interaction of carbonatitic melts with peridotite in the lower part of the lithospheric mantle. It is further speculated that this interaction may play a role in precipitating diamond, linking the low-Ca garnets *genetically* to diamond. This hypothesis should be viewed (hopefully) as a refinement of the original proposal by Boyd and

GURNEY (1982), but obviously requires further experimentation to establish its viability. An alternative possibility is that the melt is kimberlitic rather than carbonatitic in composition (MYSEN, pers. comm., 1998). Both of these possibilities merit further study.

Consequences of the presence of carbonate: Melting behavior

The widespread temporal and geographic occurrence of carbonatites is evidence that carbonate magmas and indeed that carbonate exists- or can be generated- in the mantle in different regions over geologic time. The long-standing controversy concerning the origin of carbonatites appears to have been resolved in favor of a magmatic origin (BAILEY, 1993; BARKER, 1996), although many issues, such as the relative importance of immiscibility and fractionation, remain controversial. In particular, the relationship between primary dolomitic carbonate melts observed in experiments, and natural calciocarbonatites, with extremely low Mg contents, is still contentious.

Either carbonate is present as a stable phase in the source region, or carbonatites are the product of large-scale oxidation of elemental carbon, which may result from transfer of carbon-bearing, Fe^{3+}-rich mantle to shallower depths (see earlier discussion). There have been no experimental tests of this latter hypothesis.

A large body of work has been done based on the first possibility, that carbonate is stable in the source region. For example, studies have shown that near-solidus melts of carbonated peridotite at >75 km depth are carbonatitic in nature (WYLLIE et al., 1990; WALLACE and GREEN, 1988; DALTON and WOOD, 1993B; LEE and WYLLIE, 1997). GREEN and WALLACE (1988) proposed that near-solidus carbonatitic melts could be an effective agent of metasomatism in the mantle in the 2.1–3.1 GPa, 930–1080°C region. At lower pressures, they proposed that the melts would become unstable relative to CO$_2$ fluid, and that the cations liberated by decomposition of the melt would react with orthopyroxene to form clinopyroxene + olivine ± spinel. This reaction would lead to "cryptic" metasomatism- and the liberation of CO$_2$ would allow formation of the CO$_2$-rich fluid inclusions that are ubiquitous in lower-pressure (i.e., spinel lherzolite) mantle xenoliths. Evidence for this reaction has been observed in natural wehrlite xenoliths (*e.g.,* YAXLEY et al., 1991; DAUTRIA et al., 1992; RUDNICK et al., 1992), and the reaction has been studied experimentally in natural compositions (DALTON and WOOD, 1993b; YAXLEY and GREEN, 1996). As discussed above, infiltration of carbonatitic melts *at*

higher pressures may explain the low-Ca harzburgite suite of xenoliths.

Subsequent experimental studies verified that carbonatitic melts were very mobile in mantle assemblages (HUNTER and MACKENZIE, 1989; MINARIK and WATSON, 1995), and reinforced the idea that such melts have the potential to alter the geochemistry and mineralogy of mantle through which they traverse. Petrologists studying mantle xenoliths have invoked such melts to explain mineralogic, major- and trace-element features of these rocks (*e.g.,* GREEN and WALLACE, 1988; YAXLEY *et al.*, 1991; DAUTRIA *et al.* 1992, IONOV *et al.* 1993, 1996; HAURI *et al.*, 1993; RUDNICK *et al.*, 1993; WIECHERT *et al.*, 1997). The inferred geochemical effects of such metasomatism have been incorporated into models of magma genesis (*e.g.,* FURMAN 1995).

Given the extensive invocation of this model, systematic experimentation to outline the conditions at which a carbonatitic melt may be generated from, and coexist with, peridotitic assemblages, and the geochemical and mineralogical consequences of this coexistence, is in order. This gap is starting to be addressed by studies such as SWEENEY (1994), and DALTON and PRESNALL (1998).

The groundwork for these studies has been laid in the studies to date of melting in carbonated peridotite systems, in both natural and synthetic (model) systems. This has been an active topic of research since the 1970s at $\leq$ 4 GPa by several groups, and more recently at higher pressures. In the CaO-MgO-SiO$_2$-CO$_2$ model system, the distinguishing features are a
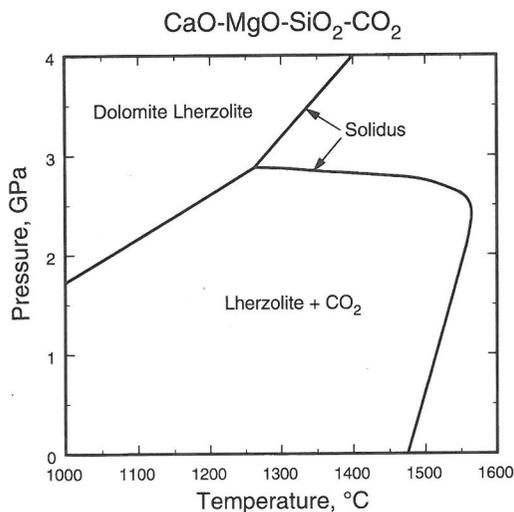
FIG. 10. Solidi for the systems CaO-MgO-SiO$_2$-CO$_2$ (labeled "CMS" in figure) and for CaO-MgO-Al$_2$O$_3$-SiO$_2$-CO$_2$ (labeled "CMAS" in figure) from CANIL and SCARFE (1990). Subsolidus assemblages are ol + cpx + carb $\pm$ opx and ol + opx + cpx + gar + carb, respectively.

pronounced depression of the solidus to lower temperatures at 2.5–3 GPa (Fig. 9, after WHITE and WYLLIE, 1992), where the near-solidus melt changes from alkali basalt at low pressure to dolomite-carbonatite at higher pressures. This depression produces a "ledge" on the solidus in P-T space, which could trap ascending melts and force them to crystallize and exsolve fluids (*e.g.,* WYLLIE, 1987a,b; EGGLER, 1987a,b).

At higher pressure, CANIL and SCARFE (1990) studied the melting behavior of CaO-MgO-SiO$_2$-CO$_2$ and CaO-MgO-Al$_2$O$_3$-SiO$_2$-CO$_2$ from 4 to ~12 GPa (Fig. 10). They found that near-solidus melts resembled kimberlites, and that magnesite was a stable solidus phase throughout this pressure interval. Recently, DALTON and PRESNALL (1998) studied the phase relations in CaO-MgO-Al$_2$O$_3$-SiO$_2$-CO$_2$ to 7 GPa, capitalizing on the fact that the assemblage *L* + *ol* + *opx* + *cpx* + *gar* + *carbonate*[1] is univariant, and can exist only at a single temperature at a given pressure, independent of the modal proportions of phases present. This allowed iterative "tailoring" of the experimental bulk composition to generate large proportions of melt, which minimizes uncertainties in analyzing the composition of the melts produced. Their results (Fig. 11) are displaced to higher temperatures compared to the results of CANIL and SCARFE (1990). DALTON and PRESNALL (1998) suggested that the difference was a result of the thermo-

CaO-MgO-SiO$_2$-CO$_2$

FIG. 9. Solidus in the system CaO-MgO-SiO2-CO$_2$ for coexisting olivine + orthopyroxene + clinopyroxene + CO$_2$ or carbonate. After WHITE and WYLLIE (1992).

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[1] the italics here and in subsequent usage indicate that the measured phase compositions are being used.

CaO-MgO-Al$_2$O$_3$-SiO$_2$-CO$_2$
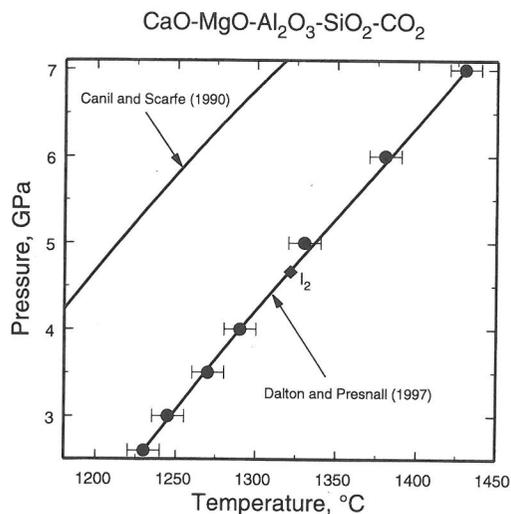
FIG. 11. Solidus in the system CaO-MgO-Al$_2$O$_3$-CO$_2$ from DALTON and PRESNALL (1998) compared to that from CANIL and SCARFE (1990). I$_2$ is the invariant point on the solidus where the exchange reaction discussed in the text intersects the solidus. The exchange reaction is not shown on this figure for clarity.

couple configurations used, with the configuration used by CANIL and SCARFE (1990), in which the thermocouple penetrates the furnace at the hot spot, being liable to underestimate temperatures. Another possibility is that the composition used by CANIL and SCARFE (1990) generated small amounts of melt near the solidus, and reliable determination of the solidus in this situation is always problematic. The technique used by DALTON and PRESNALL (1998) should be more reliable in determining solidus locations.

The melts of DALTON and PRESNALL (1998) were carbonatitic, with < 6 wt.% SiO$_2$, and the Ca/(Ca+Mg) of the melts decreased smoothly from 0.59 at 3 GPa to 0.45 at 7 GPa. As discussed previously, they did not observe an abrupt increase in Mg-content of the melt at ~5 GPa, where the coexisting solid carbonate changed from dolomite to magnesite (Fig. 6 of DALTON and PRESNALL, 1998). This result does not confirm predictions of earlier workers (BREY et al., 1983; KATSURA and ITO, 1990) that such an increase should be observed.

The melting reactions found by DALTON and PRESNALL (1998) were peritectic, changing with increasing pressure from $dol + opx + gt = ol + cpx + L$ at 3, 3.5, and 4 GPa to $mag + cpx = ol + opx + gt + L$ at 5 and 6 GPa, and then to $mag + gt + cpx = ol + opx + L$ at 7 GPa. In addition, they inferred that the decarbonation reaction in CaO-MgO-SiO$_2$-CO$_2$ (Reaction 11) becomes $dol + opx = ol + cpx + gt + CO_2$ with the addition of alumina. Similarly, the

exchange reaction (16) changes with the addition of alumina to involve small amounts of garnet and olivine: $48 opx + 49 dol + 2 gt + 1 ol = 55 cpx + 45 mag$ (the high-pressure side is on the right to be consistent with reaction (16) as written).

DALTON and PRESNALL (IN PRESS) determined melt compositions as a function of temperature at 6 GPa for the divariant assemblage $L + ol + opx + cpx + gar$ in the CaO-MgO-Al$_2$O$_3$-SiO$_2$-CO$_2$ system. They found a systematic increase in the concentrations of SiO$_2$, Al$_2$O$_3$, and MgO, and a decrease in the concentrations of CaO and CO$_2$ with increasing temperature. They propose that this systematic change in melt composition reflects an evolution from carbonatitic melts (~45 wt. % CO$_2$, ~5 wt. % SiO$_2$, Ca/(Ca + Mg) ~ 0.49) at the carbonated solidus to kimberlitic melts (~34 wt. % SiO$_2$, ~30 wt. % MgO, ~17 wt. % CaO, ~17 wt. % CO$_2$) at 125°C above the solidus.

In natural peridotite + CO$_2$ systems, the studies by WENDLANDT and MYSEN (1980) and FALLOON and GREEN (1989) are germane to the present discussion. The former authors determined the solidus temperatures at 1.5 and 3 GPa in a study concerned primarily with understanding the phase relationships above the solidus, particularly with understanding how the degree of partial melting was related to temperature and residual assemblage. The results of FALLOON and GREEN (1989) (Fig. 12) on the melting behavior of "pyrolite" + CO$_2$ show features similar to those in the simpler systems. The solidus, as expected, is shifted to lower temperatures in the presence of additional components, especially FeO and Na$_2$O. The same "ledge" in P-T space is present, formed by the depression of the solidus at ~2 GPa, but is shifted to lower pressures- as well as lower temperatures- relative to its position in the CaO-MgO-SiO$_2$-CO$_2$ system.

The solidus determined by FALLOON and GREEN (1989) is at lower temperature than that inferred by WENDLANDT and MYSEN (1980), who had attributed low-temperature melting (<5 % melting) in their experiments to the ingress of H$_2$ and formation of H$_2$O in their charges, with attendant depression of the solidus. WENDLANDT and MYSEN (1980) suggested that the solidus of PHN1611+CO$_2$ is ~1400°C at 1.5 GPa and ~1150°C for vapor-undersaturated conditions at 3 GPa (diamonds in Fig. 12). The discrepancy between the two solidi, noted by FALLOON and GREEN (1989), has not been revisited.

The low temperatures for the solidus found in the study by FALLOON and GREEN (1989) imply that carbonate-bearing lherzolite will not be stable on an average mantle adiabat, at least to pressures > 4 GPa, but rather a carbonate-bearing melt will coexist with
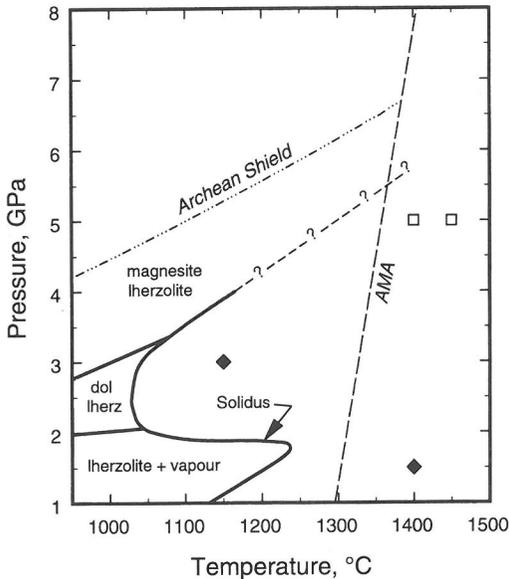
FIG. 12. Phase relations in natural peridotite + CO_2 systems. Curves and labeled fields from FALLOON and GREEN (1989) for (pyrolite- 40% olivine) + CO_2. Solidus extrapolated linearly from their low-pressure data; no data exist at > 4 GPa. Diamonds are solidus determinations from WENDLANDT and MYSEN (1980). Open squares are supersolidus experiments of RYABCHIKOV *et al.* (1989). Average mantle adiabat (AMA) and Archean Shield geotherm from MCKENZIE and BICKLE (1988).

silicate residue (Fig. 12). In contrast, the lower temperatures present in sub-cratonic mantle would allow the existence of carbonate-bearing lherzolites in these areas. If, on the other hand, the interpretation of WENDLANDT and MYSEN (1980) is correct, the solidus for carbonated peridotite must intersect the mantle adiabat between 1.5 and 3 GPa (*cf.* diamonds in Fig. 12), with peridotite + CO_2, and potentially carbonate-bearing peridotite, being stable at low pressures along the adiabat. The low temperatures for the solidus found for carbonate-bearing peridotite at 3 GPa by WENDLANDT and MYSEN (1980) would still require carbonate-bearing melt, rather than carbonate-bearing peridotite, be the stable host for carbonate in the "average" mantle at pressures > ~2 GPa.

The possibility of carbonate existing at higher pressures in "normal" mantle depends on the relative slopes in P-T space of the solidus at > 4 GPa and the mantle adiabat. Extrapolating the results of FALLOON and GREEN (1989) would lead to an intersection of the solidus and the adiabat at 4-6 GPa (Fig. 12). This extrapolation may be constrained with the results of the study of RYABCHIKOV *et al.* (1989), who report liquid coexisting with olivine + orthopyroxene + clinopyroxene + garnet at 1400°C and 1450°C at 5

GPa. These results require the solidus to be at < 1400°C at 5 GPa. Also of interest in this study is the observed change in melt composition with increasing temperature; the SiO_2 content increased from ~4 wt.% at 1400° to ~13.5 wt.% at 1450°, consistent with the findings of DALTON and PRESNALL (in press) in the synthetic $CaO-MgO-Al_2O_3-SiO_2-CO_2$ system. Therefore, magnesite-bearing peridotite will be stable at depths > ~150 km in normal, convecting mantle.

The melting reactions of carbonated non-peridotitic bulk compositions (*e.g.* eclogite) have not been studied extensively to date. YAXLEY and GREEN (1994) studied the melting behavior of a basaltic composition containing both H_2O (in amphibole) and CO_2 (in calcite or magnesite), but did not look at the anhydrous endmember. They found that carbonate was stable in equilibrium with a hydrous dacitic melt and a rutile + garnet + clinopyroxene residue at 2.5–3.5 GPa and 700–900°C.

SUMMARY

Although significant progress has been made in constraining the behavior of carbon-bearing phases in the mantle, areas of significant ignorance remain.

(1) There is a need to delineate explicitly the conditions in P-T-X space where a carbonated melt (either carbonatitic or silicate-rich) coexists with peridotitic or eclogitic bulk compositions. Exploration of the consequences of interaction of such melts with peridotite within the diamond stability field are in order to establish if there is a link between such melts and the presence of low-Ca harzburgites and diamonds.

(2) Better understanding of the controls of the oxidation state are (still) in order, as is testing experimentally the hypothesis that the relative oxidation state of the mantle decreases with depth.

(3) Efforts need to be directed towards improving the thermodynamic database at mantle pressures to allow computational exploration of some of these questions to complement experimental studies.

(4) Renewed studies of mixed-volatile systems must be conducted and should build on the "simpler" C-only studies reviewed here.

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