Near-solidus Melting of the Shallow Upper Mantle: Partial Melting Experiments on Depleted Peridotite

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We present the results of melting experiments on a moderately depleted peridotite composition (DMM1) at 10 kbar and 1250–1390°C. Specially designed experiments demonstrate that liquids extracted into aggregates of vitreous carbon spheres maintained chemical contact with the bulk charge down to melt fractions of ~0.02–0.04 and approached equilibrium closely. With increasing melt fraction, SiO2, FeO, and MgO contents of the partial melts increase, Al2O3 and Na2O contents decrease, and CaO contents first increase up to clinopyroxene-out at a melt fraction of 0.09–0.10, then decrease with further melting. A linear fit to melt fraction vs temperature data for lherzolite-bearing experiments yields a solidus of 1272 ± 11°C. The melting reaction is 0.56 orthopyroxene + 0.72 clinopyroxene + 0.24 spinel = 0.34 olivine + 0.24 liquid. Above clinopyroxene-out, the reaction is 1.24 orthopyroxene = 0.24 olivine + 1 liquid. Near the solidus, DMM1 glass compositions have lower SiO2, TiO2, Na2O, and K2O contents, higher FeO, MgO, and CaO contents, and higher CaO/Al2O3 ratios compared with glasses from low-degree melting of fertile peridotite compositions. Recent computational models predict partial melting trends generally parallel to our experimental results. We present a parameterization of 10 kbar peridotite solidus temperatures suggesting that K2O and P2O5 have greater effects on solids depression than Na2O, consistent with theoretical expectations. Our parameterization also suggests that abyssal peridotites have 10 kbar solidi of ~1278–1295°C.

KEY WORDS: depleted; experimental petrology; mantle melting; near-solidus; peridotite

INTRODUCTION

It is widely accepted that parental magmas of mid-ocean ridge basalts (MORBs) represent a mixture of liquids produced by pressure-release melting over a range of depths in the Earth’s upper mantle (e.g. McKenzie, 1984; McKenzie & Bickle, 1988; Langmuir et al., 1992). Experimental and theoretical studies indicate that small amounts of melt (~2%) are interconnected in olivine-dominated, partially molten systems (e.g. Waff & Bulau, 1979; von Bargen & Waff, 1986; Daines & Richter, 1988) and that such low degrees of melt can move relative to the residual solid phases (McKenzie, 1985, 1989; Stevenson & Scott, 1991). The extremely depleted rare earth element patterns observed in residual clinopyroxenes from dredged abyssal peridotites have been used as evidence of this mobility and that melt production beneath mid-ocean ridges can approach the limit of fractional melting (Johnson et al., 1990; Johnson & Dick, 1992; Salters & Dick, 2002). Correlations between the major element compositions of spinels and the concentrations of moderately incompatible trace elements in clinopyroxenes from abyssal peridotites also suggest that these peridotites experienced near-fractional melting (Hellebrand et al., 2000). Finally, melt inclusions with variably depleted trace element concentrations relative to average MORB (e.g. Sobolev & Shimizu, 1993; Sobolev, 1996; Shimizu, 1998) suggest that erupted MORB magmas contain a component of liquid produced by melting of depleted peridotite. Taken together, these lines of evidence suggest that...
partial melts can be extracted from the mantle beneath mid-ocean ridges at low melt fractions and that at least some components of MORBs were produced by melting of depleted sources with low concentrations of incompatible major, minor, and trace elements relative to the fertile MORB source.

Most high-pressure experimental studies of peridotite melting have focused on fertile mantle compositions, and these studies have provided information on melt compositions over a wide range of pressures and temperatures (e.g. Jaques & Green, 1980; Takahashi, 1986; Hirose & Kushiro, 1993; Baker & Stolper, 1994; Baker et al., 1995; Kushiro, 1996; Robinson et al., 1998; Walter, 1998). In addition, Pickering-Witter & Johnston (2000) and Schwab & Johnston (2001) explored the effects of pyroxene and spinel abundances and pyroxene compositions on liquid compositions, melt productivities, and melting reactions at 10 kbar, and, by varying the orthopyroxene/clinopyroxene ratios in their starting materials, they were able to work on bulk compositions spanning wide ranges of MgO, Al₂O₃, CaO, and Na₂O contents.

In a synthesis of available experimental data, Hirschmann et al. (1998a) showed the important role that alkalis play in controlling the compositions of olivine + orthopyroxene ± clinopyroxene-saturated melts of peridotite. Likewise, the broadly inverse correlation between total alkali contents of peridotites and their solidus temperatures (Herzberg et al., 2000; Hirschmann, 2000) suggests that, at a given pressure, depleted peridotites will begin to melt at higher temperatures than fertile peridotites. Because peridotites in the shallowest part of the melting zone beneath mid-ocean ridges are expected to have been depleted in incompatible major and minor elements (and especially alkalis) by prior melting, the expectation is that melts of peridotite. Likewise, the broadly inverse correlation between total alkali contents of peridotites and their solidus temperatures (Herzberg et al., 2000; Hirschmann, 2000) suggests that, at a given pressure, depleted peridotites will begin to melt at higher temperatures than fertile peridotites. Because peridotites in the shallowest part of the melting zone beneath mid-ocean ridges are expected to have been depleted in incompatible major and minor elements (and especially alkalis) by prior melting, the expectation is that such peridotites would melt to a lower degree and produce different liquids compared with melting of fertile peridotite under similar conditions.

In this paper we present the results of melting experiments on a moderately depleted peridotite composition (DMM1) at 10 kbar and 1250–1390°C; these results complement the large amount of available data on more fertile peridotite compositions. We used a variant of the diamond aggregate melt-extraction technique developed by Johnson & Kushiro (1992), Hirose & Kushiro (1993), and Baker & Stolper (1994) to study near-solidus experimental glasses unmodified by quench crystal growth. In the experiments described here, the aggregate comprised vitreous carbon spheres or fragments (Wasylkenki et al., 1996; Pickering-Witter & Johnston, 2000; Schwab & Johnston, 2001). A potential problem associated with the diamond aggregate technique in low melt fraction experiments is that pressure is initially low within the void spaces of the aggregate until the layer is completely filled with melt (Baker et al., 1996), possibly leading to the segregation of liquid that is far from equilibrium with the peridotite at the actual pressure of the experiment. The motivation for replacing the porous diamond aggregate used in our previous studies (Baker & Stolper, 1994; Baker et al., 1995) with vitreous carbon spheres is that, although vitreous carbon is strong enough to support open pore space at the start of an experiment, it is much less stiff than diamond (Noda et al., 1969; Sawa & Tanaka, 2002), so this open space collapses more quickly. Another advantage is that vitreous carbon is readily polished at the end of an experiment, allowing small pools of melt to be imaged and analyzed in situ with ease (e.g. Pickering-Witter & Johnston, 2000; Schwab & Johnston, 2001). In addition to modifying the melt-extraction technique in this way, we have addressed the controversy surrounding this technique (see Baker et al., 1996; Falloon et al., 1996, 1997, 1999; Wasylkenki et al., 1996; Pickering-Witter & Johnston, 2000) with special experiments that demonstrate the reliability and close approach to equilibrium of melt-extraction experiments.

Following the presentation of the experimental results, we consider the effects of bulk composition on 10 kbar melting reaction coefficients and on melt productivity, and we compare our experimental glass compositions for the depleted peridotite DMM1 with those produced by melting more fertile peridotite compositions at the same pressure. We also compare our experimental glass compositions with liquid compositions calculated for the DMM1 composition using four peridotite melting models. Finally, by combining our experimentally determined 10 kbar solidus temperature with solidus determinations on other peridotite compositions, we develop a simple expression for predicting the solidus temperature at 10 kbar as a function of bulk composition.

EXPERIMENTAL AND ANALYTICAL TECHNIQUES

Starting materials

Starting materials for this study were prepared by mixing mineral separates (olivine, ol; orthopyroxene, opx; clinopyroxene, cpx; spinel, sp) from a Kilbourne Hole spinel lherzolite nodule (KBH), olivine from a Hawaiian dunite nodule (H1801i), and synthetic diopside (CaMgSi₂O₆). Electron microprobe analyses of the natural minerals are reported in Table 1. The crystallinity of the synthetic diopside was verified by X-ray diffraction, and the composition reported in Table 1 is that of stoichiometric diopside. The natural minerals were hand-picked from disaggregated
Table 1: Compositions of starting materials and bulk composition of DMM1

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>TiO₂</th>
<th>Al₂O₃</th>
<th>Cr₂O₃</th>
<th>FeO*</th>
<th>MnO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>NiO</th>
<th>mg-no.</th>
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<td>KBH oil(10)</td>
<td></td>
<td></td>
<td>0-01(1)</td>
<td>0-01(1)</td>
<td>9-34(10)</td>
<td>0-12(2)</td>
<td>49-49(21)</td>
<td>0-07(11)</td>
<td></td>
<td></td>
<td>0-39(2)</td>
<td>90-4(5)</td>
</tr>
<tr>
<td>H18B01 oil(14)</td>
<td></td>
<td></td>
<td>0-01(1)</td>
<td>0-02(2)</td>
<td>12-07(71)</td>
<td>0-17(2)</td>
<td>47-55(65)</td>
<td>0-16(2)</td>
<td></td>
<td></td>
<td>0-39(4)</td>
<td>87-5(15)</td>
</tr>
<tr>
<td>KBH opx(8)</td>
<td>54-99(22)</td>
<td>10-0(2)</td>
<td>4-76(15)</td>
<td>5-50(4)</td>
<td>5-38(6)</td>
<td>0-13(2)</td>
<td>32-79(14)</td>
<td>0-86(2)</td>
<td>0-12(1)</td>
<td>0-11(2)</td>
<td>90-7(15)</td>
<td></td>
</tr>
<tr>
<td>KBH cpx(15)</td>
<td>51-99(21)</td>
<td>0-41(5)</td>
<td>6-56(11)</td>
<td>1-00(5)</td>
<td>2-81(4)</td>
<td>0-09(2)</td>
<td>15-24(10)</td>
<td>19-89(11)</td>
<td>1-58(3)</td>
<td>0-04(2)</td>
<td>90-6(8)</td>
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<tr>
<td>Diopside²</td>
<td>55-49</td>
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<td></td>
<td></td>
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<td></td>
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<td>25-89</td>
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<tr>
<td>KBH spin(11)</td>
<td>0-11(2)</td>
<td>0-11(2)</td>
<td>54-91(27)</td>
<td>12-96(20)</td>
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<td></td>
<td></td>
<td></td>
<td>0-37(2)</td>
<td>78-0(5)</td>
</tr>
<tr>
<td>DMM1³</td>
<td>44-91(11)</td>
<td>0-04(1)</td>
<td>2-38(5)</td>
<td>0-39(1)</td>
<td>8-34(15)</td>
<td>0-13(1)</td>
<td>41-59(15)</td>
<td>2-14(2)</td>
<td>0-05(3)</td>
<td>0-006(2)</td>
<td>0-28(1)</td>
<td>89-9(5)</td>
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<tr>
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<td>12-07(10)</td>
<td>0-10(2)</td>
<td>11-96(3)</td>
<td>12-06(3)</td>
<td>1-39(2)</td>
<td></td>
<td>0-01(1)</td>
<td>63-8(3)</td>
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<td>GBR⁴</td>
<td>77-7</td>
<td>0-07</td>
<td>12-9</td>
<td></td>
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<td>0-4</td>
<td>0-04</td>
<td>0-05</td>
<td>0-5</td>
<td>4-2</td>
<td>4-2</td>
<td>18-2</td>
</tr>
</tbody>
</table>

³Minerals designated by KBH were separated from a Kilbourne Hole nodule; number of electron microprobe analyses in parentheses, each analysis on a separate grain. Numbers in parentheses adjacent to each oxide value are one sample standard deviation in terms of the least units cited, e.g. 40.76(16) represents 40.76 ± 0.16. Dashes indicate that the element was not analyzed or was below the detection limit of the microprobe.

²Olive separated from a dunite nodule collected from the Hualalai 1801 flow.

Synthetic crystalline diopside; crystallinity verified by X-ray diffraction. Listed composition is for end-member diopside.

Bulk composition (with the exception of K₂O and P₂O₅) calculated from constituent mineral compositions and mineral proportions given in text. Mean bulk K₂O content calculated from liquid K₂O contents in runs 22, 12, 27C, 28C, 33C, and 42C (Table 3); phase proportions; and ol–liq, opx–liq, and cpx–liq partition coefficients from Halliday et al. (1995). Mean bulk P₂O₅ = 0-0049(12); calculated from liquid P₂O₅ contents in runs 28C, 33C, and 42C (Table 3); phase proportions; and ol–liq, opx–liq, and cpx–liq partition coefficients for P₂O₅ of 0-1, 0-03, and 0-05 (Libourel et al., 1994; Brunet & Chazot, 2001). Uncertainties (with the exception of those for K₂O and P₂O₅) are based on Monte Carlo propagations of errors on phase compositions and estimated weighing errors; uncertainty on K₂O and P₂O₅ is one sample standard deviation of the mean bulk K₂O and P₂O₅ values.

Composition of Glass Buttes rhyolite taken from Dobson et al. (1989) and Ihinger et al. (1999).

The starting DMM1 composition was chosen to represent a moderately depleted mantle peridotite. When compared with the residues in the 10 kbar melting experiments of Baker & Stolper (1994) and Baker et al. (1995), DMM1 is roughly equivalent to the residue formed by 12–13% batch melting of MM3. Figure 1 compares the concentrations of MgO, Al₂O₃, CaO, and Na₂O in DMM1 with other peridotites studied experimentally at 9–10 kbar, with estimates of the primitive mantle, and with reconstructed abyssal peridotites. DMM1 has lower Al₂O₃, CaO, and Na₂O contents than all estimates of primitive mantle, and, unlike other peridotite compositions that have been studied experimentally, it falls on the well-defined MgO–oxide trends for abyssal peridotites (Fig. 1). Figure 1a and b shows that DMM1 is lower in Al₂O₃ than all other experimentally studied peridotite compositions and lower in CaO than the others, except those investigated by Sen (1982; 5 in Fig. 1b) and by Pickering-Witter & Johnston (2000; 9 in Fig. 1b; note that this composition is far removed from the MgO–CaO trend defined by abyssal peridotites and primitive mantle estimates). Figure 1c shows that DMM1 also has lower Na₂O than most peridotite compositions previously studied.
Experimental methods

All experiments were run in a 1.27 cm piston cylinder apparatus using CaF$_2$ cells, straight-walled graphite furnaces, and inner pieces of crushable MgO dried at 1000°C for at least 8 h. Pressure was applied using the hot-piston-in technique with no friction correction. Experiments at 1300°C with identical assemblies bracketed the Ca-Tschermak breakdown reaction to lie at 11–14 kbar. This pressure range encompasses the reaction boundary (1300°C, 13 kbar) determined by Hays (1966). W$_{93}$Re$_3$/W$_{75}$Re$_{25}$ thermocouples were used to monitor and control temperature to within ~1°C of the set point. No pressure correction was applied to the nominal e.m.f.–temperature relation. Based on past experiments with double thermocouples, temperatures are estimated to be accurate to within ±15°C.

Run durations and experimental conditions are reported in Table 2. Except in experiments 1, 2, and 3, N$_2$ gas was bled into the slot in the thermocouple plate during each experiment to minimize oxidation of the thermocouple wires within and just below the steel base plug. At the end of each experiment, the thermocouple wires just below the base plug (i.e. within the run assembly) were inspected for signs of oxidation; no evidence of significant oxidation was observed on any of the wires, including those from experiments 1–3. After the power was turned off, samples cooled to below 1000°C within several seconds. As each run assembly was taken apart, the position of the capsule relative to the center of the furnace and that of the thermocouple junction relative to the top of the capsule were measured to ensure that the capsule was properly positioned within the furnace and that the thermocouple tip was 0.5–1 mm from the top of the capsule. Each capsule was sliced vertically with a diamond wafering blade, mounted in epoxy, and polished for electron microprobe analysis.

This study includes three types of melting experiments. The first type of experiment consisted of two stages (see Baker & Stolper, 1994). For the first stage, 3–6 mg of peridotite powder that had been dried in a vacuum oven at 110°C for 2 h was loaded into a graphite inner capsule. The inner capsule was then placed in a 0.15 inch o.d. Pt capsule. The composite capsule assembly was then dried and welded shut. This second-stage capsule was then run for 18–135 h at the same temperature and pressure as the first-stage capsule.

Fig. 1. MgO–oxide variation diagrams showing the bulk composition of the moderately depleted DMM1 peridotite used in this study (large filled square) and estimates of primitive upper-mantle compositions (○: Ringwood, 1979; Sun, 1982; Wänke et al., 1984; Hart & Zindler, 1986; Allègre et al., 1995; McDonough & Sun, 1995); reconstructed abyssal peridotite compositions (◇: Baker & Beckett, 1999); and other peridotitic starting materials studied experimentally at 9–10 kbar (●: 1, MM3, Baker & Stolper, 1994; 2, PHN1611, Kushiro, 1996; 3, KLB-1, 4, HK-66, Hirose & Kushiro, 1993; 5, 7P11I-1, Sen, 1982; 6, Hawaiian Pyrolite–40% olivine (HPy-40); 7, Tainquillo Lherzolite–40% olivine, Jaques & Green, 1980; 8, FER-B, 9, FER-C, 10, FER-D, 11, FER-E, Pickering-Witter & Johnston, 2000; 12, INT-A, 13, INT-B, 14, INT-D, 15, INT-E, Schwab & Johnston, 2001). MgO vs (a) Al$_2$O$_3$, (b) CaO, (c) Na$_2$O.

This study includes three types of melting experiments. The first type of experiment consisted of two stages (see Baker & Stolper, 1994). For the first stage, 3–6 mg of peridotite powder that had been dried in a vacuum oven at 110°C for ≥2 h was loaded into a graphite inner capsule. The inner capsule was then placed in a 0.15 inch o.d. Pt capsule. The composite capsule assembly was then dried and welded (see Table 2); and finally the crimped end of the Pt capsule was welded. After drying and welding, the capsule was run at temperature and pressure for ~52–136 h. For the second stage, the silicate charge was removed from the first-stage capsule and loaded into a new graphite capsule along with 80–100 μm diameter vitreous carbon spheres that had been dried for at least 1 h in a 110°C vacuum oven. The mass of vitreous carbon (Table 2) was ~3–9% of the mass of the silicate sample. The loaded second-stage graphite capsule was then placed in a Pt capsule, after which the composite assembly was dried and welded shut. This second-stage capsule was then run for ~18–135 h at the same temperature and pressure as the previous stage.
<table>
<thead>
<tr>
<th>Run</th>
<th>Temp. (°C)</th>
<th>Drying*</th>
<th>1st stage</th>
<th>2nd stage</th>
<th>Silicate (mg)</th>
<th>Glassy carbon (mg)</th>
<th>Phases present</th>
<th>Phases proportions (wt %)</th>
</tr>
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<tbody>
<tr>
<td>9</td>
<td>1390</td>
<td>300/4,300/1</td>
<td>51-7</td>
<td>59-4</td>
<td>5-01</td>
<td>0-175</td>
<td>gl, ol, opx</td>
<td>16-6(6), 68-1(1-5), 15-4(1-6)</td>
</tr>
<tr>
<td>30</td>
<td>1370</td>
<td>400/1,400/1</td>
<td>69-5</td>
<td>87-5</td>
<td>4-85</td>
<td>0-196</td>
<td>gl, ol, opx</td>
<td>13-8(5), 68-1(1-7), 18-3(1-7)</td>
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<td>1</td>
<td>1360</td>
<td>110/12+,110/3</td>
<td>72-1</td>
<td>18-5</td>
<td>4-17</td>
<td>0-261</td>
<td>gl, ol, opx</td>
<td>12-5(6), 67-5(1-5), 20-0(1-6)</td>
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<td>2</td>
<td>1330</td>
<td>110/20,300/2</td>
<td>93-4</td>
<td>37-6</td>
<td>4-32</td>
<td>0-238</td>
<td>gl, ol, opx</td>
<td>10-0(5), 67-1(1-5), 22-9(1-6)</td>
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<td>1330</td>
<td>110/12+</td>
<td>141-3</td>
<td>3-07</td>
<td>0-435 (33-8, FB)</td>
<td>gl, ol, opx</td>
<td>11-7(4), 66-9(1-5), 21-4(1-5)</td>
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<td>1325</td>
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<td>4-38</td>
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<td>25T</td>
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<td>110/12+</td>
<td>30-2/92-8</td>
<td>3-02</td>
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<tr>
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<td>1250</td>
<td>400/4,400/4</td>
<td>142-0</td>
<td>245-5</td>
<td>9-26</td>
<td>ol, opx, cpx, sp</td>
<td>62-8(1-7), 28-4(1-9), 8-1(5), 0-6(2)</td>
<td></td>
</tr>
</tbody>
</table>

Phases present: gl, glass; ol, olivine; opx, orthopyroxene; cpx, clinopyroxene; sp, spinel.

*Indicates drying procedure for loaded capsule before welding. Temperature and duration in hours (rounded to nearest hour; 12+ indicates that the capsule was dried overnight) separated by slash. Drying conditions for both stages given for two-stage runs.

† Numbers in parentheses indicate masses, in micrograms, of aggregate chips included with silicate samples in compositional-convergence runs. FB and GBR indicate glass used in aggregate chip; FB, synthetic ferrobasaltic glass; GBR, Glass Buttes rhyolite (compositions listed in Table 1).

‡ Calculated by mass balance. Numbers in parentheses indicate uncertainties; e.g. 16-6(6) represents 16.6 ± 0.6% liquid. The silica contents of 17 of the 18 olivine compositions used to calculate the modes have been adjusted using the stoichiometric constraint for ol that Si (cation %) equals 33.333. For each of these analyses, the SiO₂ (wt %) value was iteratively raised or lowered and cation % calculated until the Si value was within 0.005 units of 33.333. All oxides were then normalized to 100 wt %; it should be noted that this procedure has no effect on the Mg/(Mg + Fe) ratio of the olivines. Although the correction is relatively small (e.g. mean absolute value of the change in silica contents is 0.26 wt %), the correlation coefficients for melt fraction (F) vs ol and F vs opx increased dramatically (e.g. for F vs ol, the Pearson correlation coefficient increased from 0.05 to 0.58). Unadjusted olivine compositions are reported in Table 3.

§ Calculated using analyses for opx and cpx that were normalized to 100 wt % (see Table 3).

The second type of experiment was run as a single stage, but the temperature was changed during the experiment to evaluate whether liquid that had segregated into the interstices between the vitreous carbon spheres could respond chemically to changes in temperature; these experiments are indicated by a T next to the run number in Table 2. Graphite capsules were loaded with vitreous carbon and peridotite powder, placed in Pt outer capsules, and then dried and welded shut as for the previously described charges. Each sample was run at 10 kbar and an initial temperature as listed in Table 2 for ~26–68 h. Following this initial period, the temperature was raised either 15 or 40°C, and the charge was held at this higher temperature for an additional ~88–117 h. The potential concern...
addressed by these experiments is whether liquid segregated into the vitreous carbon at the start of the experiment is in sufficient chemical contact with the main mass of the experimental charge that its composition can change by diffusive interaction with the peridotite and its interstitial liquid.

We refer to the third type of experiment as ‘compositional-convergence’ runs; these experiments are marked with a C next to the run number in Table 2. For these seven experiments, glass-bearing vitreous carbon aggregates were prepared as follows. An oxide mix of a synthetic ferrobasalt or a powdered rhyolitic glass from Glass Buttes, Oregon (both compositions are reported in Table 1), were mixed with conchoidally fractured vitreous carbon shards (80–147 μm in size). Approximately 85% (by weight) of the material in each capsule was vitreous carbon. Each of these two mixtures was loaded into a separate Pt capsule and then held at 10 kbar and 1350°C for a few hours. At the end of these two preparatory runs, the silicate liquids had impregnated most of the pore spaces between the vitreous carbon fragments. Fragments (10–41 μg; see Table 2) of the glass-impregnated vitreous carbon aggregates were loaded into graphite–Pt capsules with DMM1 powder (~3–6 mg; see Table 2) as described above for the other two types of experiments. The samples were run for ~127–188 h. In one experiment (20C), a layer of vitreous carbon spheres was also loaded into the capsule at the opposite end of the charge from the ferrobasalt-impregnated vitreous carbon aggregate. The purpose of these experiments was to examine the degree to which the ferrobasaltic and rhyolitic glasses in the interstices of the vitreous carbon aggregate were able to converge in composition toward each other and toward the compositions of glasses within vitreous carbon aggregates that were not pre-filled with glass (i.e. glass within the layer of vitreous carbon in 20C or that in charges from the previously described experiments). Because the ferrobasaltic and rhyolitic glasses are extremely distant in composition from the equilibrium partial melts of the DMM1 peridotite, the extent to which they can shift compositionally during an experiment can be used to demonstrate that liquids segregated into vitreous carbon aggregates can maintain chemical contact with the main mass of the peridotite during an experiment. This means that even if a disequilibrium liquid migrates into the vitreous carbon aggregate at the start of an experiment, it can evolve substantially via exchange with the bulk charge over the course of the experiment. Moreover, if the initial ferrobasaltic and rhyolitic compositions converge to a single composition similar to glasses from our two-stage and temperature-change experiments, we can infer with confidence that an equilibrium liquid composition was approached closely.

Oxygen fugacity was not controlled in our experiments, but the presence of graphite inner capsules constrains $f_{\text{O}_2}$ to below the graphite–CO vapor buffer (GCO). Following the approach discussed by Bertka & Holloway (1988) and Gudmundsson et al. (1993), we placed 13 μg of platinum wire in the middle of the peridotite powder in experiment 25 (1325°C). During the experiment the Pt wire absorbed Fe. Based on the compositions of the resulting Fe–Pt alloy and coexisting orthopyroxene and olivine, and using the equations and solution models of Jamieson et al. (1992), the $\log_{10} f_{\text{O}_2}$ in run 25 was −9.2, or ~2.4 log units below the quartz–fayalite–magnetite buffer (QFM) at 10 kbar (Huebner, 1971). The slightly different activity–composition models of Gudmundsson & Holloway (1993) yielded a $\log_{10} f_{\text{O}_2}$ of ~8.5, or ~1.7 log units below QFM. The inferred $f_{\text{O}_2}$ values of our experiments are thus consistent with estimates for the MORB source region (Christie et al., 1986; Green et al., 1987; O’Neill & Wall, 1987; Mattioli & Wood, 1988; Mattioli et al., 1989).

Fig. 2. Backscattered electron photomicrographs of (a) a typical charge with vitreous carbon spheres and (b) a portion of the charge from run 28C, showing the chip of vitreous carbon aggregate that had been pre-impregnated with ferrobasalt before the experiment.
Analytical techniques
Experimental charges were analyzed at Caltech with a five spectrometer JEOI 733 electron microprobe using an accelerating voltage of 15 keV. Crystalline phases in all experiments (including the Pt alloy in run 25) were analyzed with a beam current of 30 nA and a rastered beam at magnifications greater than 40,000× (the resulting spot size is less than 2 µm × 2 µm). Glasses were analyzed with a 2-5, 5, or 10 nA beam current and a rastered area as large as possible for the glass pools being analyzed (generally ~5 µm × 5 µm). Repeated analyses on the same region of glass within several experiments indicated little or no Na loss. All data were processed using CITZAF (Armstrong, 1988). Two basaltic glasses, VG-2 and BGIO (Jarosewich et al., 1979), were analyzed as secondary standards during each microprobe session to estimate accuracy and precision of the instrument on a long-term basis; when crystalline phases were analyzed, Johnstown hypersthene and Natural Bridge diopside (Jarosewich et al., 1979) were also analyzed to provide additional estimates of accuracy and precision.

Raw oxide sums for the experimental glasses were typically 95–97%, but were occasionally lower, and in one case down to 89%. We consistently observed higher totals for glass pools that were more than ~5 µm in the shortest dimension and lower totals for smaller glass pools. The low totals probably reflect the inclusion of vitreous carbon in the electron beam analysis volume. This inference is supported by the observation that when all of the glass analyses for a given sample are normalized to 100%, there are no systematic differences in the normalized oxide concentrations as functions of the raw oxide sums. Within the vitreous carbon aggregate of a given experiment, normalized glass compositions display no systematic variation as a function of distance from the DMM1 peridotite. Mean compositions for normalized glasses, crystalline phases, and secondary standards are reported in Table 3.

Water contents of the glasses in two charges (3 and 22) were measured by secondary ion mass spectrometry with the modified Cameca IMS-3f ion microprobe at Lawrence Livermore National Laboratories using the techniques described by Kent et al. (1999). Measured H+/30Si+ ratios in our experimental glasses were converted to water contents with a calibration curve constructed by analyzing a set of Marianas back-arc basin basaltic glasses (Stolper & Newman, 1994) and synthetic MORB glasses (Dixon et al., 1995) whose water and silica contents were determined by independent techniques. Errors on the water contents of the experimental glasses are conservatively estimated at ±15% relative. Charges 3 and 22 contain 1.2 ± 0.2 and 0.3 ± 0.1 wt % water, respectively. These have not been corrected for the possible effects of vitreous carbon in the analysis volume. As vitreous carbon can dissolve hydrogen in the presence of water-bearing melt, but contains no Si (L. Wasylenki, unpublished data, 1995), such a correction would probably lead to lower estimates of the water contents of our experimental glasses.

RESULTS
Evaluation of the approach to equilibrium
Although the melt-extraction technique used in this study provides a simple way to avoid the quench modification problems encountered in conventional peridotite melting experiments close to the solidus, the technique must be applied with care. In particular, the issue of whether the glasses within the vitreous carbon aggregates (this study; Pickering-Witter & Johnston, 2000; Schwab & Johnston, 2001) or diamond aggregates (e.g. Johnson & Kushiro, 1992; Hirose & Kushiro, 1993; Baker & Stolper, 1994; Baker et al., 1995; Kushiro, 1996) actually represent equilibrium melt compositions has sparked much debate (Baker et al., 1996; Falloon et al., 1996, 1997, 1999; Wasylenki et al., 1996). For example, as explained above, one possible problem with the one-stage experiments of Baker & Stolper (1994) is that at the onset of an experiment, low pore pressure within the diamond experiments could affect the composition of liquid initially filling these pores, i.e. the initial liquid may not be in equilibrium with the bulk peridotite at the nominal pressure of the experiment. Similarly, the kinetics of melting could lead to generation of a disequilibrium liquid at the start of an experiment. In either of these cases, liquid migrating rapidly into the pores in the diamond or vitreous carbon layer might not be in equilibrium with the bulk of the material in the capsule, and, if this segregated liquid were subsequently cut off from exchange with the adjacent peridotite, results would be erroneous. Liquids segregated into diamond aggregates in short-duration, one-stage experiments do indeed differ from those produced in long-duration runs at the same temperature and pressure (Johnson & Kushiro, 1992; Baker & Stolper, 1994), so this general class of potential problems cannot be disregarded. Our two-stage experiments, however, were designed to minimize these problems in that the liquid moving into a vitreous carbon layer at the beginning of a second-stage run is remelted glass from the first-stage run and thus should represent a near-equilibrium melt.

Temperature-change experiments
Although our two-stage experiments were explicitly designed to minimize problems of melt re-equilibration
### Table 3: Experimental results

<table>
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<tr>
<th>Run</th>
<th>Phase</th>
<th>SiO₂</th>
<th>TiO₂</th>
<th>Al₂O₃</th>
<th>Cr₂O₃</th>
<th>FeO</th>
<th>MnO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>Sum</th>
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<tbody>
<tr>
<td>26C</td>
<td>gl(6)</td>
<td>50.19(28)</td>
<td>27.4(4)</td>
<td>13.78(4)</td>
<td>27.4(4)</td>
<td>7.81(21)</td>
<td>15.27(15)</td>
<td>14.10(23)</td>
<td>12.81(22)</td>
<td>56.3(3)</td>
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<td>0.16(2)</td>
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<td>0.04(1)</td>
<td>5.68(19)</td>
<td>32.79(29)</td>
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</tr>
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<td>gl(7)</td>
<td>48.21(24)</td>
<td>30.4(14)</td>
<td>16.14(16)</td>
<td>23.0(3)</td>
<td>7.61(17)</td>
<td>0.11(4)</td>
<td>14.18(17)</td>
<td>15.25(11)</td>
<td>0.56(3)</td>
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<td>25.9(6)</td>
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<td>7.4(16)</td>
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<tr>
<td>12</td>
<td>oil(8)</td>
<td>39.32(18)</td>
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<td>8.25(19)</td>
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<td>2.75(9)</td>
<td>0.02(1)</td>
<td>—</td>
<td>99.90</td>
</tr>
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in the vitreous carbon layers, we nevertheless made further efforts to demonstrate directly that liquids in the vitreous carbon layers in our experiments can change composition over the course of an experiment. The temperature-change experiments described above provide evidence of continued interaction between segregated melt and the peridotite over the course of an experiment.

We conducted three temperature-change experiments to demonstrate that segregated liquids can change composition in response to changes in experimental conditions. In each such experiment, after
initial run durations of 26–68 h at 1285 or 1310°C, temperatures were raised either 15 or 40°C and the runs continued for an additional 88–117 h. We assume that during the initial stages of these experiments, liquids in the vitreous carbon layers approached the glass compositional trends defined by the two-stage experiments at the same initial temperatures. In two of the three temperature-change experiments (17T, 1285–1300°C; 25T, 1285–1325°C), the final liquid compositions are similar to those in two-stage experiments run at the same final temperatures and different from liquid compositions expected at 1285°C (see Fig. 4). (The third experiment, 23T, appears to have had a significant temperature gradient, as evidenced by modal variations from top to bottom of the charge, and to have had a final temperature of ~1310°C rather than 1325°C; see the section ‘Phase relations and liquid compositions’ below.) Based on mass balance calculations using the quenched glass and mineral compositions and the bulk DMM1 composition, the melt fractions of 17T and 25T during their respective high-temperature steps were ~0-03 and 0-11 (Table 2). Thus, over the course of 93–117 h at these melt fractions, the segregated liquids in the vitreous carbon layers were able to change in response to the increase in temperature via diffusive exchange with liquid retained in the peridotite. We also attempted temperature-change experiments in which the temperature was lowered in the second phase of the experiment, but, as one would expect, this resulted in extensive crystallization within the vitreous carbon aggregates.

**Compositional-convergence experiments**

Successful ‘compositional-convergence’ experiments demonstrate not only that liquids in vitreous carbon aggregates can change significantly, but also by convergence that an equilibrium result has been approached from more than one direction in multi-component composition space. As described above, these experiments involved placing ~10–41 μg of a vitreous carbon aggregate that was pre-impregnated with either a synthetic ferrobasalt or a rhyolite in a capsule with DMM1 powder (Fig. 2b). Based on the results of our two-stage experiments, both the ferrobasalt and the rhyolite glass compositions were initially far from equilibrium with DMM1 at 10 kbar and any temperature. With the exceptions of K$_2$O and, to a lesser extent, Na$_2$O for the two rhyolite-bearing experiments, the few micrograms of glass added to the system have little effect on the bulk composition. The potassium budget in the two rhyolite-bearing runs (26C and 34C) is dominated by the rhyolite glass; for example, we estimate that the bulk K$_2$O content in 34C increased from ~0-006 wt % (the estimated bulk composition of DMM1) to ~0-02 wt % as a result of the addition of the rhyolite-bearing vitreous carbon aggregate. The change in the sodium content in run 34C is less extreme; the Na$_2$O concentration increased from ~0-06 to ~0-07 wt %.

![Figure 3](https://example.com/figure3.png)

Figure 3 illustrates the large shifts in composition that the ferrobasaltic and rhyolitic glasses underwent as a result of diffusive equilibration with 2–12 wt % melt in the peridotite and shows that the quenched liquids in all of these experiments define a single compositional trend approached from opposite directions in most compositional dimensions. As shown in Fig. 4, this compositional trend is consistent with the trend defined by glass compositions from the two-stage and temperature-change experiments. It is important to emphasize that the compositions of the liquids in the vitreous carbon chips in these experiments have converged to their final compositions from opposite directions in terms of several oxides and that the compositional changes achieved in these experiments are in some cases very large (e.g. SiO$_2$, CaO, MgO, and FeO* for the initially rhyolitic liquid). It is also striking that three of the convergence experiments are within <5°C of our estimated solidus for the DMM1 composition and have only ~2–5% melt (Table 2). These results should thus disperse controversy about the validity of melt-segregation experiments into diamond or vitreous carbon aggregates, as they demonstrate large compositional shifts, convergence from melts initially in the aggregates that are extremely far in composition from the final compositions, and that the results of two-stage, temperature-change, and ‘compositional-convergence’ experiments form coherent compositional trends as a function of melt fraction near the solidus.

**Homogeneity of crystalline phases**

We have also examined the compositions of the residual peridotite minerals in all of our experiments (Table 3), as true achievement of equilibrium would require homogeneous crystals and mineral compositions that are independent of distance from the glass-bearing aggregates.

In all experiments olivine grains (15–40 μm in size) were homogeneous within analytical error in each charge, both from core to rim of individual analyzed grains and from top to bottom of the residual peridotite. Orthopyroxene grains with cross-sectional diameters larger than ~10 μm often displayed small, incompletely reacted cores, visible with high-gain, backscattered electron imaging. We estimate that these cores occupy <35% of the volume of opx in a given charge. The cores have compositions between the initial KBH opx
composition and analyzed rim compositions, indicating some compositional change toward equilibrium. We did not observe any significant differences in opx core and rim compositions as a function of distance from the vitreous carbon aggregates in any of our experiments.

Clinopyroxene grains are typically \(5 \text{ to } 15 \mu m\) in size. Unreacted \(\text{cpx}\) cores were not clearly visible in back-scattered electron images, but microprobe analyses indicate that \(\text{cpx}\) grains in the run products are chemically heterogeneous. In particular, \(\text{CaO}\) and \(\text{Al}_2\text{O}_3\) contents vary within and among the \(\text{cpx}\) grains in each charge. In our study, more than 20 \(\text{cpx}\) analyses were collected from each charge, and those that clustered toward the low-Al and low-Ca end of the trend in \(\text{Al}_2\text{O}_3–\text{CaO–MgO}\) space defined by all analyses within a charge were averaged for Table 3. None of the \(\text{cpx}\) analyses from any of the run products were close in composition to the starting KBH \(\text{cpx}\) composition or pure diopside, suggesting that all of the \(\text{cpx}\) in our experiments at least partially re-equilibrated. We did not observe any systematic variations in \(\text{cpx}\) compositions as a function of distance from the vitreous carbon aggregates, but in some experiments modal \(\text{cpx}\) abundance increases with increasing distance from the top of the capsule (i.e. the end closest to the thermocouple junction). The experiments in which this modal variation occurs probably experienced larger thermal gradients than those experiments that show a more uniform \(\text{cpx}\) distribution (Lesher & Walker, 1988).

Spinel is a minor phase in our experiments and, as run temperatures fall, shows more compositional heterogeneity within runs than olivine or pyroxenes. Spinel grains in the run products are small (\(\approx 10 \mu m\) in size), and generally only 3–6 grains are visible on the polished surface of each charge. Thus we were not able to assess the degree of compositional variation within individual \(\text{sp}\) grains or as a function of the position of \(\text{sp}\) grains in the charge relative to the melt-bearing vitreous carbon aggregates. We did observe that in a given charge, grains of \(\text{sp}\) in direct contact with melt tended to be more compositionally similar than those \(\text{sp}\) grains that were not obviously in contact with melt. The compositions reported in Table 3 are averages of the \(\text{sp}\) grains that had similar compositions within each charge. As we discuss below, these mean compositions are consistent with the compositional trends of \(\text{sp}\) from other 9–12 kbar peridotite melting experiments.

Overall, although the pyroxenes and spinels in the experimental charges are not homogeneous within analytical error, our run durations were long compared with most previous peridotite melting experiments, and the observed heterogeneity is attributable to incompletely reacted cores that would be difficult to react fully without much finer starting materials or much longer experiments. As these cores do not make up a major fraction of the residual phases, it is unlikely that they have a significant influence on the results. More importantly, the compositional heterogeneities

![Fig. 3. Changes in melt compositions in 'compositional-convergence' experiments (see text): (a) SiO\(_2\) vs Al\(_2\)O\(_3\); (b) FeO\(^*\) (all Fe as FeO) vs Na\(_2\)O; (c) MgO vs CaO. The large gray square in each panel represents the initial composition of ferrobasaltic glass in aggregates of vitreous carbon particles that were loaded in capsules with DMM1 powder and run at 10 kbar for 127–184h. Smaller open and filled squares represent compositions of glasses in the vitreous carbon chips at the end of the experiments. Glass composition from the vitreous carbon layer in run 20C is also plotted (○). The large gray circle in each panel represents the initial composition of Glass Buttes rhyolite in another set of vitreous carbon aggregates run with DMM1 powder at 10 kbar for 166–188h; smaller open and filled circles represent the compositions of the glasses at the end of these experiments. Glass compositions denoted by small filled squares or circles coexist with spinel lherzolite; small open squares or circles denote harzburgite residues. Arrows show typical compositional changes in these ‘compositional-convergence’ experiments; no arrows are drawn from the initial ferrobasalt composition to the re-equilibrated melts in (c) because of the close proximity of the two sets of symbols. Melt fractions \((F)\) are given for the experiments that define each end of the compositional trends.](image-url)
observed in pyroxenes and spinel within each charge do not appear to correlate with distance from the vitreous carbon aggregates.

**Phase relations and liquid compositions**

Our experiments span the 1250–1390°C temperature range. Glass was present in all experiments run at ≥1270°C; no glass was detected in high-magnification, backscattered electron images of the 1250°C experiment (36), and although such visual determinations can be misleading, we tentatively place the solidus for DMM1 between 1250 and 1270°C. Melt coexists with ol, opx, cpx, and sp at 1270–1300°C. Experiments at 1310–1390°C contain liquid, ol, and opx, with the exception of experiment 23T (nominally 1325°C), which contains ~1 wt % cpx at the end of the capsule far from the vitreous carbon aggregate and the thermocouple.
junction. We interpret these results to indicate that $\text{cpx-out}$ (the temperature at which $\text{cpx}$ disappears from the solid residue) and $\text{sp-out}$ are at 1300–1310°C. We attribute the $\text{cpx}$ in run 23T to a deviation in nominal temperature at the limit of our stated ±15°C uncertainty, coupled with a temperature gradient along the length of the capsule. Comparison of the composition of glass in 23T with glasses from our other experiments (Fig. 4) shows that it is consistent with being just at $\text{cpx-out}$, and examination of compositional trends in 23T and the other experimental glasses with temperature (not shown) suggests that the temperature of run 23T was ~1310°C.

Figure 4 shows the concentrations of selected oxides in glasses from our experiments as functions of MgO content. At constant pressure, the MgO content of peridotite partial melts is positively correlated with temperature (e.g. Hirose & Kushiro, 1993; Baker & Stolper, 1994; Walter, 1998; Falloon et al., 1999), but our trends in glass composition are smoother when plotted against MgO content rather than temperature, presumably reflecting uncertainties in temperature in our experiments. Glass compositions from 1270 to 1390°C vary from basaltic (~11–12 wt % MgO) at the low end of the temperature range to picritic (~17 wt % MgO) at the high end. Over this range of MgO contents, SiO$_2$, Cr$_2$O$_3$, and FeO$^*$ concentrations increase with increasing MgO, whereas TiO$_2$, Al$_2$O$_3$, and Na$_2$O abundances all decrease with increasing MgO. CaO contents display a more complex pattern, first increasing with increasing MgO content until $\text{cpx-out}$, after which the CaO content of melt decreases with increasing MgO content (and temperature). Except for SiO$_2$ and TiO$_2$, the trends displayed by the glasses are qualitatively similar to those observed in near-solidus melting experiments on fertile mantle compositions at 10 kbar (e.g. Hirose & Kushiro, 1993; Baker & Stolper, 1994; Baker et al., 1995; Kushiro, 1996; Hirschmann et al., 1998a). We will return to a more detailed comparison of 10 kbar depleted and fertile peridotite melting trends in the discussion section below.

**Solid phase compositions**

**Olivine**

The $mg$-number [defined as 100 MgO/(MgO + FeO$^*$), molar] of ol in our experiments increases from ~89-8 at 1270–1275°C to 90-8 at 1390°C. $K_{\text{D,Fe-Mg}}$ values [$K_{\text{D,Fe-Mg}} = (\text{FeO}^\text{OL}/\text{FeO}^\text{LIQ})/(\text{MgO}^\text{OL}/\text{MgO}^\text{LIQ})$, where liq indicates liquid] are between ~0-28 and ~0-36, with most values between 0-30 and 0-34. For comparison with our experimental results, we have compiled mineral and glass compositions from 142 experiments conducted at 9–12 kbar and 1200–1400°C that contain the residual solid phases $\text{ol} + \text{cpx} \pm \text{sp} \pm$ plagioclase (Takahashi & Kushiro, 1983; Falloon & Green, 1987; Kinzler & Grove, 1992a; Hirose & Kushiro, 1993; Baker & Stolper, 1994; Kushiro, 1996; Gaetani & Grove, 1998; Hirschmann et al., 1998a; Wagner & Grove, 1998; Draper & Green, 1999; Falloon et al., 1999, 2001; Pickering-Witter & Johnston, 2000; Schwab & Johnston, 2001; M. B. Baker, unpublished data, 1996).
Fig. 6. Wt % Na$_2$O + K$_2$O in glasses coexisting with opx vs opx–liq $K_{D_{opx-liq}}$ values from DMM1 experiments. Symbols as in Fig. 5, except for: small filled dark gray circles are K$_2$O values from 9 to 12 kbar experiments where opx coexists with ol + opx + sp + plagioclase (1225–1400°C); small filled light gray circles with black rims represent K$_2$O values from opx coexisting with ol ± sp (1250–1400°C). Data sources listed in the caption to Fig. 5.

Orthopyroxene

With rising temperature, opx mg-numbers increase from 90–90.5 near the solidus (1270–1275°C) to ~91.5 at 1370–1390°C. Over this temperature range, $K_{D_{opx-Mg}}$ values increase with temperature from ~0.29 to ~0.32 and are also inversely correlated with Na$_2$O + K$_2$O in the coexisting glasses. Figure 6 shows that our $K_{D_{opx-Mg}}$ vs glass alkali trend is consistent with a large body of experimental data. $D_{Ca}^{opx/liq}$ values (CaO$_{opx}$/CaO$_{liq}$, both in wt %) from our experiments are consistent with values from other high-pressure experiments containing opx + ol ± opx-saturated liquids, $D_{Ca}^{opx/liq}$ from our opx-free runs show a slight decrease with rising temperature, but the mean values from the lherzolite- and harzburgite-saturated experiments are identical at 0.16 ± 0.02 (1σ). These means also overlap with the mean $D_{Al}^{opx/liq}$ values for opx-bearing and opx-free experiments from the literature (0.20 ± 0.04 and 0.16 ± 0.05, 1σ, respectively).

The opx–liq partition coefficient for Al$_2$O$_3$, $D_{Al}^{opx/liq}$, shows a weak negative correlation with temperature in our experiments, decreasing from 0.22–0.28 at 1270–1275°C to 0.15–0.23 at 1370–1390°C; the mean values from the opx-bearing and opx-free experiments overlap at the 1σ level (0.24 ± 0.06 and 0.20 ± 0.03). $D_{Al}^{opx/liq}$ values from the literature show considerable scatter, with ranges of 0.14–0.51 (opx-bearing) and 0.10–0.56 (opx-free). The mean $D_{Al}^{opx/liq}$ values for the two sets of literature data (0.30 ± 0.09 and 0.25 ± 0.07, 1σ) overlap with our lherzolite- and harzburgite-saturated experimental $D_{Al}^{opx/liq}$ values at the 1σ level.

The opx–liq partition coefficients for Na$_2$O, $D_{Na}^{opx/liq}$, from our experiments are positively correlated with temperature: ranges of $D_{Na}^{opx/liq}$ values are 0.02–0.04 (0.028 ± 0.008, 1σ) for opx-bearing assemblages and 0.03–0.07 (0.041 ± 0.012, 1σ) for opx-free assemblages. However, the uncertainty on individual determinations is large (25–50%) because of the low concentration of Na$_2$O in the orthopyroxenes (0.02–0.05 wt %; Table 3). The mean $D_{Na}^{opx/liq}$ value for all 9–12 kbar experiments compiled from the literature is 0.04 ± 0.01 (1σ), which overlaps with the mean values from our experiments (the literature mean includes all experiments containing glasses in the same range of Na$_2$O contents as our experiments, regardless of whether they contain opx). The literature data also suggest a positive correlation with temperature, although again uncertainties on individual determination are large because of the low Na$_2$O contents of the opx.

$D_{Ti}^{opx/liq}$ values in our experiments are 0.03–0.20 (0.11 ± 0.05, 1σ) for opx-bearing experiments and 0.07–0.18 (0.12 ± 0.04, 1σ) for opx-free experiments and do not correlate with temperature. Again, individual $D_{Ti}^{opx/liq}$ values have large uncertainties (25–100%), as a result of the low concentrations of TiO$_2$ in the orthopyroxenes (0.01–0.08 wt %). Mean literature values from lherzolite- and harzburgite-saturated experiments are 0.20 ± 0.07 and 0.15 ± 0.08 (both 1σ) and overlap with our results.

Clinopyroxene

$K_{D_{Fe-Mg}}$ values in our experiments are 0.29–0.36 with a mean of 0.32 ± 0.02 (1σ). Figure 7a shows that these $K_{D_{Fe-Mg}}$ values are consistent with those from the literature and both sets of data display a weak inverse correlation with alkalis in the coexisting glass. Figure 7b compares $D_{Ca}^{opx/liq}$ values from our experiments and from opx–liq pairs saturated with opx from the literature with the weight percent sum of Na$_2$O and K$_2$O in the coexisting glasses. $D_{Ca}^{opx/liq}$ values from the DMM1 opx–liq pairs are consistent with the literature values; the positive correlation between $D_{Ca}^{opx/liq}$ and Na$_2$O + K$_2$O reflects the effect of alkalis on the activity coefficient of calcium complexes in the melt (e.g. CaSiO$_3$; Hirschmann et al., 1999a).

$D_{Al}^{opx/liq}$ values from our experiments increase from ~0.28 at 1270°C to ~0.34 at 1300°C and fall in the field of literature values. Mean $D_{Al}^{opx/liq}$ calculated for our data and for the compilation of literature data overlap at the 1σ level (0.32 ± 0.03 for our DMM1 results vs 0.36 ± 0.08 for opx–liq pairs from other peridotite melting experiments). $D_{Na}^{opx/liq}$ values from our experiments and for the compilation of literature data
have identical means (0.16 ± 0.04, 1σ). $D_{\text{Na}}^{\text{cpx-liq}}$ values do not correlate with temperature in either dataset. $D_{\text{Ti}}^{\text{cpx-liq}}$ values for the DMM1 experiments have large uncertainties (~25–75%), reflecting the low concentrations of titanium in the clinopyroxenes. The mean $D_{\text{Ti}}^{\text{cpx-liq}}$ value for our data is 0.22 ± 0.05 (1σ). This is lower than the mean of the literature values (0.38 ± 0.13, 1σ), although there is considerable overlap between the two datasets. As discussed by Hirschmann et al. (1999a), at constant pressure $D_{\text{Ti}}^{\text{cpx-liq}}$ is positively correlated with the SiO$_2$ content of melt and negatively correlated with alkali content. The offset in $D_{\text{Ti}}^{\text{cpx-liq}}$ between the two sets of data thus plausibly reflects the generally lower SiO$_2$ and Na$_2$O + K$_2$O contents of the DMM1 glasses relative to the glasses in the 9–12 kbar literature compilation (47.8–48.9 vs 46.9–55.5 wt % SiO$_2$ and 0.8–2.1 vs 0.8–7.8 wt % Na$_2$O + K$_2$O, respectively).

**Spinel**

Although the spinel mg-number is a complex function of a number of variables, the most important are the mg-numbers of the coexisting phases, the partitioning of Al and Cr between $sp$ and these phases, and the $f_{\text{O}_2}$.
Algorithm that incorporates uncertainties in both the bulk composition and the compositions of the coexisting phases (Albarède & Provost, 1977). Liquid fractions increase from ~0.02–0.04 at 1270–1275°C to ~0.17 at 1390°C (Fig. 9). A weighted linear fit of melt fraction (F) vs temperature (T), using errors on both F (Table 2) and T (±15°C; Reed, 1992), of the spinel lherzolite-saturated glasses yields a solidus temperature of 1272 ± 11°C (1σ), within our experimental bracket of 1250–1270°C (because of its uncertain temperature, run 23T was not included in the fit). Weight fractions of ol and opx change from ~0.64 and ~0.27 at 1270°C to 0.69 and ~0.19 at 1390°C. Weight fractions of cpx and opx decrease from ~0.06 and 0.005 at the solidus to 0 at 1300–1310°C.

Figure 10 shows the fractions of residual solid phases plotted against melt fraction. The lines are weighted least-squares fits to the data using errors on both T and F. Equations for DMM1: 
\[ T°C = F \text{ (spinel lherzolite field); } -1.05(19) + 0.00086(14) F°C = F \text{ (harzburgite field).} \]
Equations for MM3: 
\[ -2.58(23) + 0.0021(2) F°C = F \text{ (spinel lherzolite field); } -1.44(7) + 0.0002(1) F°C = F \text{ (spinel harzburgite field).} \]
Values in parentheses are standard deviations on the y-intercepts and slopes, respectively, in terms of the least units cited.

These coefficients are compared with those based on 10 kbar data on the melting of spinel lherzolite assemblages in the literature in Table 4. The reaction relationship between ol and liquid indicated by our data for DMM1 is a robust result from all studies of spinel lherzolites. As noted by Kinzler & Grove (1992a), Baker & Stolper (1994), and Pickering-Witter & Johnston (2000), cpx reaction coefficients show little variation over a wide range of multi-component spinel lherzolite compositions (the total range is 0.72–0.82) and dominate each melting assemblage. However, as illustrated by Table 4, the values of the reaction coefficients for ol and opx are

\[
0.56(10) ol + 0.72(4) cpx + 0.04(1) sp = 0.34(10) ol + 11ig.
\]
variable (0.10–0.38 and 0.27–0.56, respectively). There is a crude inverse correlation between the mean alkali content in the glasses used in the fits for each bulk composition’s reaction coefficients and the opx and ol melting coefficients.

At temperatures above opx + sp-out, the reaction for melting of DMM1 is based on the best-fit lines in Fig. 10 and is

\[ 1.24(14) \text{ opx} = 0.24(13) \text{ ol} + 1 \text{ liq} \]

Harzburgite ± spinel melting reaction coefficients at 10 kbar for other bulk compositions are listed for comparison in Table 4. Although all the melting reactions listed in Table 4 above opx-out have olivine in reaction relation, the reaction coefficients for all three solid phases (0.88–1.3 for opx; 0.1–0.46 for ol; 0.04–0.24 for sp) are highly variable; again, there is a crude inverse correlation between alkali content in the glasses and the opx and ol melting reaction coefficients.

Isobaric melt productivity, \( \langle \partial F/\partial T \rangle_p \), is an important term in the equation describing melt production during adiabatic mantle upwelling (e.g. Asimow et al., 1997). By analogy with simple systems and based on MELTS (Ghiorso & Sack, 1995) calculations on peridotite compositions (including DMM1 and MM3), we expect a steady increase in \( \langle \partial F/\partial T \rangle_p \) up to opx-out (Hirschmann et al., 1999b). At opx-out, a discontinuous drop in productivity is expected, and the \( T \) vs \( F \) trend is expected to remain concave-up with further rises in temperature (Asimow et al., 1997; Hirschmann et al., 1999b). To determine average values for \( \langle \partial F/\partial T \rangle_p \) for ol + opx + cpx + sp-saturated and ol + opx-saturated melting of the DMM1 composition, we fitted our \( T(\text{°C}) \) vs \( F \) data (Table 2 and Fig. 9; excluding run 23T) to straight lines below and above opx-out. The best-fit average melt productivities are 0.3±0.2%/°C (1σ) for opx-saturated melting and 0.08±0.01%/°C (1σ) above opx-out. For comparison, the fertile MM3 peridotite composition has best-fit productivities of
melting. have been observed experimentally for lherzolite indeed increase with rising temperature in the spinel Johnston, 2001) suggest that melt productivities do (Pickering-Witter & Johnston, 2000; Schwab & experiments on the FER-E and INT-E compositions (1998) also yield nearly constant melt productivities systems and MELTS calculations (Asimow concave-upward curve (Fig. 9 inset) and the 15 kbar data in the spinel lherzolite field cannot be fitted with a peridotite melting experiments of Robinson concen-

The effects of peridotite composition on 10 kbar near-solidus partial melts Partial melts generated from depleted peridotite differ in several important ways from partial melts of fertile peridotite. Figure 11 illustrates some of these differences by comparing liquid compositions from this study as functions of melt fraction with trends of 10 kbar partial melt compositions from experiments on fertile peridotites. We have included the glass data of MM3 (Baker & Stolper, 1994; Baker et al., 1995; Hirschmann et al., 1998a; M. B. Baker, unpublished data, 1996), KLB-1 (Hirose & Kushiro, 1993), PHN1611 (Kushiro, 1996), and FER-E (Pickering-Witter & Johnston, 2000).

At melt fractions of 0.1–0.2, SiO₂ contents of the DMM1 experimental glasses overlap those of experimental glasses from the fertile peridotite compositions (Fig. 11a). At lower melt fractions, however, partial melts of all the fertile peridotites display increases in their silica contents, whereas the silica contents of the DMM1 partial melts continue to decrease with decreasing F. This difference in the behavior of SiO₂ in near-solidus melts of fertile and depleted peridotite reflects the effects of alkalis on the liquid silica activity coefficient [at 1 atm, these effects have been discussed by Kushiro (1975) and Ryerson (1985)]. As emphasized by Hirschmann et al. (1998a), the silica activity of opx + ol-saturated liquids varies little with melt fraction, but the activity coefficient of silica in the liquids decreases significantly with increasing alkali content. Consequently, as Na₂O + K₂O concentrations of liquids increase to high levels with decreasing F in melting experiments on fertile lherzolites, the SiO₂ concentrations likewise increase. However, the alkali contents of glasses in the DMM1 experiments are low relative to partial melts of more fertile peridotite, and the effects of increasing alkali contents on the SiO₂ contents of partial melts would only be expected to be expressed at very low melt fractions. For example, Fig. 11e shows that at F ~ 0.02, the Na₂O concentration in the DMM1 melt is only ~2 wt %, much lower than partial melts of more fertile peridotites such as MM3, where at F ~ 0.02 the Na₂O contents can reach concentrations >7 wt %. It should be noted also that the SiO₂ contents of the partial melts of the fertile peridotites begin to increase only when Na₂O contents reach ~3 wt %. Thus the lack of increasing SiO₂ contents in the DMM1 glasses at melt fractions down to ~0.02 (where Na₂O content is only ~2 wt %) is consistent with the results from fertile peridotites. MELTS calculations predict that for the DMM1 composition alkali contents build up sufficiently to cause increases in silica contents only at melt fractions lower than ~1 wt % (Hirschmann et al., 1998b).

Although we have emphasized the role of Na₂O, which is the most abundant alkaline component, concentrations of K₂O in the melts of fertile peridotite are also important: at F ~ 0.02, the 10 kbar partial melt of MM3 contains ~0.43 wt % K₂O (Hirschmann et al., 1998a); at F ~ 0.04, the 10 kbar partial melt of PHN1611 contains 3.2 wt % K₂O (Kushiro, 1996). Overall, such high values of Na₂O + K₂O can lead to significant changes in melt chemistry in addition to increasing SiO₂ contents (Fig. 11a), such as less incompatible behavior of Ti and other highly charged incompatible trace elements (e.g. U⁴⁺, Th⁴⁺, Ta⁵⁺, Hf⁴⁺) in cpx and decreasing ol–liq, opx–liq, and cpx–liq K_D-Fe-Mg values (e.g. Baker et al., 1995; Hirschmann et al., 1998a, 1999a; see Figs 5, 6, and 7). The deviation in the F vs FeO⁸⁰ trend of DMM1 partial melts relative to the trends of melts of fertile peridotites at low F (Fig. 11c) also reflects the low alkali contents in the near-solidus melts of DMM1 relative to those of fertile peridotites. At constant melt fraction a decrease in the alkali content in an ol + opx-saturated liquid decreases the stability of ol (the most Fe-rich silicate phase) relative to opx.
(Kushiro, 1975), which in turn increases the FeO* content in the melt.

Alumina contents of partial melts from the five peridotite compositions plotted in Fig. 11b decrease with increasing melt fraction, but partial melts of DMM1 contain ~2–4 wt % less Al2O3 than melts from the more fertile bulk compositions, with the deviation increasing slightly with increasing F. The lower Al2O3 contents in the partial melts of DMM1 compared with those of the fertile peridotites at all melt fractions probably reflect several different factors, including the 18–80% lower alumina content of DMM1 relative to the fertile peridotites and the effect of alkali content on the activity coefficient of Al2O3 in peridotite melts (Hirschmann et al., 1999a).

For DMM1, CaO contents in cpx-saturated liquids increase from ~13 to nearly 14 wt % with increasing melt fraction and then decrease with increasing F beyond the exhaustion of cpx (Fig. 11d). In contrast, the CaO contents of cpx-saturated partial melts of the fertile peridotites increase by up to a factor of two with increasing melt fraction from F ~ 0.02 up to the point of cpx exhaustion, after which the CaO contents of the partial melts decrease rapidly with further melting. For
DMM1 and the fertile peridotites, the maximum CaO contents occur at different melt fractions (0.09–0.10 for DMM1, 0.10–0.30 for the fertile peridotites); this is because the maximum CaO content occurs at the exhaustion of cpx from the solid residue, which occurs at different values of F for peridotites with different initial cpx contents. An important result is that the maximum CaO contents in the DMM1 partial melts are 1–2.5 wt % higher than the maximum values of melts from the more fertile compositions even though the DMM1 bulk composition has ~1–3 wt % less CaO than the more fertile mantle compositions. The elevated CaO contents of melts of the depleted DMM1 composition relative to partial melts of the fertile compositions are even more dramatic at low F; for example, at F ~0.02, partial melts of DMM1 contain ~13 wt % CaO compared with ~6.5 wt % for partial melts of MM3. The explanation for this significant difference again lies in the much higher alkali contents of near-solidus melts of fertile peridotite relative to melts of DMM1 (Hirschmann et al., 1999a). The alkali-rich partial melts of the fertile peridotites have higher CaO activity coefficients relative to alkali-poor melts of depleted lherzolite. The higher CaO activity coefficients in turn result in lower concentrations of CaO in alkali-rich, cpx-saturated liquids compared with alkali-poor, cpx-saturated liquids, as the activity of CaO is roughly fixed in lherzolite-saturated melts (Hirschmann et al., 1999a). It should be noted that the difference in CaO contents of cpx-saturated melts of fertile and depleted peridotites, first discussed quantitatively by Hirschmann et al. (1999a), is somewhat unintuitive. The fertile peridotites, although richer in CaO, generate partial melts that are poorer in CaO, and experimental confirmation of this phenomenon is an important result of this study.

CaO/Al2O3 ratios in partial melts of DMM1 and four fertile peridotite compositions are plotted in Fig. 11f. These ratios lie in a narrow band for the melts of fertile peridotite, increasing from ~0.4 to 0.7 as F increases from 0.02 to 0.15. This simple trend has led to the use of CaO/Al2O3 in primitive MORBs as a proxy for the extent of melting (e.g. Niu & Batiza, 1991; Niu & Hékinian, 1997). However, for melts of depletions peridotites, the CaO/Al2O3 ratios of low-degree partial melts of DMM1 are as high as those of high-degree melts of fertile peridotite and increase slowly with increasing F (Fig. 11f; Hirschmann et al., 1999a). The high CaO/Al2O3 ratios and their small range in the DMM1 melts reflect primarily the low degree of variation in CaO contents before cpx exhaustion compared with CaO in partial melts of fertile peridotite; above cpx-out, CaO and Al2O3 trends generally have similar slopes and thus less variation in CaO/Al2O3 ratios (Fig. 11b and d). The key point of

Comparison of experiments and mantle melting models

A wide range of models have been developed for calculating the compositions of partial melts of peridotite under upper-mantle conditions (e.g. McKenzie & Bickle, 1988; Niu & Batiza, 1991; Kinzler & Grove, 1992a, 1992b; Langmuir et al., 1992; Ghiorso & Sack, 1995; Kinzler, 1997; Ghiorso et al., 2002; Longhi, 2002). Most high-pressure experiments that have been available to calibrate these models have come from melting of fertile peridotites and pyroxene-enriched compositions, so the degree to which they can model the melting behavior of more depleted compositions is uncertain. Yet, as emphasized in the Introduction, current thinking about the dynamics of partial melting processes suggests that melt extraction occurs throughout the melting process, producing variously depletions peridotite compositions in much of the MORB source region. Therefore accurate modeling of MORB generation must handle well the melting behavior of depleted peridotitic compositions. Our experimental results provide an opportunity to evaluate the performance of these models on a depleted peridotite composition far removed from the data used to calibrate them.

Figure 12 shows melt fractions vs major element concentrations for the experimental glasses presented in this paper and compares them with the results of calculations on the DMM1 bulk composition using four of the available models of peridotite melting. Calculations are shown for the thermodynamically based MELTS (Ghiorso & Sack, 1995) and pMELTS (Ghiorso et al., 2002) algorithms; pMELTS is a better calibrated version of the MELTS model, based on a much larger high-pressure experimental dataset for calculating crystal–liquid equilibria in silicate systems by thermodynamic potential minimization. pMELTS also incorporates a revised thermodynamic model and equation of state for the silicate melt. Also shown in Fig. 12 are liquids calculated using BATCH (Longhi, 2002), based on parameterizations of multiply saturated phase boundaries and mineral–melt distribution coefficients, and the expressions of Langmuir et al. (1992), based on selected mineral–melt distribution coefficients parameterized using T, pressure (P), and liquid compositions. It should be noted that the expressions of Langmuir et al. (1992) cannot calculate liquid SiO2, Al2O3, or CaO contents.

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The four models shown in Fig. 12 were chosen because they could handle the DMM1 composition with either little [the expressions of Langmuir et al. (1992)] or no modification (MELTS, pMELTS, BATCH). Although we show the MELTS trends in Fig. 12 for completeness, we concentrate on the comparison between the calculated pMELTS liquids and DMM1 glass compositions because the MELTS–DMM1 comparison was discussed by Hirschmann et al. (1998b). The calculations for the Langmuir et al. model were performed using a spreadsheet provided by C. H. Langmuir (personal communication, 1998). In using this spreadsheet, we adjusted the variable that controls the relationship between temperature and melt fraction so as to match the experimental solidus temperature of DMM1. We also entered the modal abundance of cpx for DMM1 at its solidus (from the intercept at \( F = 0 \) of the linear fit to cpx abundance shown in Fig. 10) and changed the cpx melting reaction coefficient in the spreadsheet so as

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**Fig. 12.** Comparison of experimental glass compositions (● and ○, this study) as functions of melt fraction from melting experiments on DMM1 with partial melts calculated for the DMM1 bulk composition using several different melting models: pMELTS (Ghiorso et al., 2002; continuous curve); MELTS (Ghiorso & Sack, 1995; long-dash curve); BATCH (Longhi, 2002; dot–dash curve); and the expressions of Langmuir et al. (1992; short-dash curve). All calculations are for 10 kbar. In the pMELTS and MELTS calculations, \( f_{O_2} \) was set at QFM – 2; calculations were also carried out at QFM, but those at QFM – 2 more closely match the \( F \) vs FeO* and \( F \) vs MgO trends of the experimental glasses. ●, glasses coexisting with ol + cpx + cpx + sp; ○, glasses coexisting with only ol + cpx. Oxide error bars as in Fig. 4. Melt fraction values and uncertainties for the experimental glasses are from mass balance calculations (see Table 2); for the calculated melting paths, the melt fractions are those output by each program. A short, thick, vertical line on the calculated trends denotes cpx-out (not shown in all panels). The Langmuir et al. (1992) expressions do not calculate SiO₂, Al₂O₃, or CaO liquid contents. Melt fraction vs (a) SiO₂, (b) Al₂O₃, (c) FeO*, (c) MgO, (e) CaO, all in wt %.
For SiO$_2$ (Fig. 12a) above $cpx$-out, the liquids calculated with pMELTS match the glasses produced by melting DMM1. Although those liquids calculated with BATCH have the correct slope, they are on average $\sim$1 wt % too low. Below $cpx$-out, both calculated trends have approximately constant liquid SiO$_2$ contents for $F \geq \sim$0-02, but the pMELTS-calculated liquids are on average $\sim$0-8 wt % too high in SiO$_2$, and the BATCH-calculated liquids are on average $\sim$0-3 wt % too low. The pMELTS trend shows a slight upturn in liquid SiO$_2$ content at the lowest calculated melt fractions; as described above, this effect reflects the elevation in alkalis at very low melt fractions. It should be noted that the pMELTS-calculated occurrence of $cpx$-out at $F \sim 0-09$ corresponds well to the occurrence of $cpx$-out in our experiments ($F \sim 0-09$–0-10), indicating that pMELTS is successful at reproducing a key aspect of the melting behavior. For BATCH, $cpx$-out occurs at $F \sim 0-08$. MELTS-calculated liquids are displaced to significantly lower silica contents than the experimental data; this inaccuracy in MELTS is well known and reflects the oversaturation of $cpx$ and undersaturation of ol in the MELTS model (Hirschmann et al., 1998b; Ghiorso et al., 2002).

Al$_2$O$_3$ contents of partial melts of DMM1 calculated using MELTS, pMELTS, and BATCH are all displaced downwards, but are parallel to the experimental data (Fig. 12b). Mean absolute deviations between the calculated liquid compositions and the liquid compositions calculated using pMELTS and BATCH are 1.37 and 1.16 wt % Al$_2$O$_3$, respectively. For pMELTS, the main cause of this systematic deviation is the 3-5–4-5 times higher $sp$ contents in the calculated near-solidus residues compared with the experimental modes, and the fact that above $cpx$-out, $sp$ is still a residual phase in the pMELTS calculations over the range of F values plotted in Fig. 12 (recalling that $sp$- and $cpx$-out occur over the same melting interval in our experiments). The systematic deviations in liquid Al$_2$O$_3$ contents in the BATCH calculations reflect (at the same melt fractions) the higher Al$_2$O$_3$ contents in the calculated $cpx$ and $cpx$ compared with the Al$_2$O$_3$ contents in our experimental pyroxenes. Although $F$ vs liquid Al$_2$O$_3$ contents from both models show systematic deviations from the experimental data, both models predict the approximately linear decrease in liquid Al$_2$O$_3$ content with increasing melt fraction (Fig. 12b).

At the same melt fraction, FeO$^*$ and MgO contents of DMM1 partial melts calculated using pMELTS and BATCH are similar, but their $F$ vs FeO$^*$ and MgO trends plot above, but parallel to, the experimental glass compositions (Fig. 12c and d). The mean absolute deviations are 0-67 wt % FeO$^*$ and 1-65 wt % MgO for the pMELTS-calculated trends and 0-76 wt % FeO$^*$ and 1-55 wt % MgO for the BATCH-calculated trends. Both models reproduce the slope changes in $F$ vs FeO$^*$ and MgO at $cpx$-out. The Langmuir et al. model predicts liquids with lower FeO$^*$ and similar MgO contents to the experimental glasses. The mean absolute deviations in FeO$^*$ and MgO are 0-52 and 0-55 wt %, respectively. In contrast to the pMELTS and BATCH calculations, the $F$ vs FeO$^*$ and MgO trends of these Langmuir et al. calculations show only a subtle change in slope near $cpx$-out; the near linearity of the Langmuir et al. FeO$^*$ and MgO trends reflects the model constraint that the Mg/Fe ratio of residual olivine and the Mg/Fe ratio of the bulk residue are equal. The offsets between the MELTS trends and the experimental data in the $F$–MgO and $F$–FeO$^*$ space are, as for SiO$_2$, the result of overstabilization of $cpx$ and understabilization of ol in the MELTS model (Hirschmann et al., 1998b).

Figure 12e shows that the liquid compositions calculated with pMELTS, BATCH, and MELTS all parallel the $F$–CaO trend of the experimental DMM1 glasses, with BATCH matching most closely (as noted above, the Langmuir et al. model does not provide liquid CaO contents). Mean absolute deviations for the pMELTS and BATCH trends are 1-05 and 0-58 wt % CaO, respectively. With increasing melt fraction from the solidus up to $cpx$-out, the calculated liquid CaO contents increase gradually, as do the CaO concentrations in the experimental glasses. Above $cpx$-out, the CaO contents of the experimental glasses and all the calculated liquid compositions decrease rapidly with increasing $F$. Although BATCH reproduces the $F$ vs CaO partial melting trend of DMM1, it is less successful in reproducing the low CaO contents in experimental glasses close to the fertile peridotite solidus; for example, using BATCH with MM3 as the starting composition, the calculated 10 kbar CaO content of the liquid at $F = 0-03$ is 2-3 wt % higher than the experimental glass (Baker & Stolper, 1994; Hirschmann et al., 1998b; M. B. Baker, unpublished data, 1996). In contrast, for the same conditions, the pMELTS-calculated liquid is only 0-5 wt % low in CaO relative to the experimental results.

Although DMM1 was not included in the calibrations of either pMELTS or BATCH, both of these programs reproduce the essential characteristics of the melt fraction vs major element trends observed in the experimental glasses. The successes of these calculations include their generally close matches to the absolute values of the major oxide concentrations, their successful predictions of the overall shapes of the observed trends, their predictions of the changes in slope in the $F$ vs SiO$_2$, FeO$^*$, MgO, and CaO trends that occur at or near $cpx$-out, and their predictions of
Variations in solidus temperature as a function of peridotite bulk composition

McKenzie & Bickle (1988), Langmuir et al. (1992), Iwamori et al. (1995), Herzberg et al. (2000), and Hirschmann (2000) have compiled and parameterized available data on the solidi of fertile peridotite compositions in pressure–temperature space. The parameterizations of these studies are broadly consistent, and the rise in solidus temperature ($T_s$) with increasing pressure from 1 bar to 100 kbar is reasonably well constrained. The relationship between $T_s$ and bulk composition at any given pressure, however, is less well quantified. Qualitatively, solidus temperature at constant pressure decreases in peridotites with increasing concentrations of incompatible elements (of which Na$_2$O, K$_2$O, and H$_2$O are likely to be the most important) and decreasing mg-number (Herzberg et al., 2000; Hirschmann, 2000). Deconvolving the influence of these two compositional effects is generally difficult, as those peridotites with high alkali contents also tend to have relatively low mg-numbers. Linear fits of bulk peridotite Na$_2$O + K$_2$O vs $T_s$ and peridotite mg-number vs $T_s$ by Herzberg et al. (2000) suggest that at 15 kbar, increasing the alkali content from 0-2 to 0-4 or decreasing the mg-number from 90 to 80 will produce a 30–35°C drop in $T_s$. However, mg-numbers and bulk alkali contents in the peridotite compositions fit by Herzberg et al. (2000) show an inverse correlation (correlation coefficient = 0-68), making it difficult to evaluate independently these two parameters.

Using an idealized ternary system as a framework for considering the effects of composition on solidus temperature, Hirschmann (2000) was able to model the negative correlation between solidus temperatures and incompatible element content (e.g. Na$_2$O + K$_2$O). His analysis, based on the cryoscopic expression (e.g. Carmichael et al., 1974, pp. 170–173), showed that the bulk partition coefficients and concentrations of incompatible elements at the peridotite solidus are important parameters influencing the solidus temperature. In particular, the more incompatible an element, the larger its effect on the solidus (assuming melting is a continuous reaction). He further showed that the conclusions drawn from the idealized ternary system could be applied to understanding variations in the solidus temperatures for MM3 (Baker & Stolper, 1994; Hirschmann et al., 1998a; M. B. Baker, unpublished data, 1996), FER-B, FER-D, and FER-E (Pickering-Witter & Johnston, 2000) at 10 kbar, and MPy and Tinaquillo lherzolite (Robinson et al., 1998) at 15 kbar.

We have extended the analysis of Hirschmann (2000) by considering eight peridotites for which the 10 kbar solidus has been determined and by including the effect of P$_2$O$_5$ in addition to Na$_2$O and K$_2$O. Because P$_2$O$_5$ contents in the bulk compositions of Pickering-Witter & Johnston (2000) and Schwab & Johnston (2001) are unknown, we have not included the solidus temperatures for these bulk compositions in our parameterization. The complete dataset includes DMM1 (this study), MM3 (Baker & Stolper, 1994; Hirschmann et al., 1998a; M. B. Baker, unpublished data, 1996), syn-MM3 (Falloon et al., 1999), KLB-1 and HK-66 (Takahashi & Kushiro, 1983; Hirose & Kushiro, 1993), HPy-40 (Jaques & Green, 1980), PHN1611 (Kushiro, 1996), and DW (Bertka & Holloway, 1994; this is a model Martian mantle composition). Bulk compositions are listed in Tables 1 and 5. These peridotites have solidus temperatures ranging from 1193 to 1272°C. Their concentrations of Na$_2$O, K$_2$O, and P$_2$O$_5$ are highly variable, ranging from 0-06 to 0-95, 0 to 0-22, and 0 to 0-16, and their mg-numbers range from 90-5 to 75-0. Experimentally determined solidus assemblages at 10 kbar include both spinel lherzolite and plagioclase + spinel lherzolite.

Most of these peridotites lack the necessary experimental data to estimate near-solidus liquid compositions. Thus, we have used pMELTS (Ghiorso et al., 2002) to calculate 10 kbar near-solidus liquid compositions for these eight peridotites. The Na$_2$O, K$_2$O, and P$_2$O$_5$ contents of the pMELTS-calculated liquids at 10 kbar, QFM, and $F = 0$-005 range from 2-8 to 11-6, 0 to 11-3, and 0 to 8-6 wt %, respectively, and all of the calculated melts coexist with ol, apx, cpx, and qz. At $F = 0$-005, alkali feldspar is predicted to be a stable phase in the three peridotite compositions with the highest bulk alkali contents (PHN1611, HK-66, and HPy-40; these peridotites have bulk Na$_2$O + K$_2$O contents of 0-47–1-17 wt %). pMELTS also predicts that whitlockite is stable at $F = 0$-005 in the five bulk compositions that have >0-017 wt % P$_2$O$_5$ (PHN1611, KLB-1, HPy-40, HK-66, and DW). It should be noted that, in this respect, results from pMELTS calculations differ from the expectations of the idealized ternary system analysis of Hirschmann (2000), in which it was assumed that the incompatible components never become a major structural constituent of a crystallizing phase and that the concentrations...
Table 5: Bulk compositions used in modeling the 10 kbar peridotite solidus

<table>
<thead>
<tr>
<th>Silica</th>
<th>TiO₂</th>
<th>Al₂O₃</th>
<th>Cr₂O₃</th>
<th>FeO*</th>
<th>MnO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>P₂O₅</th>
<th>NiO</th>
<th>mg-no.¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>MM3²</td>
<td>45.5</td>
<td>0.11</td>
<td>3.98</td>
<td>0.68</td>
<td>7.18</td>
<td>0.13</td>
<td>38.3</td>
<td>3.57</td>
<td>0.31</td>
<td>0.008</td>
<td>0.004</td>
<td>0.23</td>
</tr>
<tr>
<td>syn-MM3³</td>
<td>45.5</td>
<td>0.14</td>
<td>3.98</td>
<td>0.68</td>
<td>7.18</td>
<td>0.13</td>
<td>38.3</td>
<td>3.57</td>
<td>0.31</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>KLB-1⁴</td>
<td>44.48</td>
<td>0.16</td>
<td>4.69</td>
<td>0.31</td>
<td>8.10</td>
<td>0.12</td>
<td>39.22</td>
<td>3.44</td>
<td>0.30</td>
<td>0.02</td>
<td>0.03</td>
<td>0.25</td>
</tr>
<tr>
<td>HK-66⁵</td>
<td>48.02</td>
<td>0.22</td>
<td>4.88</td>
<td>0.25</td>
<td>9.90</td>
<td>0.14</td>
<td>32.36</td>
<td>2.97</td>
<td>0.66</td>
<td>0.07</td>
<td>0.07</td>
<td>0.162</td>
</tr>
<tr>
<td>HPy40⁶</td>
<td>47.9</td>
<td>1.18</td>
<td>5.91</td>
<td>0.72</td>
<td>8.81</td>
<td>0.13</td>
<td>28.8</td>
<td>5.14</td>
<td>0.95</td>
<td>0.22</td>
<td>0.06</td>
<td>0.13</td>
</tr>
<tr>
<td>PHN161¹⁷</td>
<td>43.7</td>
<td>0.25</td>
<td>2.75</td>
<td>0.28</td>
<td>10.65</td>
<td>0.13</td>
<td>37.22</td>
<td>3.26</td>
<td>0.33</td>
<td>0.14</td>
<td>0.018</td>
<td>0.25</td>
</tr>
<tr>
<td>DW⁷</td>
<td>44.4</td>
<td>0.14</td>
<td>3.02</td>
<td>0.75</td>
<td>17.9</td>
<td>0.46</td>
<td>30.2</td>
<td>2.45</td>
<td>0.6</td>
<td>0.16</td>
<td>0</td>
<td>75.05</td>
</tr>
</tbody>
</table>

¹mg-no. = 100MgO/(MgO + FeO⁶) on a molar basis with all Fe as FeO.

²MM3: Baker & Stolper (1994); bulk K₂O and P₂O₅ contents calculated from K₂O and P₂O₅ values in glasses from experiments on MM3 and mass balance constraints (Hirschmann et al., 1998; M. B. Baker, unpublished data, 1996), mineral-liquid K₂O partition coefficients of Halliday et al. (1995), and ol–liq, opx–liq, and cpx–liq P₂O₅ partition coefficient values of 0.1, 0.03, and 0.05, respectively (Libourel et al., 1994; Brunet & Chazot, 2001).

³Syn-MM3: target composition of Falloon et al. (1999); actual bulk composition not reported.

⁴KLB-1, HK-66: Hirose & Kushiro (1993); bulk NiO content of HK-66 calculated from NiO contents of olivine, spinel, orthopyroxene, and clinopyroxene and the proportions of these phases calculated by mass balance. NiO in orthopyroxene and clinopyroxene calculated using the reported olivine NiO concentration and mean opx–ol (0.26) and cpx–ol (0.13) NiO ratios in minerals from spinel lherzolites analyzed by Stosch (1981) and Hervig & Smith (1982).

⁵HPy40: Jaques & Green (1980).

⁶PHN161: Kushiro (1996); bulk NiO content from Morgan et al. (1989); bulk P₂O₅ content calculated from garnet P₂O₅ value (Smith et al., 1993), mineral–garnet (gt) P₂O₅ partition coefficients measured in garnet lherzolites (ol–gt, 0.33; opx–gt, 0.11; cpx–gt, 0.78; Bishop et al., 1978; Hervig & Smith, 1982), and the weight fractions of olivine, orthopyroxene, clinopyroxene, and garnet calculated by mass balance.


in near-solidus melts are controlled entirely by partitioning into the major peridotite phases.

Figure 13a shows that the experimentally determined solidus temperatures are well correlated with the concentrations of alkalis plus phosphorus in the calculated near-solidus melts. In addition to calculating liquid compositions at F = 0.005, we continued each pMELTS calculation down temperature and determined the model solidus for each peridotite (Tₛ,pMELTS). Figure 13b shows that the calculated Tₛ,pMELTS values are correlated with the experimentally determined solidus temperatures, although the model temperatures are lower than the experimental determinations by ~25–70°C (the deviations are crudely correlated with the sum of the bulk alkali and phosphorus contents). The differences in temperature between the experimental and model solidi may reflect in part the difficulties in observing minute amounts of melt in experimental charges (each experimentally determined solidus temperature may be systematically too high), but they also probably reflect inaccuracies in the thermodynamic models that underpin pMELTS. The important point is that experimentally determined solidus temperatures are correlated with solidus temperatures and compositions of low-degree melts predicted by pMELTS, allowing us to utilize the thermodynamically consistent results of pMELTS as guides to the major factors controlling solidus temperature.

We have fitted the data shown in Fig. 13a to an equation of the form $T_c(°C) = a_0 + a_1(Na_2O) + a_2(K_2O) + a_3(P_2O_5)$. The choice of this linear function is based on the simple case of solidus depression of a single phase by an incompatible element at infinite dilution (e.g. Hirschmann, 2000). That concept represents an oversimplification, and the presence of minor phases in the pMELTS calculations also complicates the application of this equation. The best fit ($a_0 = 1295.8$, $a_1 = -3.628$, $a_2 = -7.218$, $a_3 = -5.100$) reproduces the experimental solidus temperatures with a mean deviation of 3°C (less than half of the temperature uncertainty associated with any of the $T_c$ determinations; Fig. 14). The largest temperature mismatch is for HK-66 (12°C), but the calculated $T_c$ value is still within the experimental solidus bracket for this bulk composition (Fig. 14). Given the compositional complexities of natural peridotites, the simple functional form of the fit, and the difficulties in determining the solidus experimentally, the quality of the fit is actually somewhat surprising.

Although the peridotite bulk compositions span a range of mg-numbers (Tables 1 and 5), inclusion of an mg-number term in the equation does not improve the fit (i.e. the mean temperature deviation remains ~5°C). It should be noted, however, that the model Martian mantle composition, DW, is the peridotite composition with the lowest mg-number, but it also
has the highest P₂O₅ content and one of the highest Na₂O contents in our dataset. Thus, as stated above, mg-number and incompatible element concentrations tend to be correlated in peridotites, making it difficult to separate the effect of mg-number from those of alkalis. However, to evaluate the effect of mg-number on solidus temperature, we increased the mg-number of DMM1 (keeping the total number of moles of FeO and MgO constant) from 89-9 to 92 and used pMELTS to calculate the solidus temperature, which changed by only 2°C. This suggests that over the limited range of mg-numbers observed in the vast majority of spinel peridotite samples (∼88–92; Herzberg et al., 1988), mg-number will have no effect on Tₛ at 10 kbar.

In our parameterization, the coefficients for K₂O and P₂O₅ have similar absolute values that are larger than that for Na₂O. The larger effects on lowering of solidus temperature of the more incompatible components is precisely what was anticipated by Hirschmann (2000), suggesting that this simple fit has some validity as a predictive tool. Our expression for Tₛ suggests that the 10 kbar solidus temperature for an alkali- and phosphorus-free peridotite will be ~1296°C. This is broadly consistent with the 1287–1299°C range for the 10 kbar solidus temperatures for the model peridotite compositions DF80 and JDS (with mg-numbers of 89-6 and 90-0, respectively) of Gudfinnsson & Presnall (2000) in CMA SF based on mass balance constraints and their experimentally calibrated expressions for liquid and solid compositions in the plagioclase lherzolite field. Many abyssal peridotites have bulk compositions more strongly depleted in alkalis than DMM1 (Baker & Beckett, 1999; Fig. 1), and using our Tₛ expression and the abyssal peridotite compositions from Baker & Beckett (1999) that have the lowest and highest MgO contents, we predict that 10 kbar abyssal peridotite solidus temperatures would lie in the range of ~1278–1295°C.

**CONCLUSIONS**

(1) We conducted melting experiments on a depleted peridotite composition (DMM1) at 10 kbar using a modification of the diamond-aggregate melt-extraction technique in which diamonds were replaced by vitreous carbon spheres. Several approaches were used to demonstrate that melts segregated into plagioclase. The lowest temperature run of Kushiro (1996) also contains plagioclase. (b) Comparison of 10 kbar experimental solidus temperatures (Tₛ °C) and the pMELTS-calculated solidus temperatures (Tₛ_pMELTS °C) for the eight peridotites listed in Tables 1 and 4. The pMELTS calculations were performed at 10 kbar and QFM. The temperature step in the pMELTS calculations was 1°C and the plotted point is the temperature at which F = 0. The diagonal continuous line is a 1:1 line shown for comparison.
to those determined for ol + opx + cpx + sp-saturated melting of fertile peridotite and analog mantle compositions in the CaO + MgO + Al₂O₃ + SiO₂ + FeO system. In particular, cpx dominates the melting reaction over a wide range of peridotite compositions, and the cpx reaction coefficient is insensitive to the modal abundance of cpx in the lherzolite. Above cpx- and sp-out, DMM1 melts via the reaction 1-24 opx = 0-24 ol + liq, which is also qualitatively similar to harzburgite melting reactions previously determined for fertile peridotites.

(4) pMELTS (Ghiorso et al., 2002), BATCH (Longhi, 2002), and the expressions presented by Langmuir et al. (1992) were used to calculate partial melts of the DMM1 composition at 10 kbar. Although melts of depleted peridotites were not included in the calibrations of either pMELTS or BATCH, both of these programs reproduce the essential characteristics of the melt fraction vs major element trends observed in experiments on DMM1. The successes of these calculations include their generally close matches to the absolute values of the major oxide concentrations, their successful predictions of the overall shapes of the observed trends, their predictions of the changes in slope of the F vs SiO₂, FeO*, MgO, and CaO trends that occur at or near cpx-out, and their predictions of the melt fraction at which cpx-out occurs. Nevertheless, liquid compositions calculated by these models display systematic offsets relative to the experimental glass compositions. The Langmuir et al. expressions provide the best match to the F vs FeO* and MgO glass trends for DMM1, but cannot be used to model SiO₂, CaO, or Al₂O₃ contents of partial melts.

(5) Combining our experimentally determined solidus temperature with solidus temperatures determined on seven other peridotites, we parameterized Tₛ at 10 kbar as a function of the Na₂O, K₂O, and P₂O₅ contents in near-solidus liquids at F = 0.005 calculated with pMELTS. The resulting equation, \( Tₛ(°C) = 1295-8 - (3.628)Na₂O - (7.218)K₂O - (5.100)P₂O₅ \) (oxide quantities in wt %), recovers the input temperatures with a mean deviation of 3°C. This expression predicts that the 10 kbar solidi of abyssal peridotites are ~1278–1295°C and is consistent with the theoretical expectation that more incompatible elements have a larger influence on the solidus.

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PARTIAL MELTING OF DEPLETED PERIDOTITE


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