THE BEHAVIOR OF $\text{Fe}^{3+}/\Sigma\text{Fe}$ DURING PARTIAL MELTING OF SPINEL LHERZOLITE

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ABSTRACT

This study presents an internally consistent model for the behavior of $\text{Fe}^{3+}/\Sigma\text{Fe}$ during partial melting of spinel lherzolite. The $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio for olivine is calculated on the basis of point defect thermodynamics, and the oxidation states of iron in the other solid phases are calculated using $\text{Fe}^{3+}/\text{Fe}^{2+}$ distribution between olivine and orthopyroxene, clinopyroxene, or spinel. Conservation of mass is used to relate the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio of partial melt to the concentrations of Fe^{3+} and Fe^{2+} in the initial and residual solids as a function of pressure, temperature, and oxygen fugacity. Results from isobaric batch melting calculations demonstrate that the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio of the partial melt decreases with increasing melt fraction. Conversely, the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio of the partial melt *increases* with increasing melt fraction during decompression batch melting. The relative oxygen fugacity of the upper mantle depends on both the oxidation state of iron and mantle potential temperature. Results from incremental decompression melting calculations in which 1% melt is produced for each 100 MPa of decompression and then removed from the residue indicate that relative oxygen fugacity calculated from the oxidation state of iron in basaltic glass does not represent a unique value for the oceanic upper mantle but, rather, reflects conditions in the lower portion of the melting regime. A 100 °C change in mantle potential temperature produces a change in relative oxygen fugacity of ~ 0.8 log units, similar to the global range inferred from mid-ocean ridge basalt glasses. It is necessary, therefore, to compare relative oxygen fugacity calculated from basaltic glass with proxies for potential temperature before drawing conclusions on heterogeneity of the oxidation state of iron in the oceanic upper mantle. Results from model calculations also suggest that the sub-arc mantle is intrinsically more oxidizing than the oceanic mantle because it is cooler. The global correlation between $\text{Fe}^{3+}/\Sigma\text{Fe}$ and H_2O in basaltic glasses may, in part, reflect the solidus-lowering influence of the latter. Secular variations in relative oxygen fugacity of the upper mantle due to cooling of the Earth over geologic

time do not appear to be large enough to have influenced the nature of volcanic outgassing significantly enough to have contributed to the Great Oxidation Event.

1. INTRODUCTION

The fugacity of oxygen (f_{O_2}) is a measure of the potential for multivalent elements – such as iron, carbon, and sulfur – to gain or lose electrons through reaction with oxygen (*e.g.*, Frost, 1991). Knowledge of the equilibrium f_{O_2} of the oceanic upper mantle constrains the valence state of redox-sensitive elements and, thereby, their geochemical behavior. Given that there is no source of “free oxygen” in the oceanic upper mantle, the valence states of these elements are interrelated through heterogeneous equilibria involving the exchange of oxygen between coexisting phases. For example, as peridotite ascends along an adiabat, reduced carbon may react with oxidized iron to produce oxidized carbon and reduced iron (*e.g.*, Wood et al., 1990; Ballhaus and Frost, 1994; Stagno and Frost, 2010; Stagno et al., 2013). In this way, upper mantle f_{O_2} influences the speciation of C-O-H-S volatiles, the point defect chemistry of minerals, and the stability of metal (*e.g.*, Stocker and Smyth, 1978; Eggler and Baker, 1982; O'Neill and Wall, 1987; Luth, 1989; Hirsch and Shankland, 1993; Holloway and Blank, 1994; Ballhaus, 1995).

Iron is the highest concentration redox-sensitive element in basalts and peridotite, existing in both relatively oxidized (trivalent iron or Fe^{3+}) and reduced (divalent iron or Fe^{2+}) forms. Initial interest in the influence of f_{O_2} on magmatic systems arose from attempts to explain the differences between tholeiitic (iron-enrichment) and calc-alkaline (iron-depletion) differentiation trends (*e.g.*, Kennedy, 1948, 1955; Osborn, 1959). The first determination of equilibrium magmatic f_{O_2} came from a comparison of the oxidation state of iron in natural lavas with that in aliquots of the same lavas equilibrated in melting experiments conducted at controlled conditions (*e.g.*, Fudali, 1965).

The ratio of trivalent-to-total iron ($Fe^{3+}/\Sigma Fe$) can be determined in basaltic glass using either wet chemistry (Muan and Osborn, 1956; Wilson, 1960) or X-ray absorption near

edge structure (XANES) spectroscopy (Berry et al., 2003; Wilke et al., 2004; Cottrell et al., 2009), and then related to f_{O_2} as a function of temperature (T), pressure (P), and composition using equilibrium thermodynamics (e.g., Sack et al., 1980; Kilinc et al., 1983; Kress and Carmichael, 1991). This makes the $Fe^{3+}/\Sigma Fe$ ratio of basaltic glass the most commonly used proxy for f_{O_2} of the asthenospheric upper mantle (e.g., Christie et al., 1986; Bézous and Humler, 2005; Cottrell and Kelley, 2011; Cottrell and Kelley, 2013; Brounce et al., 2014).

Despite the widespread use of this proxy, relating the $Fe^{3+}/\Sigma Fe$ ratio of mid-ocean ridge basalt (MORB) directly to the relative f_{O_2} of the oceanic upper mantle is unlikely to be straightforward. It relies on the assumption that a set of conditions existed at which the two were in equilibrium, whereas there is abundant evidence to suggest that erupted MORB are an aggregation of melts formed over a broad range of conditions. First, primitive MORB are very rarely found to be in equilibrium with orthopyroxene (Opx) on their liquidus, and even when they are, the equilibration P does not correspond to the lithosphere-asthenosphere boundary (e.g., Stolper, 1980; Fujii and Bougault, 1983; Elthon and Scarfe, 1984). Second, the degree of trace element depletion observed in abyssal peridotites is too strong for them to be in equilibrium with MORB (e.g., Johnson et al., 1990; Dick and Natland, 1996). Third, U-series disequilibria measured in MORB are consistent with efficient melt segregation at low residual porosities (e.g., McKenzie, 2000; Sims et al., 2002). Therefore, adiabatic decompression partial melting of peridotite beneath oceanic spreading centers is generally viewed as a polybaric, near-fractional process and MORB are thought to represent an aggregation of melts formed over a broad range of conditions (e.g., Klein and Langmuir, 1987; Grove et al., 1992; Kinzler and Grove, 1992; Langmuir et al., 1992). Further complicating this picture are results from thermodynamic calculations indicating that, for garnet lherzolite with a constant $Fe^{3+}/\Sigma Fe$ ratio, f_{O_2} decreases systematically with depth relative to redox reactions commonly used as reference buffers – such as fayalite reacting with oxygen to produce magnetite and

quartz (the FMQ buffer) (e.g., Wood et al., 1990; Ballhaus and Frost, 1994; Ballhaus, 1995; Wood et al., 1996). This implies that simply calculating f_{O_2} conditions for the oceanic upper mantle on the basis of the $Fe^{3+}/\Sigma Fe$ ratios of MORB is unlikely to provide a meaningful answer without a quantitative understanding of the relationship between $Fe^{3+}/\Sigma Fe$ and relative f_{O_2} during decompression partial melting of peridotite.

Here I present an internally consistent model that describes the behavior of $Fe^{3+}/\Sigma Fe$ during adiabatic ascent and decompression partial melting of spinel lherzolite. Results from this model provide a framework within which the $Fe^{3+}/\Sigma Fe$ ratios of MORB glasses can be related to the f_{O_2} regime of the oceanic upper mantle.

2. METHODS

In this section I provide a brief description of how model calculations are carried out. A detailed description – including an example calculation – is provided in the Supplemental Material. First, a spinel lherzolite bulk composition and mode are specified; I have chosen the depleted mid-ocean ridge basalt (MORB) mantle (DMM) of Workman and Hart (2005). The molar $Mg/(Mg + \Sigma Fe)$ ratios ($Mg\#$) of Opx, clinopyroxene (Cpx), and spinel (Sp) are calculated from an initial guess for the $Mg\#$ of olivine (Ol) using inter-mineral Fe/Mg exchange coefficients ($K_D^{Fe/Mg} = (Fe/Mg)^{Cpx,Opx,orSp} / (Fe/Mg)^{Ol}$) of 0.97 for Cpx/Ol, 0.94 for Opx/Ol, and 1.5 for Sp/Ol taken from Kinzler (1997). The weight concentrations of total Fe as FeO (FeO^*) and MgO in each mineral are calculated using the expressions:

$$C_{FeO^*}^{Cpx,Opx,Ol,orSp} = 100 \times (1 - Mg\#^{Cpx,Opx,Ol,orSp}) \times \frac{j \times MW_{FeO}}{MW_{Cpx,Opx,Ol,orSp}} \quad (1)$$

$$C_{MgO}^{Cpx,Opx,Ol,orSp} = 100 \times (1 - Mg\#^{Cpx,Opx,Ol,orSp}) \times \frac{j \times MW_{MgO}}{MW_{Cpx,Opx,Ol,orSp}} \quad (2)$$

where j is the number of Fe or Mg cations in the mineral formula, and MW is molecular weight. The $Mg\#$ of the bulk peridotite is then calculated from mass balance and compared with the actual value; the correct $Mg\#$ for Ol – and, thereby, all of the other

minerals – is then determined using a Nelder-Mead unconstrained nonlinear optimization routine (Nelder and Mead, 1965; Lagarias et al., 1998) implemented with MATLAB.

The $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio for Ol is estimated on the basis of point defect thermodynamics. Point defects are an equilibrium feature of all crystals, and may take the form of an unoccupied lattice site (a vacancy), an ion in the normally unoccupied space between lattice sites (an interstitial), or a regular lattice site occupied by a foreign cation (a substitution). The concept of a vacancy can be extended to describe the oxidized form of a multivalent cation on a lattice site normally occupied by the reduced form (an electron hole). Reactions involving point defects are written using Kröger-Vink notation, in which individual defect types are represented by X_j^i where X is the species (cation, vacancy, or interstitial), j is the lattice site (octahedral, tetrahedral, or interstice), and i represents the effective charge – relative to a normally occupied lattice site – associated with the defect ($\cdot$ for 1+, $'$ for 1-, $*$ for neutral). For example, V_{Me}'' represents a vacant octahedral (“metal”) site with an effective charge of 2- and $\text{Fe}_{\text{Me}}^\bullet$ represents trivalent iron on an octahedral site with an effective charge of 1+.

Several different lines of experimental evidence indicate that V_{Me}'' and $\text{Fe}_{\text{Me}}^\bullet$ are the most abundant point defects in Fe^{2+} -Mg Ol (e.g., Nakamura and Schmalzried, 1983; Sato, 1986; Wanamaker and Duba, 1993; Barkmann and Cemič, 1996; Chakraborty, 1997; Tsai and Dieckmann, 2002). This is consistent with a charge neutrality condition for anhydrous Ol in which $[\text{Fe}_{\text{Me}}^\bullet] = 2[V_{\text{Me}}'']$. In formulating the model presented here, I make the simplifying assumption that Ol is a pure Fe^{2+} -Mg solid solution (i.e. there is no Fe^{3+} associated with aliovalent cations). This allows the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio for Ol to be calculated as a function of f_{O_2} , temperature (T), fayalite content (X_{Fa}), and the activity of SiO_2 (a_{SiO_2}) using the point-defect model of Dohmen and Chakraborty (2007). The concentration of $\text{Fe}_{\text{Me}}^\bullet$ defects in Ol coexisting with Opx is given by:

$$\log [\text{Fe}_{\text{Me}}^\bullet] = \frac{1}{6} \left(\log K_{x(5a)} + 2 \log 2 + 4 \log X_{\text{Fa}} + \log f_{\text{O}_2} + \log a_{\text{SiO}_2} \right) \quad (3)$$

132 where $a_{SiO_2} \sim 0.83$ and is only weakly dependent on T . I use $K_{x(5a)}$ calibrated from the
 133 thermogravimetric data of Nakamura and Schmalzried (1983):

$$134 \quad \log K_{x(5a)} = -7.32 - \frac{90000}{2.303RT} \quad (4)$$

135 where T is in Kelvin. Once $[Fe_{Me}^\bullet]$ is known, $Fe^{3+}/\Sigma Fe$ for olivine is calculated as
 136 follows:

$$137 \quad Fe^{3+}/\Sigma Fe = \frac{[Fe_{Me}^\bullet]}{(2/3)X_{Fa}}. \quad (5)$$

138 Once $Fe^{3+}/\Sigma Fe$ has been calculated for Ol from Equations 3-5, it is used to calculate
 139 $Fe^{3+}/\Sigma Fe$ for the other solid phases using the distribution of Fe^{3+}/Fe^{2+} between Ol and
 140 Opx, Cpx, and Sp using expressions of the form:

$$141 \quad \ln K_D^{Fe^{3+}/Fe^{2+}} = a + b\Delta FMQ + \frac{c}{T} + dX_{Fa}^{Ol} \quad (6)$$

142 where $K_D^{Fe^{3+}/Fe^{2+}} = (Fe^{3+}/Fe^{2+})_{Opx,Cpx,orSp} / (Fe^{3+}/Fe^{2+})^{Ol}$, ΔFMQ is f_{O_2} relative to the
 143 FMQ buffer as defined by Myers and Eugster (1983) in log units, and T is in K. Due to
 144 the lack of experimental data, these exchange coefficient expressions were calibrated
 145 using a compilation of Mössbauer data for fifty-one Sp lherzolites from the literature
 146 (Dyar et al., 1989; McGuire et al., 1991; Dyar et al., 1992; Canil et al., 1994; Woodland
 147 et al., 2006; Hao and Li, 2013). Equilibration temperatures of 779 to 1141 °C were
 148 calculated using the two-pyroxene thermometer of Brey and Köhler (1990), and ΔFMQ
 149 values of -4.7 to +1.2 were calculated using the Nell-Wood oxybarometer (Wood et al.,
 150 1990) assuming a pressure of 1.5 GPa (Table S1). Note that $Fe^{3+}/\Sigma Fe$ in Ol from the
 151 spinel lherzolite xenoliths is below detection limits of Mössbauer, so that the $(Fe^{3+}/Fe^{2+})^{Ol}$
 152 ratio in the denominator of each $K_D^{Fe^{3+}/Fe^{2+}}$ value used in the model calibration was
 153 calculated using the point defect model for Ol.

154 The concentrations of Fe^{3+} and Fe^{2+} in Ol, Opx, Cpx, and Sp are calculated for a
 155 given P , T , and an initial guess for the equilibrium ΔFMQ on the basis of FeO^*
 156 concentrations and $Fe^{3+}/\Sigma Fe$ ratios. If the peridotite is a closed system with respect to

oxygen, the $\text{Fe}_2\text{O}_3/\text{FeO}$ ratio of the partial melt is related to Fe_2O_3 and FeO concentrations in the bulk peridotite and residual mineral phases through conservation of mass:

$$\frac{C_{Melt}^{Fe_2O_3}}{C_{Melt}^{FeO}} = \frac{C_{Bulk}^{Fe_2O_3} - (1-F)(X_{Ol}C_{Ol}^{Fe_2O_3} + X_{Opx}C_{Opx}^{Fe_2O_3} + X_{Cpx}C_{Cpx}^{Fe_2O_3} + X_{Sp}C_{Sp}^{Fe_2O_3})}{C_{Bulk}^{FeO} - (1-F)(X_{Ol}C_{Ol}^{FeO} + X_{Opx}C_{Opx}^{FeO} + X_{Cpx}C_{Cpx}^{FeO} + X_{Sp}C_{Sp}^{FeO})} \quad (8)$$

where X_j is the mass fraction of each solid phase, and C_j^i is the weight concentration of i in j . Equation 7 of Kress and Carmichael (1991) is then used to calculate the equilibrium ΔFMQ corresponding to that partial melt. At equilibrium, the ΔFMQ value used to calculate $\text{Fe}^{3+}/\Sigma\text{Fe}$ of the residual solid must be the same as that predicted from $\text{Fe}^{3+}/\Sigma\text{Fe}$ of the partial melt. The correct $\text{Fe}^{3+}/\text{Fe}^{2+}$ distribution can, therefore, be determined by comparing these values using a Nelder-Mead unconstrained nonlinear optimization routine, as discussed above.

The major element composition of Sp lherzolite partial melt and residual peridotite are calculated using the method of Kinzler (1997). Because the expression used by Kinzler (1997) to predict T implies an enthalpy of melting that is unreasonably large, T was calculated using the nominally anhydrous lherzolite solidus of Hirschmann (2000), an enthalpy of melting of 754 J/g, a peridotite heat capacity of 1.26 J/g °C (Hess, 1992), and an adiabat of 0.3 °C/km (e.g., Turcotte and Schubert, 2002).

3. RESULTS

Results from modeling DMM with a bulk $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio of 0.06 are summarized in Fig. 1. Spinel is assumed to be stable along the lherzolite solidus from 0.8 to 2.8 GPa on the basis of results from phase equilibria experiments (Robinson and Wood, 1998; Borghini et al., 2009). The melting regime extends from the nominally anhydrous peridotite solidus of Hirschmann (2000) to conditions at which the P-dependent Sp lherzolite melting reaction of Kinzler (1997) indicates that Cpx is eliminated from the residual solid (Cpx out). Melt fraction isopleths are assumed to be evenly spaced such

that adiabatic decompression partial melting produces 1% partial melt for every 100 MPa of decompression. The grey curves in Fig. 2a are isopleths of constant ΔFMQ . Relative f_{O_2} decreases monotonically along the nominally anhydrous solidus, from 0.09 log units above FMQ at 0.8 GPa to 2.3 log units below FMQ at 2.8 GPa. Below the solidus, constant ΔFMQ isopleths are parallel to one another, with negative P-T slopes. Upon crossing the nominally anhydrous solidus, ΔFMQ isopleths are deflected and their curvature increases. Figure 2b shows isopleths of constant $\text{Fe}^{3+}/\Sigma\text{Fe}$ in Sp, which is an important proxy for f_{O_2} in mantle peridotite (e.g., Bryndzia and Wood, 1990; Wood et al., 1990; Canil et al., 1994). These isopleths are similar in shape to the ΔFMQ isopleths, suggesting that variations in relative f_{O_2} reflect the distribution of ferric iron among co-existing phases. Below the solidus, for example, isobaric heating causes the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio in Sp to decrease as ferric iron is redistributed into the silicates, producing a decrease in relative f_{O_2} . Above the solidus, partial melt becomes an important reservoir for ferric iron, but there remains a strong correspondence between ΔFMQ and $\text{Fe}^{3+}/\Sigma\text{Fe}$ in Sp isopleths.

Figure 2a shows ΔFMQ isopleths calculated on the basis of mineral compositions predicted by the model – with Sp hosting the total Cr_2O_3 budget of the peridotite – using the Nell-Wood oxybarometer (Wood et al., 1990). These calculations quantify relative f_{O_2} on the basis of the oxidation of fayalite to produce ferrosilite and magnetite according to the reaction:

(e.g., Wood and Virgo, 1989; Wood et al., 1990). ΔFMQ calculated from the oxybarometer are similar to those predicted by the model, confirming that changes in relative f_{O_2} predicted by the model are related to the distribution of ferric iron among the co-existing phases. Isopleths for two of the most important factors influencing ΔFMQ as calculated from the Nell-Wood oxybarometer – the activity of magnetite (Fe_3O_4) in Sp and the ferrosilite (Fe_2SiO_6) content of Opx – are shown in Fig. 2b. Below the solidus,

ferrosilite in Opx is nearly constant, varying only slightly in response to the changing pyroxene mode, so that P , T , and the magnetite activity in Sp are the major controls on ΔFMQ . Above the solidus, partial melting results in significant variations in both the ferrosilite content of Opx and the activity of magnetite in Sp, deflecting the ΔFMQ isopleths and increasing their curvature.

4. DISCUSSION

4.1 Batch Melting

Batch melting is an end-member case in which the bulk composition is constant and partial melt maintains equilibrium with the residual solid. As discussed in the Introduction, however, there are several lines of evidence to indicate that melt generation in the oceanic upper mantle is a dynamic process in which melt segregates efficiently from the solid, resulting in a continuously changing bulk composition. Here I use batch melting to provide first-order insights into the behavior of $Fe^{3+}/\Sigma Fe$ and relative f_{O_2} during spinel lherzolite partial melting. Incremental decompression partial melting is explored in Section 4.4.

Isobaric heating and batch partial melting of Sp lherzolite are represented by vertical blue lines at 1.5, 2.0, and 2.5 GPa in Fig. 3a. Increasing T results in a progressive decrease of relative f_{O_2} , as the P - T paths cross systematically more reducing ΔFMQ isopleths. The *absolute* f_{O_2} of the peridotite ($\pm$ partial melt) increases less with increasing T than does the FMQ buffer, causing ΔFMQ to become progressively more negative (reducing). At 2.0 GPa, the f_{O_2} of the peridotite-melt system increases by approximately a factor of twenty as T increases from 1200 to 1400 °C, whereas the f_{O_2} that defines the FMQ buffer increases by just over two orders of magnitude (Fig. 3b). This effect is stronger at lower P . For example, 14% partial melting at 1.5 GPa produces a 0.17 log unit change in ΔFMQ whereas at 2.5 GPa the change is only 0.06 log units for the same extent of melting.

235 Similarly, the behavior of $\text{Fe}^{3+}/\Sigma\text{Fe}$ during isobaric batch melting depends on the
 236 pressure at which melting takes place (Fig. 4). At 1.5 GPa, the first increment of melt is
 237 produced at $\Delta FMQ = -0.79$. At these conditions the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio of the partial melt
 238 (0.101) is significantly higher than that of the coexisting peridotite (0.060). As the melt
 239 fraction increases in response to increasing T , the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of peridotite and partial
 240 melt both systematically decrease. When Cpx is eliminated from the residual peridotite
 241 at ~19% partial melting, the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of partial melt and residual peridotite are
 242 0.077 and 0.055, respectively. The decrease of $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios in both partial melt and
 243 solid residue reflect ΔFMQ becoming more negative by ~0.25 log units. At 2.0 GPa the
 244 first increment of melt is produced at $\Delta FMQ = -1.39$, with a $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio (0.068)
 245 similar to that of the residual peridotite (0.060). As partial melting proceeds, they
 246 converge to a ratio of ~0.06 at Cpx out. At 2.5 GPa, the first increment of melt is
 247 produced at $\Delta FMQ = -1.95$. At these reducing conditions the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio of the partial
 248 melt is lower than that of the residual peridotite (0.049 vs 0.060) and decreases slightly to
 249 0.045 at Cpx out, while $\text{Fe}^{3+}/\Sigma\text{Fe}$ of the residual peridotite increases modestly to 0.064.

250 Decompression batch melting is a process in which peridotite partially melt in
 251 response to adiabatic ascent while the solid and the partial melt maintain equilibrium.
 252 This process provides a closer approximation to melt generation beneath oceanic
 253 spreading centers than does isobaric batch melting. Adiabatic ascent and partial melting
 254 of DMM with a $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio of 0.06 is shown in Fig. 5a for potential temperatures (T_P)
 255 of 1294 °C, 1346 °C, and 1396 °C (blue curves). Adiabatically ascending peridotite
 256 cools in response to decompression, crossing ΔFMQ contours that become successively
 257 less negative with decreasing pressure. This causes the partially molten lherzolite to
 258 become progressively more *oxidized* relative to the FMQ buffer reaction with increasing
 259 melt fraction. For example, a parcel of mantle with a potential temperature of 1346 °C
 260 crosses the nominally anhydrous solidus at 2.0 GPa with a relative oxygen fugacity 1.39
 261 log units more reducing than the FMQ buffer reaction; the absolute oxygen fugacity is

1.25 $\times 10^{-8}$ MPa (Fig. 5b). When the ascending peridotite reaches 1.5 GPa, it has undergone 5% partial melting and ΔFMQ has decreased to -0.85; absolute oxygen fugacity remains nearly constant. At 0.8 GPa, the peridotite has undergone 12% partial melting and ΔFMQ is -0.17; absolute oxygen fugacity has dropped slightly to 9.95×10^{-9} MPa (Fig 5b). Results for adiabatic decompression of DMM with T_P of 1396 °C – crossing the solidus at 2.5 GPa – and 1294 °C – crossing the solidus at 1.5 GPa – are similar to those for T_P of 1346 °C, but ΔFMQ values are systematically more reducing and oxidizing – respectively – at a given extent of partial melting. When compared at a constant P , the change in ΔFMQ becomes systematically larger with increasing T_P because the peridotite has undergone greater extents of partial melting. For example, peridotite crossing the solidus at 2.5 GPa becomes more oxidizing by 1.66 log units upon decompression to 0.8 GPa, whereas peridotite crossing the solidus at 1.5 GPa is only 0.75 log units more oxidizing at 0.8 GPa.

The behavior of $Fe^{3+}/\Sigma Fe$ during decompression batch melting closely follows ΔFMQ because they are interrelated. The $Fe^{3+}/\Sigma Fe$ ratio of the partial melt increases with increasing extent of partial melting for all three T_P 's, while that of the peridotite decreases (Fig. 6). For example, the first increment of melt produced upon crossing the solidus at 2.0 GPa has a $Fe^{3+}/\Sigma Fe$ ratio of 0.069. With further decompression, this increases to 0.126 at 12% partial melting. At a given extent of partial melting, the $Fe^{3+}/\Sigma Fe$ ratio of the melt becomes systematically larger as T_P decreases – and ΔFMQ becomes less negative.

Modeling results for batch melting illustrate two important points. First, there is a sharp contrast in behavior of $Fe^{3+}/\Sigma Fe$ during isobaric versus decompression partial melting. In the isobaric case, the absolute f_{O_2} of the system does not increase as much as the FMQ buffer with increasing extent of partial melting, leading to progressively more reducing conditions and a decrease in the $Fe^{3+}/\Sigma Fe$ ratio of the melt. In the decompression case, the absolute f_{O_2} of the system does not decrease as much as the

FMQ buffer with increasing extent of partial melting, causing conditions to become more oxidizing and the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio of the melt to increase. Second, during decompression partial melting relative oxygen fugacity is sensitive to both the bulk $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio of the peridotite and T_P of the ascending mantle. A potential temperature difference of 102 °C (i.e. 1396 °C versus 1294 °C) changes ΔFMQ at the solidus by 1.16 log units (i.e. from -1.95 at 2.5 GPa to -0.79 at 1.5 GPa) for a bulk $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio of 0.06. At 7% partial melting, the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio of the melt is lower for the hotter mantle (0.071 versus 0.138), and that of the residual peridotite is higher (0.059 versus 0.056). This implies that the ΔFMQ values recorded by MORB glasses reflect a combination of the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio and the T_P of their source region.

4.2 Partitioning of Fe^{3+} during peridotite partial melting

The results discussed above indicate that, for peridotite with a given $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio, ΔFMQ of the oceanic upper mantle varies systematically as a function of P and T. Given that the behavior of Fe^{3+} is reflected in ΔFMQ , it cannot be modeled using a single solid-melt partition coefficient. It is useful, however, to consider how the partition coefficient for Fe^{3+} between peridotite and silicate melt ($D_{\text{Peridotite-Melt}}^{\text{Fe}^{3+}} = C_{\text{Peridotite}}^{\text{Fe}^{3+}} / C_{\text{Melt}}^{\text{Fe}^{3+}}$) varies as a function of P, T, and ΔFMQ in order to understand its behavior during spinel lherzolite partial melting.

The most commonly cited $D_{\text{Peridotite-Melt}}^{\text{Fe}^{3+}}$ value is 0.1, which Canil et al. (1994) estimated by modeling the Fe_2O_3 contents of mantle peridotites as the residues of partial melting, assuming an average Fe_2O_3 concentration for MORB of 0.75 wt% (taken from the data of Christie et al., 1986). Subsequent studies of the oxidation state of iron in MORB glasses have concluded that the lack of a strong correlation between $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios and indicators of extent of partial melting (e.g., $\text{Na}_{8,0}$) make such incompatible behavior untenable (Bézos and Humler, 2005; Kelley and Cottrell, 2009). The modeling results presented here suggest that Fe^{3+} is more compatible during partial melting than previously thought, and that $D_{\text{Peridotite-Melt}}^{\text{Fe}^{3+}}$ varies as a function of ΔFMQ . For a Sp

lherzolite with $\text{Fe}^{3+}/\Sigma\text{Fe} = 0.06$ that has undergone 5% partial melting, $D_{\text{Peridotite-Melt}}^{\text{Fe}^{3+}}$ increases smoothly from ~ 0.6 at 0.8 GPa and $\Delta\text{FMQ} = 0$, to ~ 1.1 at 2.8 GPa and $\Delta\text{FMQ} = -2.3$. The variability of $D_{\text{Peridotite-Melt}}^{\text{Fe}^{3+}}$ is primarily due to a decrease in the concentration of Fe^{3+} in the partial melt as ΔFMQ becomes more negative, while the concentration in the peridotite remains relatively constant. In general, increasing the bulk $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio of the peridotite tends to increase $D_{\text{Peridotite-Melt}}^{\text{Fe}^{3+}}$ at a given ΔFMQ .

4.3 Comparison with results from pMELTS

While it is difficult to “ground truth” results from the modeling presented in this study, it is instructive to compare them with results from an independent approach to modeling the behavior of $\text{Fe}^{3+}/\Sigma\text{Fe}$ in Sp lherzolite. Figure 7 shows results from modeling batch partial melting of DMM – on a K_2O -free basis – with pMELTS, which uses free energy minimization to predict the distribution of Fe^{3+} and Fe^{2+} among coexisting phases (Ghiorso et al., 2002). Given a predicted $\text{Fe}^{3+}/\text{Fe}^{2+}$ distribution, f_{O_2} can be calculated in one of two ways. If melt is present, the default method implemented in pMELTS relies on the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio of the melt to calculate f_{O_2} as a function of P , T , and melt composition using Equation 7 of Kress and Carmichael (1991). Alternatively, f_{O_2} can also be calculated via heterogeneous equilibria involving only the solid phases (Asimow and Ghiorso, 1998). This is the default method implemented in pMELTS below the solidus. When melt is present, these two methods are not in agreement (Fig. S2). Given that only the latter approach is possible below the solidus, I have chosen this method – as implemented in alphaMELTS (Smith and Asimow, 2005) – in order to maintain internal consistency, while acknowledging that there is an inconsistency between f_{O_2} calculated on the basis of the melt versus the solid phases. Crystallization of plagioclase and garnet were suppressed so that Sp remains on the solidus from 0.8 to 2.8 GPa.

The salient features of ΔFMQ isopleths predicted in this study are also predicted by pMELTS when f_{O_2} is calculated on the basis of mineral equilibria. Relative f_{O_2}

systematically decreases along the peridotite solidus, although the decrease between 0.8 and 2.8 GPa predicted by pMELTS is smaller (0.79 log units versus 2.36 log units). Both models predict that ΔFMQ isopleths are parallel and define a nearly linear, negative relationship between P and T below the peridotite solidus. Upon crossing the solidus, ΔFMQ isopleths are deflected and their curvature increases. Adiabatically ascending peridotite crosses ΔFMQ contours that become successively more positive with decreasing pressure, causing the partially molten lherzolite to become progressively more oxidizing with increasing extent of partial melting (Fig. 7a). The principal difference between predictions from the two models is that pMELTS indicates a significantly stronger T -dependence for absolute f_{O_2} of the peridotite (Fig. 7b). Moving forward, therefore, it will be important to further constrain the magnitude of intrinsic ΔFMQ variability expected for the shallow oceanic upper mantle. This will require an experimental determination of the Fe^{3+}/Fe^{2+} distribution among peridotite minerals and partial melts that can be used to instruct future models.

4.4 Incremental Decompression Melting

As discussed in the Introduction, there are numerous lines of evidence indicating that decompression partial melting beneath oceanic spreading centers is a polybaric, near-fractional process (e.g., Klein and Langmuir, 1987; Grove et al., 1992; Kinzler and Grove, 1992; Langmuir et al., 1992). To simulate this, incremental partial melting calculations were performed in which 1% melt is produced for each 100 MPa of decompression and then removed from the residue. The residual peridotite is taken as the new bulk composition, and the process is repeated at successively lower pressures.

To provide a frame of reference for understanding the influence of partial melting on ΔFMQ , adiabatic ascent paths were calculated for DMM with $Fe^{3+}/\Sigma Fe$ ratios of 0.04 and 0.06 for T_P of 1294 °C and 1396 °C with no partial melting (Fig. 8a). Results from these calculations demonstrate the dependence of ΔFMQ on both $Fe^{3+}/\Sigma Fe$ ratio and mantle T_P . For peridotite with a given $Fe^{3+}/\Sigma Fe$ ratio, a decrease in T_P produces more oxidizing

370 conditions, so that each combination of $\text{Fe}^{3+}/\Sigma\text{Fe}$ and T_P produces a unique ΔFMQ ascent
 371 path.

372 The dependence of ΔFMQ on both $\text{Fe}^{3+}/\Sigma\text{Fe}$ and T_P means that it is difficult to infer
 373 the oxidation state of iron in the oceanic upper mantle on the basis of $\text{Fe}^{3+}/\Sigma\text{Fe}$ in MORB
 374 glasses alone. Consider, for example, the melting paths of DMM with a $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio of
 375 0.06 for T_P of 1396 °C and 1294 °C, a T difference comparable to global estimates for
 376 oceanic spreading centers that are not influenced by hot spots (~100 °C according to
 377 Dalton et al., 2014). Peridotite with a T_P of 1396 °C crosses the nominally anhydrous
 378 solidus at 2.5 GPa, whereas partial melting begins at 1.5 GPa for a T_P of 1294 °C. Once
 379 the peridotite has crossed the solidus, partial melting produces a downward deflection in
 380 T relative to the adiabat due to the influence of the enthalpy of melting, producing an
 381 upward deflection in ΔFMQ (Fig. 8b). The partial melting process, therefore, influences
 382 the relative oxygen fugacity of the upper mantle, with increasing extents of partial
 383 melting producing progressively more oxidizing conditions for peridotite with a given
 384 initial $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio and T_P .

385 Results from these calculations can be used to evaluate the relationship between
 386 ΔFMQ calculated on the basis of $\text{Fe}^{3+}/\Sigma\text{Fe}$ in MORB glasses and f_{O_2} conditions in their
 387 source region. The compositions of aggregated polybaric partial melts produced by each
 388 ascent path were used to calculate ΔFMQ at 1200 °C and 0.1 MPa using Equation 7 of
 389 Kress and Carmichael (1991). Comparison of these values to conditions within the
 390 melting regimes that produced the basalts leads to two important conclusions. First,
 391 relative f_{O_2} calculated from a MORB glass does not represent a unique value for the
 392 oceanic upper mantle, but should reflect conditions near the base of the melting regime.
 393 Second, for peridotite with a constant $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio, a 100 °C change in T_P produces a
 394 change in apparent ΔFMQ of ~0.8 log units, similar to the global range inferred from
 395 MORB glasses (e.g., Cottrell and Kelley, 2011). It is necessary, therefore, to compare

ΔFMQ calculated from MORB glasses with proxies for T_P before drawing conclusions on heterogeneity in the oxidation state of iron in the oceanic upper mantle.

4.4 Oxidation State of the Sub-Arc Mantle

It has long been recognized that $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of subduction-related lavas are higher than those in MORB (e.g., Osborn, 1959; Wood et al., 1990; Carmichael, 1991; Arculus, 1994; Kelley and Cottrell, 2009), and that peridotites from the sub-arc mantle record higher ΔFMQ values than those from the oceanic mantle (e.g., Wood et al., 1990; Brandon and Draper, 1996; Parkinson and Arculus, 1999; Evans et al., 2012). Correlations among $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of arc basalt glasses and proxies for input from subducted oceanic crust – such as H_2O and Ba/La – are generally interpreted as indicating that a “subduction component” plays a role in increasing the oxidation state of iron in the sub-arc mantle (Kelley and Cottrell, 2009; Brounce et al., 2014; Brounce et al., 2015). There is, however, no consensus as to the mechanism responsible for this increase. Simple H_2O addition cannot explain the relatively oxidizing nature of the sub-arc mantle because it is a very inefficient oxidizing agent (e.g., Frost and Ballhaus, 1998; Kelley and Cottrell, 2009) – an important example of a case in which correlation does not imply causation. Perhaps the most plausible oxidizing agent is SO_4^{2-} carried into the mantle wedge by slab-derived fluids. In the sub-arc mantle, S^{6+} could be reduced to S^{2-} , most likely via a redox couple with Fe^{2+} . This mechanism has the potential to oxidize eight moles of Fe^{2+} for every mole of SO_4^{2-} that is reduced (e.g., Kelley and Cottrell, 2009; Evans and Tomkins, 2011; Evans, 2012; Brounce et al., 2015).

That upper mantle ΔFMQ depends on T_P as well as $\text{Fe}^{3+}/\Sigma\text{Fe}$ indicates, however, that the differences in relative f_{O_2} between the oceanic and sub-arc mantles should – at least in part – reflect differences in T_P . To test whether this effect could be significant, I carried out calculations for 5% partial melt coexisting with a Sp lherzolite residue at 2.0 GPa in the oceanic and sub-arc mantle, with the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio of the peridotite arbitrarily set so that ΔFMQ of the oceanic mantle is zero. The T at which 5% partial melt coexists

with Sp lherzolite in the sub-arc mantle (1225 °C versus 1391 °C for the oceanic mantle) was taken from Fig. 1 of Grove et al. (2009). It is important to recognize that results from these calculations likely provide only a crude approximation, as they do not take the influence of H₂O into account. While dissolved H₂O does not influence the Fe³⁺/ΣFe ratio of silicate melt (Moore et al., 1995), it could affect inter-mineral Fe³⁺/Fe²⁺ distribution. Further, the presence of H₂O has significant influence on the major element composition of partial melt that has not been accounted for, and this will affect the f_{O_2} predicted for the partial melt by Equation 7 of Kress and Carmichael (1991).

Results from these calculations suggest that – at upper mantle conditions – the sub-arc mantle is ~0.9 log units more oxidizing than the oceanic upper mantle for the same bulk Fe³⁺/ΣFe ratio (Fig. 9). Calculating ΔFMQ at 0.1 MPa and 1200 °C on the basis of Fe³⁺/ΣFe ratios of the partial melts exaggerates this difference slightly to ~1.0 log units (Fig. 9). This represents a significant portion of the inferred relative f_{O_2} difference between MORB and subduction-related basalts (e.g., Fig. 8 of Brounce et al., 2014), suggesting that T_P may play an important role in setting the relative f_{O_2} of the sub-arc mantle. If this is indeed the case, the observed correlation between H₂O and the oxidation state of iron in basaltic glasses may reflect the solidus lowering influence of the former. The addition of H₂O causes peridotite to partially melt at lower temperatures, which are intrinsically more oxidizing. Therefore, before the influence of slab-derived fluids on relative f_{O_2} of the sub-arc mantle can be properly evaluated, the influence of T_P must be understood.

4.5 Secular Variations in Upper Mantle f_{O_2}

The dependence of ΔFMQ in Sp lherzolite on both Fe³⁺/ΣFe and T_P suggests that there should have been secular variations in relative f_{O_2} as the upper mantle cooled over geologic time even if Fe³⁺ extracted by basaltic volcanism was efficiently recycled during subduction. The expectation is that as T_P decreased in response to cooling of the Earth, the upper mantle would have become more oxidizing. Identifying secular variations in

the relative f_{O_2} of the upper mantle could potentially have an important impact on the speciation of C-O-H-S volatiles during high- T volcanic outgassing. At present day relative f_{O_2} values near FMQ, high temperature volcanic gasses are comprised dominantly of H_2O , CO_2 , and SO_2 . If the mantle was significantly more reducing in the past, however, volcanoes would have outgassed primarily H_2 , CO , and H_2S . The oxygen content of Earth's atmosphere is a balance between sources and sinks, and at present day upper mantle f_{O_2} conditions, volcanic outgassing is an important source of oxygen (e.g., Catling and Claire, 2005). Holland (2002) proposed that oxygenation of the atmosphere (i.e. the Great Oxidation Event) occurred in response to a gradual change in upper mantle f_{O_2} that resulted in a shift from reduced to oxidized volcanic gasses. This idea is at odds, however, with studies of Cr and V in lavas and peridotites, which seem to indicate that upper mantle f_{O_2} has remained relatively constant since the Archean (Delano, 2001; Canil, 2002; Lee et al., 2003).

The magnitude of the influence of T_P on ΔFMQ of the upper mantle was investigated by calculating relative f_{O_2} for peridotite with a constant $Fe^{3+}/\Sigma Fe$ ratio at 1.8 GPa – near the center of the spinel stability field for mantle peridotite. The $Fe^{3+}/\Sigma Fe$ ratio of the peridotite was arbitrarily set so that present day upper mantle T_P results in relative f_{O_2} equal to the FMQ buffer at 1.8 GPa. While this is a very simplified approach to the problem, it should provide a reasonable first-order estimate for the magnitude of ΔFMQ variability over Earth's history. Potential temperatures were taken from the secular cooling model of Korenaga (2008) for present-day ratios of internal heat production to surface heat flux (Urey ratios) ranging from 0.08 to 0.38 (Fig. 10a). Relative f_{O_2} decreases from the present through the mid-Archean – where Korenaga's model predicts a T_P maximum – and then begins to increase. The magnitude of the ΔFMQ decrease depends on the present-day Urey ratio used in the calculations. Herzberg et al. (2010) compared these mantle evolution curves with T_P values calculated from basalts, and found that a Urey ratio of 0.38 provides the best match. On the basis of that T_P evolution

curve, the most negative ΔFMQ values would have been ~ 1 log unit more reducing than the present-day upper mantle, which is too oxidizing to produce volcanic outgassing of reduced volatile species. That studies of Cr and V in basalts and peridotite suggest that upper mantle f_{O_2} has remained relatively constant since the Archean may be an indication that Earth's present-day Urey ratio is greater than 0.38.

5. CONCLUSIONS

Results from calculations carried out using a new model for the behavior of $Fe^{3+}/\Sigma Fe$ during partial melting of spinel lherzolite provide important new insights into the relationship between the oxidation state of iron in MORB glasses and the relative f_{O_2} of their mantle source region. During isobaric batch melting, $Fe^{3+}/\Sigma Fe$ in the melt and ΔFMQ both decrease with increasing extent of partial melting, whereas both increase during adiabatic decompression batch melting. Results from incremental melting calculations indicate that ΔFMQ calculated from the oxidation state of iron in MORB glasses depends on T_P as well as $Fe^{3+}/\Sigma Fe$. Further, these ΔFMQ values do not represent a unique value for the oceanic upper mantle, but likely reflect conditions in the lower portion of the melting regime. Relative differences in ΔFMQ are likely indicative of source region differences. It is necessary, however, to investigate relationships between T_P and ΔFMQ calculated from MORB glasses before drawing conclusions on heterogeneity in the oxidation state of iron in the oceanic upper mantle. The sub-arc mantle is intrinsically more oxidizing than the oceanic mantle because it is cooler, and this effect must be taken into account when evaluating the impact of slab-derived fluids on ΔFMQ in the mantle wedge. The dependence of ΔFMQ on T_P suggests that the upper mantle may have been more reducing in the past, but this is likely limited to ~ 1 log unit or less. This variability was probably not large enough to have contributed significantly to the Great Oxidation Event via changes in the nature of volcanic outgassing.

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FIGURE CAPTIONS

FIGURE 1. Pressure-temperature diagrams showing results from modeling batch melting of DMM with a $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio of 0.06. (a) Isopleths of constant ΔFMQ (gray curves). (b) Isopleths of constant $\text{Fe}^{3+}/\Sigma\text{Fe}$ in spinel (gray curves). The nominally anhydrous solidus of Hirschmann (2000) and clinopyroxene-out – calculated using the spinel lherzolite melting reaction of Kinzler (1997) – are shown as heavy red curves. Light red curves are melt fraction isopleths with an even spacing of 0.02.

Figure 2. Pressure-temperature diagrams as in Fig. 1 showing isopleths of (a) constant ΔFMQ calculated using the Nell-Wood oxybarometer (gray curves) and (b) ferrosilite in orthopyroxene (green curves) and $\log a_{\text{Fe}_3\text{O}_4}^{\text{spinel}}$ (gray curves).

FIGURE 3. (a) Pressure-temperature diagram as in Fig. 1 showing isobaric batch melting paths at pressures of 1.5, 2.0, and 2.5 GPa (blue vertical lines). (b) Comparison of the FMQ buffer (red line) with variation in absolute oxygen fugacity during isobaric heating and batch melting at 2.0 GPa (blue curve).

FIGURE 4. Variation in the oxidation state of iron in (a) partial melt and (b) residual peridotite during batch melting at 1.5, 2.0, and 2.5 GPa.

FIGURE 5. (a) Pressure-temperature diagram as in Fig. 1 showing decompression batch melting paths for peridotite at T_p of 1396 °C (blue curve crossing the solidus at 2.5 GPa), 1346 °C (blue curve crossing the solidus at 2.0 GPa), and 1294 °C (blue curve crossing the solidus at 1.5 GPa). (b) Comparison of the FMQ buffer (red curve) with variation in absolute oxygen fugacity during adiabatic decompression and partial melting of DMM with a T_p of 1346 °C (blue curve).

FIGURE 6. Variation in the oxidation state of iron in (a) partial melt and (b) residual peridotite during decompression batch melting of DMM at T_p of 1396 °C, 1346 °C, and 1294 °C.

FIGURE 7. (a) Pressure-temperature diagram calculated for batch melting DMM with a $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio of 0.06 using pMELTS. Shown are decompression batch melting paths for peridotite at T_P of 1410 °C (blue curve crossing the solidus at 2.5 GPa), 1365 °C (blue curve crossing the solidus at 2.0 GPa), and 1296 °C (blue curve crossing the solidus at 1.5 GPa). The nominally anhydrous solidus and clinopyroxene-out are shown as heavy red curves. Light red curves are melt fraction isopleths with a spacing of 0.02. (b) Comparison of the FMQ buffer (red curve) with variation in absolute oxygen fugacity during adiabatic decompression and partial melting of DMM with a T_P of 1365 °C calculated using pMELTS (blue curve).

FIGURE 8. (a) Comparison of relative oxygen fugacities for peridotites with bulk $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of 0.04 and 0.06 along adiabats corresponding to T_P of 1294 °C and 1396 °C. (b) The influence of incremental decompression partial melting of DMM on ΔFMQ of the upper mantle. Red curves represent adiabats corresponding to potential temperatures of 1294 and 1396 °C for DMM with $\text{Fe}^{3+}/\Sigma\text{Fe} = 0.06$. Blue curves represent decompression partial melting paths. Open circles are ΔFMQ values for accumulated polybaric partial melts calculated at 1200 °C and 0.1 MPa using Equation 7 of Kress and Carmichael (1991).

FIGURE 9. Comparison of $\text{Fe}^{3+}/\Sigma\text{Fe}$ and ΔFMQ for 5% partial melting of DMM at 2.0 GPa for temperatures of 1391 °C (MORB) and 1225 °C (arc basalt) (blue symbols). Also shown are ΔFMQ values calculated for the same basalts at 1200 °C and 0.1 MPa using Equation 7 of Kress and Carmichael (1991) (red symbols).

FIGURE 10. (a) Variations in T_P over the past 4 Ga for present-day Urey ratios of 0.08, 0.23, and 0.38 from the model of Korenaga (2008). (b) Relative oxygen fugacities for DMM calculated at 1.8 GPa for the T_P curves shown in (a). The bulk $\text{Fe}^{3+}/\Sigma\text{Fe}$ was arbitrarily set so the present-day T_P gives an oxygen fugacity equivalent to the FMQ buffer.

Figure 1

Gaetani Fig. 1

Figure 2

Gaetani Fig. 2

Figure 3

Gaetani Fig. 3

Figure 4

Gaetani Fig. 4

Figure 5

Gaetani Fig. 5

Figure 6

Gaetani Fig. 6

Figure 7

Gaetani Fig. 7

Figure 8

Gaetani Fig. 8

Figure 9

Figure 10

Gaetani Fig. 10