

This PDF file is subject to the following conditions and restrictions:

Copyright © 2005, The Geological Society of America, Inc. (GSA). All rights reserved. Copyright not claimed on content prepared wholly by U.S. government employees within scope of their employment. Individual scientists are hereby granted permission, without fees or further requests to GSA, to use a single figure, a single table, and/or a brief paragraph of text in other subsequent works and to make unlimited copies for noncommercial use in classrooms to further education and science. For any other use, contact Copyright Permissions, GSA, P.O. Box 9140, Boulder, CO 80301-9140, USA, fax 303-357-1073, editing@geosociety.org. GSA provides this and other forums for the presentation of diverse opinions and positions by scientists worldwide, regardless of their race, citizenship, gender, religion, or political viewpoint. Opinions presented in this publication do not reflect official positions of the Society.

Carbonate-rich melts in the oceanic low-velocity zone and deep mantle

Dean C. Presnall*

*Department of Geosciences, University of Texas at Dallas, P.O. Box 830688, Richardson, Texas 75083-0688, USA,
and Geophysical Laboratory, 5251 Broad Branch Rd., N.W., Washington, D.C. 20015-1305, USA*

Gudmundur H. Gudfinnsson*

Geophysical Laboratory, 5251 Broad Branch Rd., N.W., Washington, D.C. 20015-1305, USA

ABSTRACT

Deep extensions of low seismic velocities in the mantle beneath volcanic centers are commonly attributed to high temperatures and have been used as a possible characteristic of hot plumes originating at the core-mantle boundary. To address this issue, we examine the effect of volatiles on melting to determine if regions of low seismic velocities may also be interpreted as regions of melting without elevated temperatures. We find that for the very small amounts of H₂O in the oceanic mantle, the effect on solidus temperatures is a reduction of at most ~13 °C, which can be neglected. In contrast, even the smallest amount of carbonate reduces solidus temperatures more than 300 °C at pressures greater than 1.9 GPa. The close match between detailed seismic imaging of the upper boundary of the low-velocity zone on the East Pacific Rise and the sharp temperature decrease for the carbonated lherzolite solidus at ~1.9 GPa supports earlier suggestions that the low-velocity zone (~70–150 km depth) is caused by melting due to the presence of carbonate. For locally elevated concentrations of carbonate subducted into the mantle along with oceanic crust, melting of the resulting carbonated lherzolite and carbonated eclogite could also occur at greater depths, possibly into the lower mantle, without elevated temperatures. Thus seismic imaging of deep low-velocity regions may reveal the locations of old subducted crust rather than hot plumes.

Keywords: plume, carbon dioxide, mantle melting, carbonatite, low-velocity zone

INTRODUCTION

The presence of small amounts of carbon in the Earth's mantle has a profound effect on melting behavior. Carbon shows almost no solubility in any mantle phase (Keppler et al., 2003). Therefore, under oxidizing conditions it forms a separate phase,

carbonate, which melts at temperatures far below the melting temperatures of silicates. During melting of the carbonate, the silicate mantle behaves as an imperfect capsule that reacts only a small amount with its contents. When carbonate is present at pressures greater than ~1.9 GPa, the mantle melts initially at temperatures at least 300 °C lower than those associated with

*E-mails: d.presnall@gl.ciw.edu; g.gudfinnsson@gl.ciw.edu.

the generation of basaltic magmas, and these initial melts are carbonatitic. It is these low-temperature, low-volume melts that are discussed here, not basaltic melts.

We first address the effect of water in controlling temperatures of melting in the oceanic mantle. We then examine the effect of carbonate and combine this with seismic observations to develop a model for melting in the upper 300 km of the oceanic mantle. This includes the depth range of the seismic low-velocity zone, which has long been thought to be caused by melting (Anderson and Sammis, 1970). However, agreement about this is not complete (Karato and Jung, 1998).

Deep low-velocity regions beneath volcanic centers extend, in some cases, to ~700 km (Ritsema and Allen, 2003) and at Iceland have been explained by partial melting or a combination of partial melting and elevated temperature (Foulger et al., 2001). The claim that some low-velocity features extend to the core-mantle boundary (Montelli et al., 2004) and represent evidence for hot plumes has been the focus of some disagreement. On the basis of recent experimental studies at high pressures, we examine the possibility that low-velocity anomalies extending to depths of ~700 km and possibly into the lower mantle may be caused by small amounts of melting without enhanced temperatures.

EFFECT OF WATER ON SOLIDUS TEMPERATURES

Michael (1988) found that the maximum amount of H₂O in the least fractionated mid-ocean ridge basalt glasses (MORBs) is ~0.21 wt.% and concluded from this that the amount of H₂O in the oceanic mantle source for enriched MORBs is ~350 ppm, an amount similar to that estimated by others. Table 1 shows that this is less than the bulk solubility of H₂O in garnet lherzolite. This result is less ambiguous than the discussion in Presnall et al. (2002) because of the recent revision of the infrared calibration for determination of H₂O in olivine (Bell et al., 2003), which increases the solubility limits for this mineral by a factor of 3.5.

Therefore, all the H₂O would normally be taken up by the nominally anhydrous phases, and none would be available for the formation of amphibole or phlogopite, a conclusion consistent with the complete absence of primary hydrous phases in abyssal peridotites (Dick et al., 1984). This absence of primary hydrous phases simplifies consideration of the shape of the solidus curve in the discussion of the MORB solidus that follows, and we suggest that this is the normal situation in the oceanic mantle. However, the mantle beneath Hawaii is different. Amphibole has been found in Hawaiian pyroxenite and pyroxenite-veined lherzolite xenoliths at Salt Lake Crater, Oahu, Hawaii (Sen, 1988; Sen et al., 1996), which is consistent with the elevated concentration of H₂O in Hawaiian lavas (Dixon and Clague, 2001). The difference in H₂O content between Hawaiian lavas and MORBs sampled from many localities suggests that the mantle beneath Hawaii is anomalous for the ocean basins.

In the absence of hydrous phases, H₂O lowers melting temperatures of peridotite. A well-constrained result for a simple system is provided by the study of Egglar and Rosenhauer (1978). They determined the liquidus of the system CaMgSi₂O₆-H₂O at 2 and 3 GPa and found that the melting curve of diopside is slightly concave at both pressures. At 2 GPa, 0.2% H₂O in the melt reduces the diopside liquidus by 7 °C, and at 3 GPa the reduction is 12 °C. Thus, a pressure effect exists, but for the small amount of H₂O considered here, it is not important. Another approach is to use the parameterization of Katz et al. (2003), an average of several studies on the depression of the solidus for natural peridotite compositions. Their parameterization, which ignores the effect of pressure, yields a solidus reduction of 13 °C for 0.2% H₂O in the melt. As both of these methods yield temperature reductions that are very small and in good agreement, the effect of H₂O on oceanic mantle melting behavior will be ignored. Even at Hawaii, where the amount of H₂O in primitive melts is ~0.4%, the equation of Katz et al. (2003) gives a solidus suppression of only 22 °C.

TABLE 1. H₂O IN NOMINALLY ANHYDROUS MANTLE MINERALS

	Maximum, natural minerals (ppm)	Maximum solubility observed experimentally	
		ppm	Conditions
Olivine	240 ¹	1800 ² 473 ³ 1736 ³	1000–1100 °C, 1.5 GPa 1100 °C, 2.5 GPa 1100 °C, 5 GPa
Orthopyroxene	650 ⁴	870 ²	1000–1100 °C, 1.5 GPa
Clinopyroxene	515 ⁴	2600–4100 ²	1000–1100 °C, 1.5 GPa
Pyrope	226 ⁴	430–1010 ⁵	1000 °C, 2.5–6 GPa
Bulk ⁶	360	620–1580	

Notes:

¹Bell et al. (2003).

²Kohn (1996).

³D. L. Kohlstedt (2004, personal commun.), who used the data of Kohlstedt et al. (1996) with the infrared calibration of Bell et al. (2003).

⁴Rossman (1996).

⁵Withers et al. (1998).

⁶65% olivine, 28% orthopyroxene, 3% clinopyroxene, 4% garnet (McDonough, 1990).

EFFECT OF CARBONATE ON SOLIDUS TEMPERATURES

The behavior of CO_2 is very different from that of H_2O . As C has a maximum solubility of only 1–5 ppm in normal mantle phases at 1.5–6 GPa, 900–1300 °C (Keppler et al., 2003), it occurs in the upper mantle as graphite, diamond, CO_2 vapor, carbonate minerals, or carbonate-rich melt. For a natural carbonated lherzolite, the transition at the solidus from CO_2 -rich vapor to dolomite has been found to occur at 1.9 GPa (Fig. 1). At lower solidus pressures, the instability of carbonate means that small amounts of CO_2 do not have a significant effect on solidus temperatures. However, at pressures above 1.9 GPa and oxygen fugacities (f_{O_2}) consistent with carbonate stability, even the smallest amounts of carbonate reduce the mantle solidus at least 300 °C below the carbonate-free solidus and the initial melt is carbonatitic (Wyllie and Huang, 1975; Eggler, 1978; Falloon and Green, 1989; Dalton and Presnall, 1998a). No separate vapor phase is present. The abrupt temperature reduction of the solidus at 1.9 GPa occurs because dolomite becomes stable at this pressure and the melting temperature of dolomite is far below the solidus of the silicate phase assemblage. The key feature of carbonate is that, unlike the case for H_2O , the amount of solidus suppression at pressures above 1.9 GPa is not a function

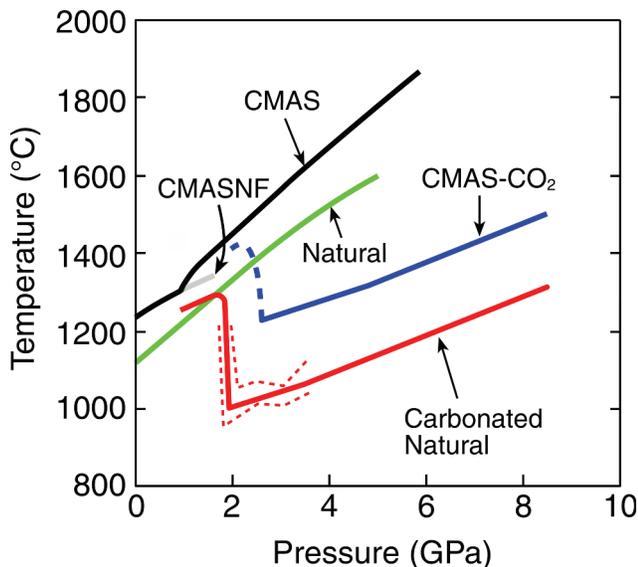


Figure 1. Solidus curves for various natural and model-system lherzolite compositions: Natural (green)—volatile-free natural lherzolite using the 5 GPa temperature from Leshner et al. (2003) and the 1 atm temperature and higher-pressure curvature from Hirschmann (2000); CMAS—model lherzolite in the $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ system (Presnall et al., 2002); CMASNF (gray)—model lherzolite for the plagioclase-spinel lherzolite transition (olivine + orthopyroxene + clinopyroxene + spinel + plagioclase + liquid) in the $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-Na}_2\text{O-FeO}$ system (Presnall et al., 2002); CMAS- CO_2 (blue)—model carbonated lherzolite (Dalton and Presnall, 1998b; Gudfinnsson and Presnall, 2005); carbonated natural (red)—carbonated natural lherzolite solidus showing limits of bracketing experiments (Falloon and Green, 1989).

of the amount present. Because C is almost totally excluded from all mantle minerals, even the smallest amount produces the full temperature reduction as soon as dolomite becomes stable. Recognition of the importance of carbonate is demanded by the fact that 75%–97% of the vapor in MORB vesicles is CO_2 (Javoy and Pineau, 1991), and these vesicles, in the experience of H.J.B. Dick (2003, personal commun.), are always present in MORBs at the scale of a single dredge haul. Also, CO_2 is abundant in Hawaiian tholeiitic eruptions (~0.7%; Gerlach and Graeber, 1985; Gerlach et al., 2002) and is probably present at some level in all volcanic eruptions.

SUBCRATONIC AND OCEANIC MANTLE CARBONATE STABILITY

The stability of dolomite at lherzolite solidus temperatures starts at 1.9 GPa (Falloon and Green, 1989) and extends to 4.8 GPa at the $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-CO}_2$ lherzolite solidus (Dalton and Presnall, 1998a) but only to ~3.5 GPa on the real mantle solidus (Fig. 2). This difference is caused by the steeply positive slope of the curve along which dolomite converts to magnesite with increasing pressure. Magnesite then remains stable to pressures in excess of 100 GPa at temperatures above 2000 °C (Biellmann et al., 1993; Isshiki et al., 2004). Therefore, in the absence of coexisting phases that might react with the carbonate and reduce it to graphite or diamond, carbonate is stable throughout most of the upper and lower mantle.

Wood et al. (1990) suggested that in the garnet lherzolite field the amount of Fe^{3+} in garnet increases with pressure, and that this is accomplished by reduction of carbonate to graphite or diamond. Canil and O'Neill (1996) determined the amounts of Fe^{3+} in all the coexisting phases for a suite of subcratonic garnet lherzolites and confirmed that the amount of Fe^{3+} in garnet progressively increases with temperature and pressure. They also found that the whole-rock Fe_2O_3 content remains relatively constant with temperature and attributed the increase of Fe^{3+} in garnet to a corresponding loss of Fe^{3+} from orthopyroxene and clinopyroxene. For some of their samples that contain graphite or diamond, part of the Fe^{3+} in garnet would appear to be present at the expense of carbonate.

In general agreement with these results, the f_{O_2} of garnet peridotites and pyroxenites from the Fennoscandian, South African, and Slave cratons have been determined to be about FMQ (fayalite-quartz-magnetite oxygen buffer) – 3 log units, with a progressive decrease from roughly FMQ to FMQ – 4 log units as pressure increases from 2 to 7 GPa (Gudmundsson and Wood, 1995; Woodland and Peltonen, 1999; McCammon et al., 2001; Woodland and Koch, 2003; McCammon and Kopylova, 2004). As the minimum f_{O_2} for carbonate stability is about FMQ – 1.7 log units (Wood et al., 1990), these studies suggest that beneath cratons an f_{O_2} sufficiently high for carbonate stability normally persists for only a limited pressure range into the garnet lherzolite field, perhaps to ~3 GPa.

Regions of the mantle with sufficient carbonate to exceed

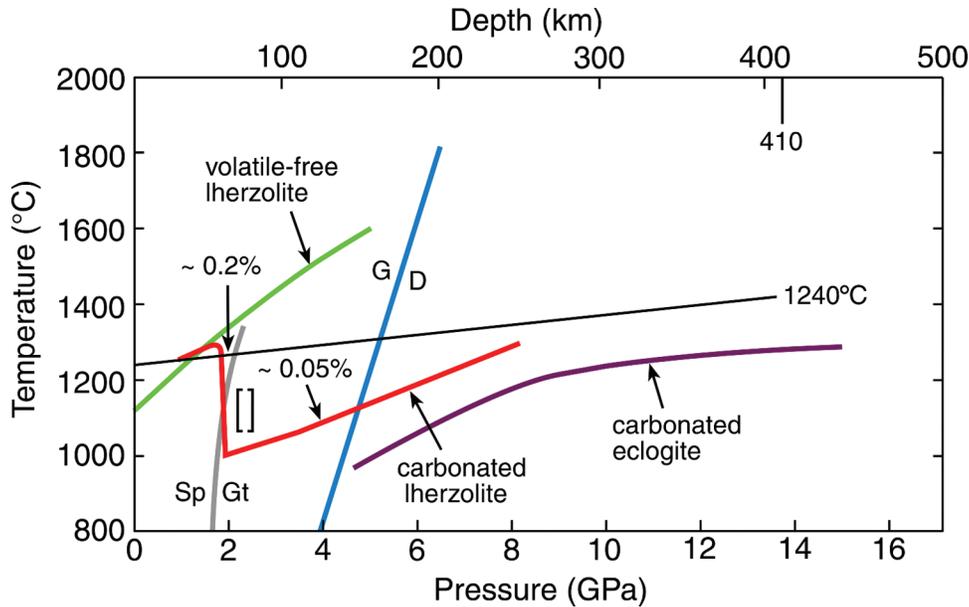


Figure 2. Solidus curves for natural compositions. Adiabats at a potential temperature of 1240 °C is the lower limit of the range indicated by Presnall et al. (2002) for generation of mid-ocean ridge basalts. Deflection of the adiabat at the solidus curve is not shown because the amount of melt is very small. The carbonated eclogite curve is from Shirasaka and Takahashi (2003). The data of Dasgupta et al. (2004) at 4–8.5 GPa are consistent with the solidus of Shirasaka and Takahashi (2003) within experimental uncertainty. Brackets at 70–80 km are the depth of maximum off-ridge reduction of shear velocity at the MELT (Mantle Electromagnetic Tomography) experiment on the East Pacific Rise (Conder et al., 2002). The values of 0.2% and 0.05% indicate estimates, based on the data of Gudfinnsson and Presnall (2005), of the amount of melt on the 1240 °C adiabat at 2 GPa and along the entire solidus above 1.9 GPa for the assumption of a lherzolite with 200 ppm CO₂. G/D—graphite-diamond transition (Bundy et al., 1961); Sp/Gt—spinel lherzolite–garnet lherzolite transition (O’Hara et al., 1971).

the reducing capacity of the garnet would preserve high fO_2 values to greater depths. Indeed, the xenoliths that have indicated a progressively decreasing fO_2 with depth beneath cratons were brought to the surface by deeper kimberlite melts containing large amounts of carbonate. Experimental studies (Dalton and Presnall, 1998a,b; Gudfinnsson and Presnall, 2005) strongly support the formation of kimberlite magmas by melting of a carbonated lherzolite mantle, and the data of Gudfinnsson and Presnall (2005) suggest a depth of origin for some kimberlites of greater than 250 km. Furthermore, carbonatitic melts and carbonate minerals have been found as inclusions in diamonds (Schrauder and Navon, 1994; Wang et al., 1996; Sobolev et al., 1997; Stachel et al., 1998; Leost et al., 2003), and it has been shown experimentally that diamonds will grow in a carbonate melt at high pressures (Arima et al., 1993; Pal’yanov et al., 1999; Sokol et al., 2001). Thus, even though the subcratonic mantle appears generally to decrease in fO_2 with depth so that carbonate is no longer stable, local enrichment in carbonate that exceeds the reducing capacity of garnet must exist to at least ~220 km depth (~7 GPa), the approximate maximum recovery depth of peridotite xenoliths.

A rough estimate of the amount of carbonate necessary for

persistence at significant depths into the garnet lherzolite stability field is instructive. We assume initially that all of the Fe³⁺ in garnet comes at the expense of carbonate. Typical garnet lherzolites average ~4%–5% garnet (Boyd and Nixon, 1972; McDonough, 1990), and the Fe₂O₃ content of mantle garnets in high-temperature garnet lherzolites ranges from 0.20% to 1.56% (Luth et al., 1990; Canil and O’Neill, 1996; Woodland and Koch, 2003). For this amount of Fe₂O₃ an average garnet lherzolite would convert ~13–100 ppm CO₂ to diamond. Much less would be reduced if coexisting pyroxenes rather than carbonate were the main contributors to Fe³⁺ in garnet (Canil and O’Neill, 1996). Thus, garnet lherzolites beneath cratons with very low fO_2 values would be expected to have very small amounts of graphite or diamond but no carbonate. This is consistent with the presence of diamond or graphite in some garnet lherzolite xenoliths (Pearson et al., 1994), the extreme rarity of carbonate in these xenoliths (Canil, 1990), and the generally depleted character of much of the mantle beneath cratons. The isolation of this part of the mantle from the actively convecting mantle and its attachment to the overlying crust for 1–3 b.y. (Pearson et al., 2003) would commonly prevent it from being resupplied with subducted carbonate. This suggests that the

oceanic mantle may be more oxidized than the cratonic upper mantle.

The stability of carbonate in the oceanic mantle has also been examined. Wood et al. (1990) found that the average fO_2 of the MORB mantle, as determined from abyssal spinel peridotites, averages about FMQ – 0.9 log units. This is in general agreement with values determined from MORB glasses (Christie et al., 1986) and is consistent with the stability of carbonate. Unfortunately, the complete absence of garnet-bearing peridotite samples at ridges prevents direct determination of fO_2 at depths greater than that of the garnet-spinel lherzolite transition at ~1.9 GPa (Fig. 2).

Estimates of the amount of CO_2 in the oceanic mantle are based on the amount of CO_2 in oceanic basalts and various kinds of modeling (Gerlach and Graeber, 1985; Greenland et al., 1985; Marty and Jambon, 1987; Gerlach, 1989; Bottinga and Javoy, 1990; Blundy et al., 1991; Trull et al., 1993; Zhang and Zindler, 1993; Canil et al., 1994; Gerlach et al., 2002; Saal et al., 2002). Values range from 72 to 3700 ppm, and there is no consensus. Given that carbonate is recycled back into the mantle at subduction zones (Becker and Altherr, 1992; Zhang et al., 2002), it is expected to be present in the oceanic mantle, and strong heterogeneity is likely. Carbonate has been described in xenoliths from the Canary Islands (Frezzotti et al., 2002), and Keshav and Sen (2003) found evidence for kimberlitic melts at Hawaii. A carbonatite volcano even occurs at Santiago, Cape Verde Islands (Silva et al., 1981), and carbonatite eruptions have occurred at Fuerteventura, Canary Islands (Hoernle et al., 2002). As carbonatitic melts in equilibrium with lherzolite are stable only at pressures greater than 1.9 GPa, these magmas must have originated in the garnet lherzolite field (Fig. 2). Microdiamonds in a garnet pyroxenite xenolith from Salt Lake Crater, Oahu, Hawaii (Wirth and Rocholl, 2003), indicate a pressure greater than ~6 GPa, and Bizimis et al. (2003) found carbonate in another garnet pyroxenite xenolith from this locality.

Because samples of the oceanic mantle at depths greater than that of the spinel lherzolite facies are rare, the variation in oxidation state with depth is not known. Therefore, we assume that progressive reduction with depth, like that found in the cratonic mantle, is the normal situation in the ocean mantle. However, the occasional presence of deep carbonate, as at Hawaii and the Canary and Cape Verde Islands, indicates that local carbonate enrichments extend to depths of at least 200 km and probably much deeper. The most likely situation for the oceanic mantle is that the amount of CO_2 varies strongly but is commonly ~100–200 ppm, which is within the extremes of proposed values. This amount would generally not exceed the reducing capacity of Fe^{3+} in garnet and would probably result in the exhaustion of carbonate at a depth less than ~150–200 km.

OCEANIC MANTLE SOLIDUS CURVE

Figure 1 shows model system and natural composition data used for construction of an oceanic solidus curve for carbonated

lherzolite. The effect of water is neglected at all pressures, and the effect of carbonate is neglected at pressures less than 1.9 GPa. Important features are (1) the nearly identical slopes of the CaO-MgO- Al_2O_3 - SiO_2 (CMAS) model-system lherzolite solidus (black) and the average volatile-free lherzolite solidus (green) determined from experiments on natural peridotites, and also (2) the nearly identical forms of the CMAS- CO_2 model lherzolite solidus (blue) and the solidus (dotted red brackets) determined on a natural carbonated lherzolite. The lower pressure for the steeply negative slope of the natural carbonated lherzolite solidus is caused by the positive slope of the subsolidus decarbonation reaction (not shown) that intersects both solidus curves and defines the base of the steeply negative slope in each case (Dalton and Presnall, 1998a). Although the portion of the solidus with the steeply negative slope has not been experimentally bracketed in the CMAS system, it has been shown to have this shape in the slightly simpler CaO-MgO- SiO_2 - CO_2 system (Eggler, 1978). For the natural carbonated lherzolite solidus, temperatures are well constrained at low pressures, but the slope at higher pressures is not. For the model system solidus, temperatures are too high for natural conditions, but the slope of the solidus at high pressures is well constrained. Therefore, to construct a “best” solidus (red curve) for a wide pressure range under natural conditions, we combine (1) the volatile-free lherzolite solidus at 0.9–1.5 GPa in the system CaO-MgO- Al_2O_3 - SiO_2 - Na_2O -FeO reduced by 60 °C to account for additional components (from Presnall et al., 2002), (2) the solidus data of Falloon and Green (1989) from 1.9 to 3.5 GPa, and (3) an extension of the Falloon and Green (1989) solidus to higher pressures using the slope of the CMAS- CO_2 lherzolite solidus.

THE OCEANIC LOW-VELOCITY ZONE

The oceanic low-velocity zone (LVZ) is particularly strong along the oceanic ridge system (Ekström and Dziewonski, 1998; Montagner and Ritsema, 2001; Ritzwoller et al., 2001; Ritsema et al., 2004) and has long been attributed to partial melting (Anderson and Sammis, 1970; Lambert and Wyllie, 1970; Wyllie and Huang, 1975; Eggler, 1976; Forsyth, 1992; Webb and Forsyth, 1998). In a detailed tomographic image of the upper part of the LVZ near 17°S on the East Pacific Rise, Conder et al. (2002) showed that the lowest off-ridge shear velocities just west of the ridge occur at a depth of ~70 km, and just east of the ridge at ~80 km (brackets in Fig. 2). In a later tomographic image, Dunn and Forsyth (2003) showed an essentially similar result but with slightly revised contouring. Figure 2 shows that the depth range of lowest velocity coincides with the depth of greatest solidus reduction (the largest melt fraction along an adiabat). Also, the abrupt decrease of solidus temperatures at 60–65 km depth provides a simple explanation for the sharp decrease of seismic velocity at approximately this depth for the MELT (Mantle Electromagnetic Tomography) area as well as elsewhere (Gaherty and Jordan, 1996; Conder et al., 2002; Dunn and Forsyth, 2003). This excellent agreement strongly supports the suggestion

(Wyllie and Huang, 1975; Egger, 1976) that melting caused by the presence of carbonate is the explanation for the LVZ. In the western Pacific, Revenaugh and Jordan (1991) found that the depth of the upper boundary of the LVZ (the G discontinuity) varies between 50 and 100 km. The depth of 60–65 km for the sharp decrease in solidus temperature (Fig. 2) is well within this range, and would vary somewhat depending mainly on the proportions of MgO, CaO, and FeO in the carbonate phase. For example, note the increase in depth to ~80 km (Fig. 1, dashed blue curve) for a composition containing no iron oxide. Thus, the variation in the depth of the G discontinuity is an expected consequence of a compositionally heterogeneous mantle.

Karato and Jung (1998) calculated that the crystalline residue produced by melting in the LVZ would have a higher seismic velocity than that of the unmelted rock, and concluded that the LVZ is not caused by melting. However, they excluded the melt from this calculation, which is not a condition that would exist in a mantle that has a porosity threshold for melt migration (Faul, 2001). Furthermore, in order to produce basalts, melting must occur along ridges at temperatures close to the volatile-free lherzolite solidus (Fig. 2). Because the temperature of the carbonated lherzolite solidus abruptly drops at 1.9 GPa to values far below any temperature on the volatile-free lherzolite solidus, there is no adiabat capable of producing basalts that would fail to produce small amounts of carbonate-rich melt in the depth range of the LVZ. For a mantle containing ~200 ppm CO₂, the amount of carbonatitic melt produced at the solidus would be ~0.05 wt% (Dalton and Presnall, 1998b; Gudfinnsson and Presnall, 2005).

To further test the validity of carbonate-rich melt as the cause of the LVZ, it would be desirable to compare the observed reduction of shear velocity in the LVZ with that expected by carbonate-induced melting. This would require a knowledge of the amount of melting and the relationship between shear velocity and amount of melt. Both are uncertain. Directly beneath ridges, the modeling of Presnall et al. (2002) involves large amounts of melting to produce basaltic melts in the depth range of ~30–45 km. This shallow and laterally restricted region of basalt production is not of concern here. In the LVZ, which lies beneath the region of basalt production, the maximum amount of carbonate-rich melt along a 1240 °C adiabat would occur at a depth just greater than the abrupt decrease in the carbonated lherzolite solidus temperature at ~60 km (Fig. 2). For a mantle with 200 ppm CO₂ at this depth, the data of Gudfinnsson and Presnall (2005) yield a rough estimate of ~0.2% melt, but this value is likely to be highly variable depending on the local amount of carbonate. Anderson and Spetzler (1970) indicate that for 0.2% melt, the observed reduction of ~6% in shear velocity at the G discontinuity (Dunn and Forsyth, 2003) would require very flattened melt volumes with an aspect ratio of ~10⁻³. Although Faul et al. (1994) found that an aspect ratio of ~0.05 is appropriate for low melt fractions, Drury and Fitz Gerald (1996) observed, for an experimentally deformed olivine-orthopyroxene rock at 1500 K, 300 MPa, that melt occurs in

films 1.0–1.5 nm thick along all grain boundaries as well as in tubes along grain edges and in layers 50–500 nm thick. An additional complication (Cmíral et al., 1998) is dihedral angles that vary as a function of grain size and melt fraction. Also, Cmíral et al. (1998) found that these angles, excluding those for planar crystal faces, range from 0 to 10°, much lower than values reported earlier, which ranged from 20 to 50°. Thus, it appears that the variation of seismic velocity with melt fraction is a complex problem that cannot presently be quantified reliably.

For the lower boundary of the LVZ to be caused by the intersection of the solidus with a solid adiabat, the depth typically would be in the vicinity of 300 km for the very low potential temperature of 1240 °C (Fig. 2). This is roughly twice the normal depth of 150 km (Ritsema and Allen, 2003). An intersection at ~150 km would require an adiabat with a potential temperature less than ~1100 °C, which would be incapable of generating basalts. Therefore, we propose that the lower boundary is best explained by exhaustion of carbonate due to reduction to carbon, with variations in the depth of the lower boundary being the expected result of variations in the amount of carbonate, the reducing capacity of the mantle, or both. The progressive reduction of carbonate to carbon with increasing depth, as documented for the mantle beneath cratons, is consistent with the usual representation of the lower boundary of the oceanic LVZ as a gradual increase of velocity with depth (for example, Gaherty and Jordan, 1996).

THE TRANSITION ZONE

In addition to the progressive reduction of oxygen fugacity with depth discussed earlier, an additional abrupt reducing effect occurs at the 410 km discontinuity, assuming that this transition is caused by the olivine to wadsleyite transformation. Olivine in mantle xenoliths has no detectable Fe³⁺ (Dyar et al., 1989), whereas in wadsleyite and its transformation product, ringwoodite, at slightly higher pressures, the amount of Fe³⁺ is expected to be large (O'Neill et al., 1993). Since Fe³⁺ can easily enter the abundant wadsleyite and ringwoodite phases, it is not forced into minor phases. Therefore, the oxygen fugacity is very low (O'Neill et al., 1993). In this environment carbonate would normally be completely converted to diamond except in the case of a carbonate anomaly large enough to overcome even the enhanced reducing capacity of this part of the mantle. For such an anomaly, the solidus curves of a carbonated eclogite or possibly even carbonated lherzolite (Fig. 2) are low enough that melting could occur without enhanced temperatures.

Regions of low shear velocity have been reported beneath the Sea of Japan, the Yellow Sea, and adjoining parts of Asia (Revenaugh and Sipkin, 1994), southeastern Africa (Vinnik and Farra, 2002), and the Arabian plate (Vinnik et al., 2003), although the result of Revenaugh and Sipkin (1994) has been questioned by Vinnik et al. (1996). All have a consistent lower boundary at ~410 km, which suggests that they may be due to melting of carbonate concentrations sufficient to survive reduc-

tion to diamond at depths of less than 410 km, but not the abrupt increase in reducing capacity at the olivine-wadsleyite transition. The depths of the upper boundaries are somewhat variable at ~330 km (Sea of Japan, Yellow Sea, East Asia), 280–300 km (southeastern Africa), and 350 km (Arabian plate). These boundaries may simply locate the upper limit of a region of enhanced carbonate.

Plumes are necessarily hot, and Sleep (1990) modeled plumes using an excess temperature of 225 °C. On the basis of low shear velocity anomalies extending to ~700 km depth beneath Afar, Bowie, Easter, Hawaii, Iceland, Louisville, MacDonald, and Samoa, Ritsema and Allen (2003) considered these volcanic centers possible locations for hot plumes. Similarly, low shear velocities beneath volcanic centers at 500 km depth were used by Courtillot et al. (2003) as an indication of high temperatures and as a possible plume diagnostic.

Figure 2 shows that temperatures of the carbonated lherzolite solidus are more than 300 °C below the volatile-free lherzolite solidus, and the carbonated eclogite solidus (Shirasaka and Takahashi, 2003) is an additional 100 °C lower. At 10–15 GPa the latter is essentially parallel to a solid adiabat. As the carbonated lherzolite and carbonated eclogite solidus curves have nearly identical slopes at pressures less than 8 GPa and both are controlled dominantly by the melting behavior of carbonate, the carbonated lherzolite curve may have a slope at 10–15 GPa similar to that of the carbonated eclogite. In this case, for a localized region of the mantle with an amount of carbonate sufficient to survive reduction to diamond, very deep melting extending into the transition zone could occur at quite low temperatures.

On the basis of the oxygen isotopic composition of coesite inclusions in eclogitic diamonds, some mantle eclogites have been unequivocally shown to have a crustal origin (Schulze et al., 2003). Also, concurrent subduction of basaltic crust and carbonate to produce carbonated eclogite in the mantle is supported by the observation of magnesite in eclogite from an ultra-high-pressure metamorphic locality in China (Zhang et al., 2002). The melting temperature would be very low (Fig. 2), and the carbonatitic melts would probably be present in small amounts. Thus, instead of imaging temperature or major-element compositional heterogeneities, seismic tomography may frequently image regions with minor amounts of carbonatitic melt. Regions of low velocity may be a better indicator of old subducted crust than hot plumes. In this regard, it is interesting that at depths greater than ~200 km the low-velocity anomaly beneath Iceland extending to ~600–700 km (Ritsema and Allen, 2003) has the shape of a slab elongated parallel to the Mid-Atlantic Ridge (Foulger et al., 2001). The issue of eclogite in the Iceland source region is discussed further by Foulger et al. (this volume).

THE LOWER MANTLE

Wood et al. (1996) argued that the low oxygen fugacity expected in the transition zone does not continue into the lower mantle. Instead, they suggested that oxygen fugacity is elevated,

as in the upper mantle, so that magnesite would be stabilized rather than diamond. The reasoning is that Fe has been found to be concentrated more strongly in magnesiowüstite than in perovskite (Ito and Takahashi, 1989). Because magnesiowüstite would be present in small amounts relative to perovskite and can accept a large amount of Fe³⁺, the oxygen fugacity would be high and magnesite would be stabilized. Melting in the lower mantle is generally dismissed because silicate compositions melt at temperatures far higher than those in the lower mantle. However, at high oxygen fugacities, solidus temperatures would be controlled by the low-temperature melting behavior of magnesite rather than the high-temperature melting behavior of perovskite and magnesiowüstite, a situation comparable to that in the upper mantle.

Although temperatures for the carbonated mantle solidus at lower mantle pressures are not known, the controlling low-melting phase, magnesite, remains stable without any phase changes to at least 100 GPa (Isshiki et al., 2004). Therefore, the temperature-pressure slopes of the carbonated solidus curves in Figure 2 would be only weakly affected by phase changes at 410 and 660 km. In this case, temperatures of the solidus curves would increase only gradually with pressure, and might lie fairly close to the 1240 °C adiabat in the lower mantle. For the more commonly used adiabat of ~1400 °C, melting in the lower mantle would be even more likely. Therefore, caution is necessary in using low seismic velocities in the lower mantle as an unambiguous indication of elevated temperature.

SUMMARY OF CONCLUSIONS

1. On the assumption that the amount of H₂O in the oceanic upper mantle is less than ~350 ppm, H₂O will be completely taken up by nominally anhydrous phases. In this case phlogopite and amphibole are expected to be absent as primary phases in the oceanic mantle. A possible exception to this is Hawaii, where the amount of H₂O is elevated. When hydrous phases are absent, the effect of this amount of H₂O on solidus temperatures is negligible.
2. At ~1.9 GPa, even the smallest amount of carbonate abruptly lowers mantle solidus temperatures by ~300 °C and melts at and near the solidus are carbonatitic. For a mantle containing ~200 ppm CO₂, the amount of melt produced directly at the solidus is ~0.05 wt%, and on the 1240 °C adiabat at the top of the LVZ it is ~0.2 wt%.
3. The depth range and sharpness of the upper boundary (G discontinuity) of the low-velocity zone are in excellent agreement with the abrupt decrease in the solidus temperature of carbonated lherzolite at ~1.9 GPa. This strongly supports melting of carbonated lherzolite as the cause of the LVZ. However, even in the absence of any seismic constraints, petrological considerations require melting beneath ridges in the depth range of the LVZ. The depth of the upper boundary would vary as a function of the relative proportions of CaO, MgO, and FeO in the mantle because these

three oxides control the subsolidus stabilization pressure of carbonate. The more gradual lower boundary of the LVZ is explained by progressive elimination of carbonate-rich melt by conversion of carbonate to carbon as the mantle becomes more reducing with depth. The depth of the lower boundary would vary as a function of the amount of CO₂ and the reducing capacity of the mantle.

4. Extrapolations of carbonated lherzolite and carbonated eclogite solidus curves to lower mantle pressures suggest that regions of low seismic velocity anywhere in the upper or lower mantle can be caused by low-degree melting (<1%) of eclogite or lherzolite that contains enough carbonate to exceed the local reducing capacity of the mantle. Such regions may indicate the locations of cool, carbonated, and partially melted subducted slabs rather than hot plumes. No elevated temperatures are required.

ACKNOWLEDGMENTS

We thank Gill Foulger, Jim Natland, Shantanu Keshav, and especially Don Anderson for continuing and very stimulating conversations on issues related to this paper. We thank P. Asimow and B. Wood for very useful formal reviews and L. Vinnik for valuable comments on seismological issues. Financial support was provided by National Science Foundation grant EAR-0106645. Contribution no. 1052, Department of Geosciences, University of Texas at Dallas.

REFERENCES CITED

- Anderson, D.L., and Sammis, C.G., 1970, Partial melting in the upper mantle: *Physics of the Earth and Planetary Interiors*, v. 3, p. 41–50, doi: 10.1016/0031-9201(70)90042-7.
- Anderson, D.L., and Spetzler, H., 1970, Partial melting and the low-velocity zone: *Physics of the Earth and Planetary Interiors*, v. 4, p. 62–64.
- Arima, M., Nakayama, K., Akaishi, M., Yamaoka, S., and Kanda, H., 1993, Crystallization of diamond from a silicate melt of kimberlite composition in high-pressure and high-temperature experiments: *Geology*, v. 21, p. 968–970, doi: 10.1130/0091-7613(1993)021<0968:CODFAS>2.3.CO;2.
- Becker, H., and Altherr, R., 1992, Evidence from ultra-high-pressure marbles for recycling of sediments into the mantle: *Nature*, v. 358, p. 745–748, doi: 10.1038/358745a0.
- Bell, D.R., Rossman, G.R., Makedner, J., Endisch, D., and Rauch, F., 2003, Hydroxide in olivine: A quantitative determination of the absolute amount and calibration of the IR spectrum: *Journal of Geophysical Research*, v. 108, p. 2105, doi: 10.1029/2001JB000679.
- Biellmann, C., Gillet, P., Guyot, F., Peyronneau, J., and Reynard, B., 1993, Experimental evidence for carbonate stability in the Earth's lower mantle: *Earth and Planetary Science Letters*, v. 118, p. 31–41, doi: 10.1016/0012-821X(93)90157-5.
- Bizimis, M., Sen, G., and Salters, V.M.M., 2003, Volatile-rich mineral phases in the Hawaiian lithosphere: Phlogopites and carbonates in 0-age garnet pyroxenite xenoliths from Salt Lake Crater (Oahu, Hawaii): *Eos (Transactions, American Geophysical Union)*, v. 84, p. F1607.
- Blundy, J., Brodholt, J., and Wood, B.J., 1991, Carbon fluid equilibria and the oxidation state of the upper mantle: *Nature*, v. 349, p. 321–324, doi: 10.1038/349321a0.
- Bottinga, Y., and Javoy, M., 1990, Mid-ocean ridge basalt degassing: Bubble nucleation: *Journal of Geophysical Research*, v. 95, p. 5125–5130.
- Boyd, F.R., and Nixon, P.H., 1972, Ultramafic nodules from the Thaba Putsoa kimberlite pipe: *Carnegie Institution of Washington (D.C.), Year Book*, v. 71, p. 362–373.
- Bundy, F.P., Bovenkerk, H.P., Strong, H.M., and Wentorf, R.H., Jr., 1961, Diamond-graphite equilibrium line from growth and graphitization of diamond: *The Journal of Chemical Physics*, v. 35, p. 383–391, doi: 10.1063/1.1731938.
- Canil, D., 1990, Experimental study bearing on the absence of carbonate in mantle-derived xenoliths: *Geology*, v. 18, p. 1011–1013, doi: 10.1130/0091-7613(1990)018<1011:ESBOTA>2.3.CO;2.
- Canil, D., and O'Neill, H.St.C., 1996, Distribution of ferric iron in some upper-mantle assemblages: *Journal of Petrology*, v. 37, p. 609–635.
- Canil, D., O'Neill, H.St.C., Pearson, D.G., Rudnick, R.L., McDonough, W.F., and Carswell, D.A., 1994, Ferric iron in peridotites and mantle oxidation states: *Earth and Planetary Science Letters*, v. 123, p. 205–220, doi: 10.1016/0012-821X(94)90268-2.
- Christie, D.M., Carmichael, I.S.E., and Langmuir, C.H., 1986, Oxidation states of mid-ocean ridge basalt glasses: *Earth and Planetary Science Letters*, v. 79, p. 397–411, doi: 10.1016/0012-821X(86)90195-0.
- Cmiral, M., Fitz Gerald, J.D., Faul, U.H., and Green, D.H., 1998, A close look at dihedral angles and melt geometry in olivine-basalt aggregates: a TEM study: *Contributions to Mineralogy and Petrology*, v. 130, p. 336–345, doi: 10.1007/s004100050369.
- Conder, J.A., Forsyth, D.W., and Parmentier, E.M., 2002, Asthenospheric flow and asymmetry of the East Pacific Rise, MELT area: *Journal of Geophysical Research*, v. 107, 2344, doi: 10.1029/2001JB000807.
- Courtillot, V., Davaille, A., Besse, J., and Stock, J., 2003, Three distinct types of hotspots in the Earth's mantle: *Earth and Planetary Science Letters*, v. 205, p. 295–308, doi: 10.1016/S0012-821X(02)01048-8.
- Dalton, J.A., and Presnall, D.C., 1998a, Carbonatitic melts along the solidus of model lherzolite in the system CaO-MgO-Al₂O₃-SiO₂-CO₂ from 3 to 7 GPa: *Contributions to Mineralogy and Petrology*, v. 131, p. 123–135, doi: 10.1007/s004100050383.
- Dalton, J.A., and Presnall, D.C., 1998b, The continuum of primary carbonatitic-kimberlitic melt compositions in equilibrium with lherzolite: Data from the system CaO-MgO-Al₂O₃-SiO₂-CO₂ at 6 GPa: *Journal of Petrology*, v. 39, p. 1953–1964, doi: 10.1093/petrology/39.11.1953.
- Dasgupta, R., Hirschmann, M.M., and Withers, A.C., 2004, Deep global cycling of carbon constrained by the solidus of anhydrous, carbonated eclogite under upper mantle conditions, v. 227, p. 73–85.
- Dick, H.J.B., Fisher, R.L., and Bryan, W.B., 1984, Mineralogical variability of the uppermost mantle along mid-ocean ridges: *Earth and Planetary Science Letters*, v. 69, p. 88–106, doi: 10.1016/0012-821X(84)90076-1.
- Dixon, J.E., and Clague, D.A., 2001, Volatiles in basaltic glasses from Loihi Seamount, Hawaii: Evidence for a relatively dry plume component: *Journal of Petrology*, v. 42, p. 627–654, doi: 10.1093/petrology/42.3.627.
- Drury, M.R., and Fitz Gerald, J.D., 1996, Grain boundary melt films in an experimentally deformed olivine-orthopyroxene rock: Implications for melt distribution in upper mantle rocks: *Geophysical Research Letters*, v. 23, p. 701–704, doi: 10.1029/96GL00702.
- Dunn, R.A., and Forsyth, D.W., 2003, Imaging the transition between the region of mantle melt generation and the crustal magma chamber beneath the southern East Pacific Rise with short-period Love waves: *Journal of Geophysical Research*, v. 108, no. B7, 2352, doi: 10.1029/2002JB002217.
- Dyar, M.D., McGuire, A.V., and Ziegler, R.D., 1989, Redox equilibria and crystal chemistry of coexisting minerals from spinel lherzolite mantle xenoliths: *American Mineralogist*, v. 74, p. 969–980.
- Eggler, D.H., 1976, Does CO₂ cause partial melting in the low-velocity layer of the mantle?: *Geology*, v. 4, p. 69–72, doi: 10.1130/0091-7613(1976)4<69:DCCPMI>2.0.CO;2.
- Eggler, D.H., 1978, The effect of CO₂ upon partial melting of peridotite in the system Na₂O-CaO-Al₂O₃-MgO-SiO₂-CO₂ to 35 kb, with an analysis of melting in a peridotite-H₂O-CO₂ system: *American Journal of Science*, v. 278, p. 305–343.

- Egglar, D.H., and Rosenhauer, M., 1978, Carbon dioxide in silicate melts, II: Solubilities of CO₂ and H₂O in CaMgSi₂O₆ (diopside) liquids and vapors at pressures to 40 kb: *American Journal of Science*, v. 278, p. 64–94.
- Ekström, G., and Dziewonski, A.M., 1998, The unique anisotropy of the Pacific upper mantle: *Nature*, v. 394, p. 168–172, doi: 10.1038/28148.
- Falloon, T.J., and Green, D.H., 1989, The solidus of carbonated, fertile peridotite: *Earth and Planetary Science Letters*, v. 94, p. 364–370, doi: 10.1016/0012-821X(89)90153-2.
- Faul, U.H., 2001, Melt retention and segregation beneath mid-ocean ridges: *Nature*, v. 410, p. 920–923, doi: 10.1038/35073556.
- Faul, U.H., Toomey, D.R., and Waff, H.S., 1994, Intergranular basaltic melt is distributed in thin, elongated inclusions: *Geophysical Research Letters*, v. 21, p. 29–32.
- Forsyth, D.W., 1992, Geophysical constraints on mantle flow and melt generation beneath mid-ocean ridges, in Morgan, J.P., Blackman, D.K., and Sinton, J.M., eds., *Mantle flow and melt generation at mid-ocean ridges*: Washington, D.C., American Geophysical Union, Geophysical Monograph 71, p. 1–65.
- Foulger, G.R., Pritchard, M.J., Julian, B.R., Evans, J.R., Allen, R.M., Nolet, G., Morgan, W.J., Bergsson, B.H., Erlendsson, P., Jakobsdottir, S., Ragnarsson, S., Stefansson, R., and Vogfjord, K., 2001, Seismic tomography shows that the upwelling beneath Iceland is confined to the upper mantle: *Geophysical Journal International*, v. 146, p. 504–530, doi: 10.1046/j.0956-540x.2001.01470.x.
- Frezzotti, M.L., Touret, J.L.R., and Neuman, E.-R., 2002, Ephemeral carbonate melts in the upper mantle: Carbonate-silicate immiscibility in microveins and inclusions within spinel peridotite xenoliths, La Gomera: Canary Islands: *European Journal of Mineralogy*, v. 14, p. 891–904, doi: 10.1127/0935-1221/2002/0014-0891.
- Gaherty, J.B., and Jordan, T.H., 1996, Seismic structure of the upper mantle in a central Pacific corridor: *Journal of Geophysical Research*, v. 101, p. 22,291–22,309, doi: 10.1029/96JB01882.
- Gerlach, T.M., 1989, Degassing of carbon dioxide from basaltic magma at spreading centers, I: Afar transitional basalts: *Journal of Volcanology and Geothermal Research*, v. 39, p. 211–219, doi: 10.1016/0377-0273(89)90060-7.
- Gerlach, T.M., and Graeber, E., 1985, Volatile budget for Kilauea volcano: *Nature*, v. 313, p. 273–277, doi: 10.1038/313273a0.
- Gerlach, T.M., McGee, K.A., Elias, T., Sutton, A.J., and Doukas, M.P., 2002, Carbon dioxide emission rate of Kilauea Volcano: Implications for primary magma and the summit reservoir: *Journal of Geophysical Research*, v. 107, 2189, doi: 10.1029/2001JB000407.
- Greenland, L.P., Rose, W.I., and Stokes, J.B., 1985, An estimate of gas emissions and magmatic gas content from Kilauea volcano: *Geochimica et Cosmochimica Acta*, v. 49, p. 125–129, doi: 10.1016/0016-7037(85)90196-6.
- Gudfinnsson, G.H., and Presnall, D.C., 2005, Continuous gradations among primary carbonatitic, kimberlitic, melilititic, basaltic, picritic, and komatiitic melts in equilibrium with garnet lherzolite at 3–8 GPa: *Journal of Petrology*, doi: 10.1093/petrology/egi029.
- Gudmundsson, G., and Wood, B.J., 1995, Experimental tests of garnet peridotite oxygen barometry: *Contributions to Mineralogy and Petrology*, v. 119, p. 56–67, doi: 10.1007/s004100050027.
- Hirschmann, M.M., 2000, Mantle solidus: Experimental constraints and the effects of peridotite composition: *Geochemistry, Geophysics, Geosystems*, v. 1, no. 10, doi: 10.1029/2000GC000070.
- Hoernle, K., Tilton, G., Le Bas, M.J., Duggen, S., and Garbe-Schönberg, D., 2002, Geochemistry of oceanic carbonatites compared with continental carbonatites: Mantle recycling of oceanic crustal carbonate: *Contributions to Mineralogy and Petrology*, v. 142, p. 520–542.
- Isshiki, M., Irifune, T., Hirose, K., Ono, S., Ohishi, Y., Watanuki, T., Nishibori, E., Takata, M., and Sakata, M., 2004, Stability of magnesite and its high-pressure form in the lowermost mantle: *Nature*, v. 427, p. 60–62, doi: 10.1038/nature02181.
- Ito, E., and Takahashi, E., 1989, Post-spinel transformations in the system Mg₂SiO₄-Fe₂SiO₄ and some geophysical implications: *Journal of Geophysical Research*, v. 94, p. 10,637–10,646.
- Javoy, M., and Pineau, F., 1991, The volatiles record of a “popping” rock from the Mid-Atlantic Ridge at 14°N: Chemical and isotopic composition of gas trapped in the vesicles: *Earth and Planetary Science Letters*, v. 107, p. 598–611, doi: 10.1016/0012-821X(91)90104-P.
- Karato, S.-I., and Jung, H., 1998, Water, partial melting and the origin of the seismic low velocity and high attenuation zone in the upper mantle: *Earth and Planetary Science Letters*, v. 157, p. 193–207, doi: 10.1016/S0012-821X(98)00034-X.
- Katz, R.F., Spiegelman, M., and Langmuir, C.H., 2003, A new parameterization of hydrous mantle melting: *Geochemistry, Geophysics, Geosystems*, v. 4, 1073, doi: 10.1029/2002GC000433, 19 pp.
- Keppler, H., Wiedenbeck, M., and Shcheka, S.S., 2003, Carbon solubility in olivine and the mode of carbon storage in the Earth’s mantle: *Nature*, v. 424, p. 414–416, doi: 10.1038/nature01828.
- Keshav, S., and Sen, G., 2003, A rare composite xenolith from Salt Lake Crater, Oahu: High-pressure fractionation and implications for kimberlitic melts in the Hawaiian mantle: *Contributions to Mineralogy and Petrology*, v. 144, p. 548–558.
- Kohlstedt, D.L., Keppler, H., and Rubie, D.C., 1996, Solubility of water in the α, β, and γ phases of (Mg,Fe)₂SiO₄: *Contributions to Mineralogy and Petrology*, v. 123, p. 345–357, doi: 10.1007/s004100050161.
- Kohn, S., 1996, Solubility of H₂O in nominally anhydrous mantle minerals using ¹H MAS NMR: *American Mineralogist*, v. 81, p. 1523–1526.
- Lambert, I.B., and Wyllie, P.J., 1970, Low-velocity zone of the Earth’s mantle: Incipient melting caused by water: *Science*, v. 169, p. 764–766.
- Leost, I., Stachel, T., Brey, G.P., Harris, J.W., and Ryabchikov, I.D., 2003, Diamond formation and source carbonation: Mineral associations in diamonds from Namibia: *Contributions to Mineralogy and Petrology*, v. 145, p. 15–24.
- Leshner, C.E., Pickering-Witter, J., Baxter, G., and Walter, M., 2003, Melting of garnet peridotite: Effects of capsules and thermocouples, and implications for the high-pressure mantle solidus: *American Mineralogist*, v. 88, p. 1181–1189.
- Luth, R.W., Virgo, D., Boyd, F.R., and Wood, B.J., 1990, Ferric iron in mantle-derived garnets: *Contributions to Mineralogy and Petrology*, v. 104, p. 56–72, doi: 10.1007/BF00310646.
- Marty, B., and Jambon, A., 1987, C/He³ in volatile fluxes from the solid Earth. Implications for carbon geodynamics: *Earth and Planetary Science Letters*, v. 83, p. 16–26, doi: 10.1016/0012-821X(87)90047-1.
- McCammon, C.A., and Kopylova, M.G., 2004, A redox profile of the Slave mantle and oxygen fugacity control in the cratonic mantle: *Contributions to Mineralogy and Petrology*, v. 148, p. 55–68, doi: 10.1007/s00410-004-0583-1.
- McCammon, C.A., Griffin, W.L., Shee, S.H., and O’Neill, H.S.C., 2001, Oxidation during metasomatism in ultramafic xenoliths from the Wesselton kimberlite, South Africa: Implications for the survival of diamond: *Contributions to Mineralogy and Petrology*, v. 141, p. 287–296.
- McDonough, W.F., 1990, Constraints on the composition of the continental lithospheric mantle: *Earth and Planetary Science Letters*, v. 101, p. 1–18, doi: 10.1016/0012-821X(90)90119-I.
- Michael, P.J., 1988, The concentration, behavior and storage of H₂O in the suboceanic upper mantle: Implications for mantle metasomatism: *Geochimica et Cosmochimica Acta*, v. 52, p. 555–566, doi: 10.1016/0016-7037(88)90110-X.
- Montagner, J.-P., and Ritsema, J., 2001, Interactions between ridges and plumes: *Science*, v. 294, p. 1472–1473, doi: 10.1126/science.1067486.
- Montelli, R., Nolet, G., Dahlen, F.A., Master, G., Engdahl, E.R., and Hung, S.-H., 2004, Finite-frequency tomography reveals a variety of plumes in the mantle: *Science*, v. 303, p. 338–343, doi: 10.1126/science.1092485.
- O’Hara, M.J., Richardson, S.W., and Wilson, G., 1971, Garnet-peridotite stability and occurrence in crust and mantle: *Contributions to Mineralogy and Petrology*, v. 32, p. 48–68, doi: 10.1007/BF00372233.

- O'Neill, H.St.C., Rubie, D.C., Canil, D., Geiger, C.A., Ross, C.R., II, Seifert, F., and Woodland, A.B., 1993, Ferric iron in the upper mantle and in transition zone assemblages: Implications for relative oxygen fugacities in the mantle, *in* Takahashi, E., Jeanloz, R., and Rubie, D., eds., *Evolution of the Earth and Planets: Washington, D.C., American Geophysical Union, Geophysical Monograph 74; International Union of Geodesy and Geophysics*, v. 14, p. 73–88.
- Pal'yanov, Yu.N., Sokol, A.G., Borzdov, Yu.M., Khokhryakov, A.F., and Sobolev, N.V., 1999, Diamond formation from mantle carbonate fluids: *Nature*, v. 400, p. 417–418, doi: 10.1038/22678.
- Pearson, D.G., Boyd, F.R., Haggerty, S.E., Pasteris, J.D., Field, S.W., Nixon, P.H., and Pokhilenko, N.P., 1994, The characterisation and origin of graphite in cratonic lithospheric mantle: A petrological carbon isotope and Raman spectroscopic study: *Contributions to Mineralogy and Petrology*, v. 115, p. 449–466, doi: 10.1007/BF00320978.
- Pearson, D.G., Canil, D., and Shirey, S.B., 2003, Mantle samples included in volcanic rocks: Xenoliths and diamonds, *in* Holland, H.D., Turekian, K.K., and Carlson, R.W., eds., *Treatise on geochemistry*, vol. 2: The mantle and core, p. 171–275: Amsterdam, Elsevier.
- Presnall, D.C., Gudfinnsson, G.H., and Walter, M.J., 2002, Generation of mid-ocean ridge basalts at pressures from 1 to 7 GPa: *Geochimica et Cosmochimica Acta*, v. 66, p. 2073–2090, doi: 10.1016/S0016-7037(02)00890-6.
- Revenaugh, J., and Jordan, T.H., 1991, Mantle layering from ScS reverberations, 3: The upper mantle: *Journal of Geophysical Research*, v. 96, p. 19,781–19,810.
- Revenaugh, J., and Sipkin, S.A., 1994, Seismic evidence for silicate melt atop the 410-km mantle discontinuity: *Nature*, v. 369, p. 474–476, doi: 10.1038/369474a0.
- Ritsema, J., and Allen, R.M., 2003, The elusive mantle plume: *Earth and Planetary Science Letters*, v. 207, p. 1–12, doi: 10.1016/S0012-821X(02)01093-2.
- Ritsema, J., van Heijst, H.J., and Woodhouse, J.H., 2004, Global transition zone tomography: *Journal of Geophysical Research*, v. 109, doi: 10.1029/2003JB002610.
- Ritzwoller, M.H., Shapiro, N.M., Levshin, A.L., and Leahy, G.M., 2001, Crustal and upper mantle structure beneath Antarctica and surrounding oceans: *Journal of Geophysical Research*, v. 106, p. 30,645–30,670, doi: 10.1029/2001JB000179.
- Rossmann, G.R., 1996, Studies of OH in nominally anhydrous minerals: *Physics and Chemistry of Minerals*, v. 23, p. 299, doi: 10.1007/BF00207777.
- Saal, A.E., Hauri, E.H., Langmuir, C.H., and Perfit, M.R., 2002, Vapor undersaturation in primitive mid-ocean-ridge basalt and the volatile content of Earth's upper mantle: *Nature*, v. 419, p. 451–455, doi: 10.1038/nature01073.
- Schrauder, M., and Navon, O., 1994, Hydrous and carbonatitic mantle fluids in fibrous diamonds from Jwaneng, Botswana: *Geochimica et Cosmochimica Acta*, v. 58, p. 761–771, doi: 10.1016/0016-7037(94)90504-5.
- Schulze, D.J., Harte, B., Valley, J.W., Brenan, J.M., Channer, D.M., and De, R., 2003, Extreme crustal oxygen isotope signatures preserved in coesite in diamond: *Nature*, v. 423, p. 68–70, doi: 10.1038/nature01615.
- Sen, G., 1988, Petrogenesis of spinel lherzolite and pyroxenite suite xenoliths from the Koolau Shield, Oahu, Hawaii: Implications for the petrology of the post-eruptive lithosphere beneath Oahu: *Contributions to Mineralogy and Petrology*, v. 100, p. 61–91, doi: 10.1007/BF00399440.
- Sen, G., Macfarlane, A., and Srimal, N., 1996, Significance of rare hydrous alkaline melts in Hawaiian xenoliths: *Contributions to Mineralogy and Petrology*, v. 122, p. 415–427, doi: 10.1007/s004100050137.
- Shirasaka, M., and Takahashi, E., 2003, A genesis of carbonatitic melt within subducting oceanic crusts: High-pressure experiments in the system MORB-CaCO₃, 8th International Kimberlite Conference, Victoria, British Columbia, Canada, June 23–28, 2003, Extended Abstracts, FLA-0043, CD-ROM.
- Silva, L.C., Le Bas, M.J., and Robertson, A.H.F., 1981, An oceanic carbonatite volcano on Santiago, Cape Verde Islands: *Nature*, v. 294, p. 644–645, doi: 10.1038/294644a0.
- Sleep, N.H., 1990, Hotspots and mantle plumes: Some phenomenology: *Journal of Geophysical Research*, v. 95, p. 6715–6736.
- Sobolev, N.V., Kaminsky, F.V., Griffin, W.L., Yefimova, E.S., Win, T.T., Ryan, C.G., and Botkunov, A.I., 1997, Mineral inclusions in diamonds from the Sputnik kimberlite pipe: Yakutia: *Lithos*, v. 39, p. 135–157, doi: 10.1016/S0024-4937(96)00022-9.
- Sokol, A.G., Borzdov, Y.M., Pal'yanov, Y.N., Khokhryakov, A.F., and Sobolev, N.V., 2001, An experimental demonstration of diamond formation in the dolomite-carbon and dolomite-fluid-carbon systems: *European Journal of Mineralogy*, v. 13, p. 893–900, doi: 10.1127/0935-1221/2001/0013/0893.
- Stachel, T., Harris, J.W., and Brey, G.P., 1998, Rare and unusual mineral inclusions in diamonds from Mwadue, Tanzania: *Contributions to Mineralogy and Petrology*, v. 132, p. 34–47, doi: 10.1007/s004100050403.
- Trull, T., Nadeau, S., Pineau, F., Polve, M., and Javoy, M., 1993, C-He systematics in hotspot xenoliths: Implications for mantle carbon contents and carbon recycling: *Earth and Planetary Science Letters*, v. 118, p. 43–64, doi: 10.1016/0012-821X(93)90158-6.
- Vinnik, L., and Farra, V., 2002, Subcratonic low-velocity layer and flood basalts: *Geophysical Research Letters*, v. 29, doi:10.1029/2001GL014064.
- Vinnik, L., Kosarev, G., and Petersen, N., 1996, Mantle transition zone beneath Eurasia: *Geophysical Research Letters*, v. 23, p. 1485–1488, doi: 10.1029/96GL01261.
- Vinnik, L., Kumar, M.R., Kind, R., and Farra, V., 2003, Super-deep low-velocity layer beneath the Arabian plate: *Geophysical Research Letters*, v. 30, doi: 10.1029/2002GL016590.
- Wang, A., Pasteris, J.D., Meyer, H.O.A., and DeleDuboi, M.L., 1996, Magnesite-bearing inclusion assemblage in natural diamond: *Earth and Planetary Science Letters*, v. 141, p. 293–306.
- Webb, S.C., and Forsyth, D.W., 1998, Structure of the upper mantle under the EPR from waveform inversion of regional events: *Science*, v. 280, p. 1227–1229, doi: 10.1126/science.280.5367.1227.
- Wirth, R., and Rocholl, A., 2003, Nanocrystalline diamond from the Earth's mantle underneath Hawaii: *Earth and Planetary Science Letters*, v. 211, p. 357–369, doi: 10.1016/S0012-821X(03)00204-8.
- Withers, A.C., Wood, B.J., and Carroll, M.R., 1998, The OH content of pyrope at high pressure: *Chemical Geology*, v. 147, p. 161–171, doi: 10.1016/S0009-2541(97)00179-4.
- Wood, B.J., Bryndzia, L.T., and Johnson, K.E., 1990, Mantle oxidation state and its relationship to tectonic environment and fluid speciation: *Science*, v. 248, p. 337–345.
- Wood, B.J., Pawley, A., and Frost, D.R., 1996, Water and carbon in the Earth's mantle: *Philosophical Transactions of the Royal Society of London (Ser. A): Mathematical and Physical Sciences*, v. 354, p. 1495–1511.
- Woodland, A.B., and Koch, M., 2003, Variation in oxygen fugacity with depth in the upper mantle beneath the Kaapvaal craton, Southern Africa: *Earth and Planetary Science Letters*, v. 214, p. 295–310, doi: 10.1016/S0012-821X(03)00379-0.
- Woodland, A.B., and Peltonen, P., 1999, Ferric iron contents of garnet and clinopyroxene and estimated oxygen fugacities of peridotite xenoliths from the Eastern Finland Kimberlite Province, *in* Gurney, J.J., Gurney, J.L., Pascoe, M.D., and Richardson, S.H., eds., *The P.H. Nixon volume, Proceedings of the 7th International Kimberlite Conference, Red Roof Design, Cape Town*, p. 904–911.
- Wyllie, P.J., and Huang, W.L., 1975, Influence of mantle CO₂ in the generation of carbonatites and kimberlites: *Nature*, v. 257, p. 297–299.
- Zhang, Y., and Zindler, A., 1993, Distribution and evolution of carbon and nitrogen in the Earth: *Earth and Planetary Science Letters*, v. 117, p. 331–345, doi: 10.1016/0012-821X(93)90088-Q.
- Zhang, L., Ellis, D.J., Williams, S., and Jiang, W., 2002, Ultra-high pressure metamorphism in western Tianshan, China, Part II: Evidence for magnesite in eclogite: *American Mineralogist*, v. 87, p. 861–866.