Partitioning of Fe$_2$O$_3$ in peridotite partial melting experiments over a range of oxygen fugacities elucidates ferric iron systematics in mid-ocean ridge basalts and ferric iron content of the upper mantle

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Abstract
Basalts and peridotites from mid-ocean ridges record $f_{O_2}$ near the quartz-fayalite-magnetite buffer (QFM), but peridotite partial melting experiments have mostly been performed in graphite capsules (~ QFM-3), precluding evaluation of ferric iron’s behavior during basalt generation. We performed experiments at 1.5 GPa, 1350–1400 °C, and $f_{O_2}$ from about QFM-3 to QFM+3 to investigate the anhydrous partitioning behavior of Fe$_2$O$_3$ between silicate melts and coexisting peridotite mineral phases. We find spinel/melt partitioning of Fe$_2$O$_3$ ($D_{\text{sp}}/\text{melt}^{\text{Fe}_2\text{O}_3}$) increases as spinel Fe$_2$O$_3$ concentrations increase, independent of increases in $f_{O_2}$, and decreases with temperature, which is consistent with new and previous experiments at 0.1 MPa. We find $D_{\text{opx}}/\text{melt}^{\text{Fe}_2\text{O}_3} = 0.63 \pm 0.10$ and $D_{\text{cpx}}/\text{melt}^{\text{Fe}_2\text{O}_3} = 0.78 \pm 0.30$. MORB Fe$_2$O$_3$ and Na$_2$O concentrations are consistent with a modeled MORB source with Fe$_2$O$_3 = 0.48 \pm 0.03$ wt% (Fe$^{3+}/\Sigma$Fe = 0.053 ± 0.003) at potential temperatures ($T_P$) from 1320 to 1440 °C. The temperature-dependence of the $D_{\text{sp}}/\text{melt}^{\text{Fe}_2\text{O}_3}$ function alone allows ~ 40% of the variation in MORB compositions. If we allow $D_{\text{opx}}/\text{melt}^{\text{Fe}_2\text{O}_3}$ and $D_{\text{cpx}}/\text{melt}^{\text{Fe}_2\text{O}_3}$ to also vary with temperature by tying them to spinel Fe$_2$O$_3$ through intermineral partitioning, then all the MORB data are within error of the model. Our model Fe$_2$O$_3$ concentration for the MORB source would require that the convecting mantle be more oxidized at a given depth than recorded by continental mantle xenoliths. Our result is supported by thermodynamic models of mantle with Fe$^{3+}/\Sigma$Fe = 0.03 that predict $f_{O_2}$ of ~ QFM-1 near the garnet-spinel transition, which is inconsistent with $f_{O_2}$ of MORB. Our results support previous suggestions that redox melting may occur between 200 and 250 km depth.

Keywords  MORB · Oxygen fugacity · Experimental petrology · Mantle petrology

Introduction
Estimates of upper mantle oxygen fugacity ($f_{O_2}$) and the bulk ferric iron content of the upper mantle inform petrological and geophysical models of the mantle. For example, the depth of redox melting in the mantle will be deeper if the mantle is more oxidized (Dasgupta et al. 2013; Stagno et al. 2013), potential temperatures inferred from magma compositions are lower under more oxidized conditions (Herzberg and Asimow 2008; Asimow 2021), and increased olivine ferric concentrations and associated defects may reduce seismic wave velocities and increase seismic attenuation (Cline II et al. 2018). The absence of a deep xenolith record from the convecting mantle forces workers to assume that the continental xenolith record (e.g., Frost and McCammon, 2008) can stand in for the $f_{O_2}$-depth profile of the convecting oceanic upper mantle; however, the absence of a deep xenolith record from the convecting mantle prevents evaluation of this assumption or even any direct assessment of the $f_{O_2}$ of the unmelted oceanic upper mantle. This shortfall in the geologic record highlights the importance of ridge $f_{O_2}$ as an anchor for modeling $f_{O_2}$ deeper in the convecting mantle.

Although key for understanding $f_{O_2}$ at depth, $f_{O_2}$ measurements of MORB (Christie et al. 1986; Bézos and Humler 2005; Cottrell and Kelley 2011; Berry et al. 2018; O’Neill
et al. 2018; Zhang et al. 2018) and ridge peridotites (Bryndzia and Wood 1990; Birner et al. 2018) cannot be directly related to the \( f_{O2} \) of unmelted, convecting upper mantle. Even correcting for the effects of depressurization upon ascent, which are well-characterized for ascending melts (Kress and Carmichael 1991) but poorly understood for peridotites (Birner et al. 2018), does not account for the redistribution of \( \text{Fe}_2\text{O}_3 \) between minerals and melt during partial melting and melt extraction.

The \( f_{O2} \) of MORB, and their \( \text{Fe}^{3+}/\Sigma\text{Fe} \) ratios when corrected for crystal-fractionation, span a relatively narrow range and appear insensitive to variations in extent of melting or mantle temperature (Bézos and Humler 2005; Cottrell and Kelley 2011; O’Neill et al. 2018). Possible reasons for this include reactions that limit changes in \( f_{O2} \) as peridotites undergo partial melting (Davis and Cottrell 2018; Sorbadere et al. 2018) or buffering by the presence of sulfides in the MORB source (Cottrell and Kelley 2011). In contrast, \( \text{Fe}_2\text{O}_3 \) does show systematic variations in MORB, which may provide a clue to what processes affect redox during MORB generation. If \( \text{Fe}_2\text{O}_3 \) in the MORB source could be modeled as an incompatible element with a static bulk partition coefficient, then \( \text{Fe}_2\text{O}_3 \) and \( \text{Na}_2\text{O} \) in MORB at an \( \text{MgO} \) concentration of 8 wt% should correlate positively. Observing the opposite in MORB, Bezos and Hummer (2005) suggested that \( \text{Fe}_2\text{O}_3 \) could not be modeled using simple mineral/melt partitioning. Cottrell and Kelley (2011) confirmed a negative correlation between \( \text{Fe}_2\text{O}_3(8) \) and \( \text{Na}_2\text{O}(8) \) and suggested that it could be explained if bulk \( \text{Fe}_2\text{O}_3 \) partitioning varied strongly as a function of mantle potential temperature (\( T_p \)).

The suggestion being that, while \( \text{Fe}_2\text{O}_3 \) cannot be modeled by a single partition coefficient, inversion of the partial melting process may be achievable with knowledge of \( \text{Fe}_2\text{O}_3 \) mineral/melt partition coefficients over a range of conditions and compositions. Experimental measurements of \( \text{Fe}_2\text{O}_3 \) partition coefficients are few (McCanta et al. 2004; Mallmann and O’Neill 2009; Davis and Cottrell 2018; Sorbadere et al. 2018). Testing Cottrell and Kelley’s (2011) mechanism for MORB \( \text{Fe}_2\text{O}_3 \) systematics requires experiments under mantle pressures and temperatures at variable \( f_{O2} \) and techniques for measuring \( \text{Fe}_2\text{O}_3 \) in the experimental melts and minerals. Only then will we be able to invert ridge \( f_{O2} \) measurements into measurements of convecting upper mantle \( f_{O2} \).

Unfortunately, controlling oxygen fugacity in solid media, high-pressure experiments at the moderate \( f_{O2} \) appropriate to Earth’s mantle is difficult. The conventional approach to controlling \( f_{O2} \) in a solid-apparatus employs graphite; however, this limits the \( f_{O2} \) to below the graphite–\( \text{CO}_2 \) buffer (Holloway et al. 1992). If MORB source \( f_{O2} \) were consistent with graphite saturation, as once believed (Christie et al. 1986; Blundy et al. 1991; Ballhaus 1993), graphite capsules would serve as ideal containers. It is now widely recognized, however, that MORB chemistry is inconsistent with graphite saturation in the mantle, because basalts and peridotites record more oxidized conditions near the quartz-fayalite-magnetite (QFM) buffer (Cottrell and Kelley 2011; Birner et al. 2018; O’Neill et al. 2018; Zhang et al. 2018) and because carbon behaves incompatibly during MORB genesis (Hauri et al. 2019). The \( f_{O2} \) enforced by graphite capsules is much lower than conditions in the MORB source region (Fig. 1).

To vary \( f_{O2} \) at high pressure or to access \( f_{O2}^5 \) more comparable to the MORB source, experimentalists can enforce discrete \( f_{O2}^5 \)s defined by metal-oxide buffers, such as nickel-nickel oxide (NNO), so long as \( f_{\text{H}_2\text{O}} \) of the buffer equals \( f_{\text{H}_2\text{O}} \) of the sample or \( f_{\text{H}_2\text{O}} \) within the capsule can be calculated (Eugster 1957; Blatter et al. 2013). Because this technique requires saturation in a hydrous fluid, it is an unsatisfying method of \( f_{O2} \) control when the system of interest is nominally anhydrous, as is true for magma genesis at ridges.

Here, we describe and apply a new technique for controlling \( f_{O2} \) in anhydrous experiments by encapsulating experiments in Pt-Fe alloy capsules, which we have used to saturate basaltic melts in several mantle minerals at \( f_{O2} \) between QFM + 0.25 and QFM + 3 at 1.5 GPa. The technique combines the method of estimating equilibrium melt and alloy compositions developed by Kessel et al. (2001) with a method for pre-saturating Pt-Fe alloy capsules used by Ford (1978). We additionally performed more reduced experiments at about QFM-3 in graphite capsules, and we performed experiments at 0.1 MPa near QFM at 1300 and 1400 °C to isolate effects of temperature on spinel–melt partitioning of \( \text{Fe}_2\text{O}_3 \). We measured \( \text{Fe}^{3+}/\Sigma\text{Fe} \) ratios of

![Fig. 1](attachment:image)
experimental glasses and spinels and calculated indirectly the Fe$_2$O$_3$ concentrations of the experimental pyroxenes in equilibrium with olivine. We used these partition coefficients, derived from experiments on mantle-like compositions under relevant pressures and temperatures, and results from the literature, in simple forward models of MORB genesis. Our results suggest that Fe$_2$O$_3$-Na$_2$O systematics in MORB can be accounted for by variations in Fe$_2$O$_3$ partitioning with temperature. Bulk Fe$_2$O$_3$ in the MORB source required to match the model to observations in MORB suggest the MORB source may be richer in Fe$_2$O$_3$ than previously thought.

**Experimental and analytical methods**

**Piston cylinder experiments**

Using data from Kessel et al. (2001), we equilibrated Pt tubing with magnetite in a gas-mixing furnace to achieve specific Pt-Fe alloy compositions, such that our capsules were already in near-equilibrium with our melts at the $f_{O_2}$ targeted in our high pressure and temperature runs. We prepared the tubing using methods adopted from Ford (1978). We cut 2-mm outer diameter, 1.4 mm inner diameter Pt tubing into 4.5–6 mm lengths. These tubes were packed and surrounded with a mixture of 70% by weight reagent grade magnetite and 30% sodium metasilicate (Na$_2$SiO$_3$), which allowed wetting of the capsule by a melt that acted as the transfer medium for Fe while maintaining saturation in magnetite. We suspended the tubes in Pt boats at 0.1 MPa and at the appropriate T-$f_{O_2}$ conditions to achieve our desired alloy composition (pre-saturation conditions are given in Supplementary Table S1).

After pre-saturation, we dissolved the mixture of magnetite and silicate glass from the tube by bathing in warm hydrofluoric or hydrochloric acid for 24–48 h. We coned, sealed, and flattened each end of the tube loaded with starting materials. We also ran experiments in graphite-lined 4-mm Pt capsules so that we would have experimental runs under relatively reducing conditions for comparison.

We designed our starting materials to begin with a base residue composition, SPR-1, which had a bulk composition roughly equivalent to a mixture of olivine, orthopyroxene (opx), clinopyroxene (cpx), and spinel in the proportions 30:30:30:10. We based the individual mineral compositions in this mixture on the residual minerals of fertile peridotite partial melting experiment MPY #39 of Robinson et al. (1998), adding Fe only as FeO. To this base composition, we added a powder representative of the melt phase in proportions intended to produce an experimental melt fraction of about 70%, and all Fe$_2$O$_3$ added to the experiments was added as a part of these mixtures. Experiments PC105-107 contained only the melt mixture with no peridotite residue component.

The starting materials were mixtures of reagent grade oxides and carbonates (SiO$_2$, TiO$_2$, Al$_2$O$_3$, Cr$_2$O$_3$, Fe$_2$O$_3$, FeO, MnCO$_3$, MgO, CaCO$_3$, Na$_2$CO$_3$, K$_2$CO$_3$). We doped most of these experiments with a mixture of first-row transition elements at a concentration of about 100 ppm each (Sc, V, Co, Ni, Zn, Ga, Ge). We mixed each starting composition over several steps. During each mixing step, we homogenized powders by grinding in an agate mortar and pestle under ethanol for 30 min to an hour. Before adding FeO and Fe$_2$O$_3$, we decarbonated the starting mixtures in a muffle furnace at 1000 °C overnight. We weighed powders before and after decarbonation to check that all carbon had been removed from the powders. Compositions of the starting materials are in Supplementary Table S2.

We performed high-pressure experiments in a Rockland Research end-loaded piston cylinder apparatus at the Smithsonian Institution National Museum of Natural History with a 1/2” pressure vessel. Assemblies comprised MgO spacers, a straight-walled graphite furnace, BaCO$_3$ pressure sleeves, and an outer layer of Pb foil. We controlled temperature to within ± 10 °C using type-D thermocouple. Positions of the capsule and thermocouple are equidistant from the furnace hotspot. Friction correction required for the BaCO$_3$ assembly on this piston cylinder device was tested using falling Pt spheres in NaCl to find the melting point of NaCl. The resulting friction correction matches that of Fram and Longhi (1992).

We mounted experimental assemblies in epoxy, vertically sectioned them, and polished them for electron microprobe analysis. We also wafered samples to approximately 100 μm thickness for analysis by X-ray absorption near-edge structure spectroscopy (XANES). We give additional details of the experimental design and methods in the Supplement and the run conditions of all experiments can be found in Table 1.

**0.1 MPa gas-mixing experiments**

We performed experiments at 0.1 MPa, 1306 and 1400 °C, and $f_{O_2}$ of QFM + 0.6 (Table 1) in a Del-Tech vertical gas-mixing furnace at the Smithsonian Institution National Museum of Natural History. We controlled $f_{O_2}$ to within ±0.05 log units using a mix of CO and CO$_2$ gas and monitored $f_{O_2}$ during the experiment using a ZrO$_2$-Pt oxygen sensor, referenced to air. We calibrated the sensor against a gas mixture of 50% CO, 50% CO$_2$. We monitored temperature inside the furnace tube using a PtRh thermocouple and controlled to within ± 2 °C of 1225 °C. The thermocouple was calibrated against the melting point of Au wire. Experimental charges were hung from Pt-loops by mixing starting powders with polyvinyl alcohol and
partially fusing in air at 1400 °C. Each Pt loop was pre-saturated in Fe by equilibrating with experimental starting powder at the run temperature and gas mix of each experiment for 24 h. After pre-saturation, run products were removed from the loops by soaking in hydrofluoric acid overnight. Pt loops were then reloaded with starting powder and hung in the furnace under the conditions given in Table 1. We quenched experiments by dropping the loop into a water bath without exposing the samples or gas mix in the furnace to air. We mixed starting compositions from reagent-grade oxides as described above for piston cylinder experiments.

### Analytical methods

**Electron probe microanalysis (EPMA)**

We analyzed experimental phases for major elements by wavelength dispersive spectrometry (WDS) using a JEOL 8900 Superprobe and a JEOL JXA-8530F Hyperprobe

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**Table 1** Experimental run conditions

| Expt # | Starting mix | P (GPa) | T (°C) | Pt-Fe capsule | Phase assemblage | Preferred $f_{O_2}$ relative to QFM$^a$ | Err | % Relative change in Fe | Err |
|--------|--------------|---------|--------|---------------|------------------|---------------------------------|-----|-----------------|-----|
| Melt with no added residue—capsule meant for QFM + 1 | | | | | | | | | |
| PC105  | SPR-1 Melt QFM + 1 | 1.5 | 1350 | 8 | glass + spl + cpx + grt | +2.13 | ±0.65 | −20 | ±5.5 |
| PC106  | SPR-1 Melt QFM + 1 | 1.5 | 1380 | 9 | glass + spl | +2.13 | ±0.65 | −20.5 | ±1.7 |
| PC107  | SPR-1 Melt QFM + 1 | 1.5 | 1370 | 10 | glass + spl + cpx | +2.1 | ±0.65 | −26.6 | ±3.2 |
| Graphite capsule | | | | | | | | | |
| PC128  | SPR-1 Mix Graphite | 1.5 | 1380 | N/A | glass + spl + opx | | | −5.2 | ±2.3 |
| PC130  | SPR-1 Mix Graphite | 1.5 | 1350 | N/A | glass + spl + opx + cpx | | | −9.4 | ±6.2 |
| PC216  | SPR-1 Mix2 Graphite | 1.5 | 1380 | N/A | glass + spl + ol + opx + cpx | −2.85 | +1.21, −2.86 | −10.1 | ±1.9 |
| Capsule meant for QFM-1 | | | | | | | | | |
| PC256  | SPR-1 mix1 QFM-1 | 1.5 | 1380 | 60 | glass + spl + ol + opx + cpx | +1.48 | ±0.44 | | |
| PC261  | SPR-1 mix3 QFM-1 | 1.5 | 1380 | 63 | glass + spl + ol + opx + cpx | +1.29 | ±0.45 | −20.1 | ±5.7 |
| Capsule meant for QFM | | | | | | | | | |
| PC112  | SPR-1 Mix QFM | 1.5 | 1380 | 18 | glass + spl + opx + cpx | +0.84 | ±0.65 | −19.1 | ±5.1 |
| PC126  | SPR-1 Mix2 QFM | 1.5 | 1380 | 23 | glass + spl + ol + opx + cpx | +0.25 | ±0.50 | −12.1 | ±2.2 |
| Capsule meant for QFM + 1 | | | | | | | | | |
| PC108  | SPR-1 Mix QFM + 1 | 1.5 | 1380 | 11 | glass + spl + opx + cpx | +2.04 | ±0.65 | −26.8 | ±5.5 |
| PC109  | SPR-1 Mix2 QFM + 1 | 1.5 | 1380 | 13 | glass + spl + ol + opx | +1.51 | ±0.48 | −28.7 | ±3.7 |
| PC110  | SPR-1 Mix2 QFM + 1 | 1.5 | 1380 | 16 | glass + spl + ol + opx + cpx | +0.85 | ±0.49 | −22.9 | ±6.5 |
| PC124  | SPR-1 Mix3 QFM + 1 | 1.5 | 1380 | 14 | glass + spl + opx | +1.65 | ±0.65 | −49.2 | ±1.3 |
| PC127  | SPR-1 Mix2 QFM + 1 | 1.5 | 1380 | 26 | glass + spl + ol + opx | +1.26 | ±0.47 | −19.8 | ±3.3 |
| PC231  | SPR-1 Mix5 QFM | 1.5 | 1380 | 50 | glass + spl + ol + opx + cpx | +1.66 | ±0.43 | −6.8 | ±7.4 |
| Capsule meant for QFM + 2 | | | | | | | | | |
| PC242  | SPR-1 Mix1 QFM + 2 | 1.5 | 1380 | 58 | glass + spl + ol + opx + cpx | +3.01 | ±0.44 | −6.6 | ±7.2 |
| PC247  | SPR-1 Mix1 QFM + 2 | 1.5 | 1400 | 57 | glass + spl + ol + opx + cpx | +2.8 | ±0.45 | −13.9 | ±2.7 |
| 0.1 MPa experiments | | | | | | | | | |
| SpCr1300 | CxSp11300 | 0 | 1306 | | glass + spl | +0.53 | ±0.05 | | |
| SpCr1400 | CxSp11400 | 0 | 1400 | | glass + spl | +0.60 | ±0.05 | | |

$^a$Preferred $f_{O_2}$ in piston cylinder experiments is determined by spinel-olivine-opx equilibrium when those phases were present and alloy-melt equilibrium otherwise. Preferred $f_{O_2}$ in the 0.1 MPa experiments is the $f_{O_2}$ of the gas-mix measured by ZrO$_2$-Pt oxygen sensor

$^b$Furnace conditions for capsule pre-saturation given in Supplemental Table S15
We measured Fe$_3^+$/$\Sigma$Fe ratios in experimental glasses using Fe-XANES at station 13-ID-E at the Advanced Photon Source (APS), Argonne National Laboratory, USA., following the method of Cottrell et al. (2009) modified to mitigate beam damage (Cottrell et al. 2018). We prepared samples to a thickness of about 100 μm.

We calculated Fe$_3^+$/$\Sigma$Fe ratios in the glass from the centroids of the pre-edge doublet and using the basalt standard glasses of Cottrell et al. (2009) and the calibration curve of Zhang et al. (2018). Standard glass LW_0 was analyzed repeatedly throughout each analytical session and we corrected pre-edge centroid energies such that the centroid of LW_0 (Cottrell et al. 2009) was 7112.3 eV. In addition to choosing optically clear glass for analysis, we also examined all spectra for evidence of crystal interference and discarded any spectra with unusual short-range order. XANES spectral data are given in Supplementary Table S4.

Experiments in graphite returned Fe$_3^+$/$\Sigma$Fe ratios below the detection limit with XANES (near QFM-2.5, Cottrell and Kelley, 2011). We have calculated glass Fe$_3^+$/$\Sigma$Fe ratios from PC216 using Eq. 7 of Kress and Carmichael (1991) and $f_{O_2}$ calculated from spinel-olivine-opx equilibrium.

**Calculation of $f_{O_2}$**

We calculated $f_{O_2}$ for the experimental assemblages by three independent methods (Supplementary Table S5). In all cases, when we give $f_{O_2}$ relative to the quartz-fayalite-magnetite buffer (QFM), we calculate the buffer using the formulation of Frost (1991). When spinel, olivine, and orthopyroxene were all present, we calculated $f_{O_2}$ from the equilibrium between these phases (Mattioli and Wood 1988) following the method described by Davis et al. (2017). When a large glass pool was available, we calculated $f_{O_2}$ from the glass composition, deriving the Fe$_3^+$/$\Sigma$Fe ratio of the glass from Fe-XANES and applying the algorithm of Kress and Carmichael (1991). In most experiments, we were also able to calculate $f_{O_2}$ from the equilibrium between the Pt-Fe alloy capsule and melt.

To calculate alloy-melt $f_{O_2}$, we calculated the activity coefficient of Fe in the alloy using Eq. 11a of Kessel et al. (2001) and included a pressure term described in the Supplementary text. We calculated log$f_{O_2}$ using Eqs. 3 and 4 of Médard et al. (2008). We also calculated log$f_{O_2}$ of this reaction using the $\Delta G_{rxn}$ from Holzheid et al. (1997) with a pressure term added using the molar volume of Fe metal (Robie et al. 1995) and FeO in silicate melt (Ghiorso and Kress 2004) and the activity coefficient for FeO in silicate melt ($f_{FeO}^{liq}$) from O’Neill and Eggins (2002). The two methods both rely on $\Delta G_{rxn}$ from Holzheid et al. (1997), and so only differ in the calculation of $f_{FeO}^{liq}$. We found that log$f_{O_2}$ of these two methods agree to within less than ±0.1 log units (Supplementary Table S5).

**Fe$_3^+$ in pyroxenes**

We estimate the Fe$_3^+$ concentration in the pyroxenes from the change in the apparent Fe$_2^+$–Mg exchange coefficient between coexisting pyroxenes and olivines as a function of $f_{O_2}$. Given the small range of temperatures and the limited compositional range of our experiments, we expect the true olivine-pyroxene Fe$_2^+$–Mg exchange coefficients ($K_D^{Fe-Mg} = [X_{Fe^2+}^{olv}X_{Mg}^{pyx}]/[X_{Mg}^{olv}X_{Fe-Mg}^{pyx}])$ to be constant. Because we expect little Fe$_3^+$ in olivine but significant Fe$_3^+$ in pyroxenes, the apparent olivine-pyroxene $K_D^{Fe-Mg}$, in which all Fe is treated as Fe$_2^+$, should decrease as a function of $f_{O_2}$ because the Fe$_3^+$ concentration in the pyroxene should increase as $f_{O_2}$ increases. The degree of deviation between the true $K_D^{Fe-Mg}$ and $K_D^{Fe-Mg}$ can be used to estimate the amount of Fe$_3^+$ in the pyroxene. Although indirect, this method has the potential to be more accurate than calculating Fe$_3^+$ from pyroxene stoichiometry, because it relies upon only the Fe and Mg measurements in each phase rather than being affected by the individual errors of every element in the analysis, which has been shown to be untenable for pyroxenes (Canil and O’Neill 1996).

**Results**

**Experimental products, Fe-loss, $f_{O_2}$, and approach to equilibrium**

All experiments contained a glass or crystallized quench melt and spinel ± olivine ± opx ± cpx. PC105, which did not have the SPR-1 residue added to its starting composition, yielded glass + garnet + spinel + cpx. All experiments contained large glass pools, similar to those pictured in Fig. 2, that allowed us to analyze glasses by EPMA and XANES at least 100 μm away from crystals or quench mattes. Silicate
minerals had diameters between 10 and 180 µm in most experiments (Fig. 2).

Mass balance indicates that experiments lost 5.7–49.2% of their total Fe to the capsule, though the majority lost less than 25% (Table 1 and Supplementary Table S6). Fe exchange with the capsule is probably unavoidable with this experimental design, and although we did not observe it, Fe-gain should be possible too. To meet some experimental objectives, Fe-loss must be strictly avoided (Grove 1981). In our case, Fe-loss did not compromise our experimental objectives, but did lead to adjustments to our experimental plan. Fe-loss led to an increase in bulk Si/(Mg + Fe2+), which can cause the melt to become too silica rich to remain saturated in olivine. We did observe this phenomenon, and several of the experiments that lost a large fraction of their starting Fe did not stabilize olivine (Table 1). Starting compositions for experiments performed later in the series were informed by phase compositions of the earlier experiments, which allowed us to better predict the compositions of equilibrium phase assemblages at higher fO2. Diminished Fe-loss and consistent saturation in a four-phase solid residue in the higher numbered experiments (Table 1) are evidence that our ability to make these predictions improved. We considered whether Fe-loss could have led to disequilibrium between the experimental phases. Because the environment external to the capsule is Fe-poor, there is a sink that will continue to draw Fe out of the capsule over the entire course of the experiment and true equilibrium will never be reached (more information about the compositional profiles through the alloy capsules is given in the Supplement, in Supplementary Figure S1, and the compositions of the capsule interiors are given in Supplementary Table S7). But if the loss of Fe from the silicate to the capsule is slow compared to the time required for the silicate and oxide phases to reequilibrate, then equilibrium can be approached and Fe2O3 partition coefficients will still be equal to equilibrium values. Below we demonstrate that our experiments, including those with high degrees of Fe-loss, have approached redox and Fe equilibrium.

Several observations can be combined to demonstrate the experiments have made a close approach to equilibrium. One of the strongest pieces of evidence is the good agreement between different methods of calculating fO2 from different phases. The three methods we used to calculate log fO2 all agree to within 2σ. There is close agreement between fO2 calculated from spinel-olivine-opx equilibrium and alloy-melt equilibrium (Fig. 3a), which agree to within 1σ for all experiments where both methods could be applied. There is similarly close agreement between fO2 calculated from spinel-olivine-opx equilibrium and XANES (Fig. 3b). Although all methods of calculating fO2 agree to within 2σ, log fO2 calculated from XANES are systematically offset to lower log fO2 when compared to spinel-olivine-opx equilibrium by about 0.4 log units on average (Fig. 3b). Davis and Cottrell (2018) showed that these two methods agree, with no systematic offset, in experiments conducted on a basaltic andesite composition at 0.1 MPa. Although we do not know the reason for the systematic offset observed at high pressure, possible reasons include: (1) Eq. 7 in Kress and Carmichael (1991) underestimates the effect of pressure on fO2; (2) Eq. 7 in KC91 underestimates fO2 for this particular glass composition; (3) our Fe-XANES calibration, which is based on 0.1 MPa experiments, shifts with pressure. This last possibility seems unlikely because Zhang et al. (2017) collected Fe-XANES and Mössbauer spectroscopy data on high-pressure experimental andesite glasses and found that coordination number for Fe2+ increases with pressure, while coordination of Fe3+ is unaffected. This change in coordination suggests that the 0.1 MPa glass XANES calibration of Cottrell et al. (2009), modified by Zhang et al. (2018),
would overestimate, not underestimate, Fe$_{3+}$/ΣFe ratios in high-pressure glasses. We considered the possibility of beam damage, but beam damage during XANES analyses would lead to overestimation, not underestimation, of the Fe$_{3+}$/ΣFe ratio (Cottrell et al. 2018). This leaves us with options (1) and (2), and potentially other issues we have not considered. We note that neither the pressure term deduced by O’Neill et al. (2006) nor the pressure term of Kress and Carmichael (1991) adequately models the high-pressure experiments conducted at the Ru-RuO$_2$ buffer (itself carrying uncertainty with pressure) by O’Neill et al. (2006) or Zhang et al. (2017), making option (1) plausible but difficult to test further. Option (2) is plausible, though application of the Borisov et al. (2018) algorithm for the relationship between composition and $f$$_O$$^2$ applied to the experiments in this study results in a similar offset to the one shown in Fig. 3b. We conclude that the effect of pressure on Fe$_{3+}$/ΣFe ratio bears further investigation, but given the excellent agreement overall amongst the three methods we have used to constrain $f$$_O$$^2$ (XANES, Pt-Fe alloy, and spinel-oxybarometry), we can move forward with confidence in our analysis.

The close agreement between spinel-olivine-opx and alloy-melt equilibria gives us confidence that $f$$_O$$^2$ is well-constrained in these experiments because these methods of calculating $f$$_O$$^2$ are completely independent. Moreover, we infer a close approach to redox equilibrium because the crystalline silicate and oxide phases record the same $f$$_O$$^2$ as the capsule-melt couple, despite their different kinetic limitations. The likeliest source of disequilibrium in the experiments would result from rapid loss of Fe from the melt to the capsule, which would raise $f$$_O$$^2$ locally, and incomplete communication of the new $f$$_O$$^2$ to the crystalline solids. Good agreement of these oxybarometers suggests that redox is communicated throughout the sample quickly compared to the rate of Fe-loss to the capsule, and $f$$_O$$^2$ approaches equilibrium.

It is possible that the crystalline phases and melt-capsule couple could reach redox equilibrium without attaining equilibrium partitioning of FeO and Fe$_2$O$_3$ between the crystalline and melt phases. This could result in crystals with appropriate Fe$_{3+}$/ΣFe ratios but too high ΣFe to have equilibrated with a melt that lost Fe to the capsule. We think this is unlikely because there are crystal-chemical constraints that disallow Fe to change valence without either charge-balancing coupled substitutions or defect migration. However, to account for this possibility, we further demonstrate that Fe$_{2+}$ equilibrium is approached between the melt and the silicate minerals by comparing the Fe$_{2+}$–Mg exchange coefficient between olivine and liquid ($K_D^{Fe-Mg}$) to expected values. We report both liquid Fe$_{3+}$/ΣFe ratios and olivine saturation in six experiments. Olivine-liquid $K_D^{Fe-Mg}$ in those experiments varies from 0.330 to 0.347 (Table S8 and Fig. 4), well within the model error of 0.31–0.32 ± 0.03 predicted by Toplis (2005). If mineral Fe$_{3+}$/ΣFe ratios are a function of $f$$_O$$^2$ and both $f$$_O$$^2$ and FeO have approached equilibrium, then Fe$_2$O$_3$ must have as well. Given this result, Fe$_2$O$_3$ partition coefficients are likely near-equilibrium values even in our experiments that have lost significant Fe. We, therefore, present all our experimental data and include all measurements of Fe$_2$O$_3$ partition coefficients in our analysis. In some instances, it is
useful to have the data from experiments with greater degrees of Fe-loss. For example, we will show below that spinel–melt partitioning of Fe$_2$O$_3$ is dependent on the Fe$_2$O$_3$ concentration of the spinel. We can distinguish the effect of Fe$_2$O$_3$ concentration from the effect of $f_{O_2}$ because some experiments have both high $f_{O_2}$ and spinel with low Fe$_2$O$_3$ concentration. This is possible because high $f_{O_2}$ experiments that experience high Fe-loss have spinels with oxidized Fe$^{3+}$/ΣFe ratios while still having low Fe$_2$O$_3$ because the experiment is low in total Fe.

Because we have multiple equilibria available to calculate $f_{O_2}$ in some experiments, we had to choose which methods we prefer for the purpose of plotting a single value for $f_{O_2}$ in our figures. Given the close agreement and independence of spinel-olivine-opx and alloy-melt oxybarometry, we adopt the spinel-olivine-opx $f_{O_2}$ as our preferred value of $f_{O_2}$ and alloy-melt $f_{O_2}$ when olivine was not present (Table 1 and Supplementary Table S5).

**Major element phase compositions**

Major element compositions of the silicates glasses and minerals vary little over the >4 log unit range in $f_{O_2}$. Notable exceptions are a bimodality in SiO$_2$ and Al$_2$O$_3$ concentrations between melts that crystalized olivine and those that did not and a range of variation in Mg# due to $f_{O_2}$-driven variations in FeO and Fe-loss. Spinel vary in Cr# (Cr/\[Al + Cr\]) from 0.094 to 0.334. Spinel Fe$^{3+}$/ΣFe ratios correlate strongly with log$f_{O_2}$ ($R^2 = 0.685$, $p$ value < 0.0001) and range from 0.064 to 0.639. Average phase compositions are tabulated in Supplementary Tables S8–S12.

**Fe$_2$O$_3$ in pyroxenes**

Our method for estimating Fe$_2$O$_3$ in pyroxenes relies on a correlation between the apparent olivine-pyroxene Fe–Mg exchange coefficients, which we note as $K_{D}^{Fe-Mg}$ (in which we have treated all Fe as Fe$^{2+}$) and log$f_{O_2}$. Apparent $K_{D}^{Fe-Mg}$ between olivine and opx and between olivine and cpx are both significantly correlated with log$f_{O_2}$ relative to QFM (for opx: $R^2 = 0.86$, $p$ value < 0.001; for cpx $R^2 = 0.87$, $p$ value = 0.006; Fig. 5). Having established that $K_{D}^{Fe-Mg}$ is a function of $f_{O_2}$, we can estimate the concentration of Fe$^{3+}$ in the pyroxene by comparison with the “true” $K_{D}^{Fe-Mg}$, in which only Fe$^{2+}$ is considered. If the true $K_{D}^{Fe-Mg}$ is known, then we can calculate Fe$^{3+}$ in pyroxene from the following equation:

$$X_{Fe^{3+}}^{pyx} = X_{mol}^{pyx} X_{Fe^{3+}}^{Fe^{2+}/Mg} \left( \frac{1}{K_{D}^{Fe-Mg}} - \frac{1}{K_{D}^{Fe-Mg_{true}}} \right),$$

where $X^n$ is the cations per formula unit (based on six oxygens for pyroxenes and four oxygens for olivine) of cation $i$ in phase $n$. Although true $K_{D}^{Fe-Mg}$ is likely close to the apparent value in the experiments performed in graphite, we leave open the possibility of significant Fe$^{3+}$ in those pyroxenes as well. Instead, we estimate the value of true $K_{D}^{Fe-Mg}$ by assuming that there is little enough Fe$^{3+}$ in the pyroxenes that the Fe$^{3+}$ pyroxene/melt partition coefficient will follow Henry’s law behavior; that is, we assume there will be a linear function describing the relationship between $X_{Fe^{3+}}^{melt}$ and $X_{Fe^{3+}}^{melt}$ that passes through the origin. Using the relationship $X_{Fe^{3+}}^{pyx} = D_{Fe^{3+}/melt}^{pyx} * X_{Fe^{3+}}^{melt}$ with Eq. 1 and rearranging terms, we were able to calculate true $K_{D}^{Fe-Mg}$ through multiple linear regression. The resulting values are olivine-opx $K_{D}^{Fe-Mg}$ = 1.05 ± 0.02 and olivine-cpx $K_{D}^{Fe-Mg}$ = 0.99 ± 0.01. Our estimate of olivine-opx $K_{D}^{Fe-Mg}$ compares favorably with $K_{D}^{Fe-Mg}$ predicted from the equations of von Seckendorff and O’Neill (1993) of 1.11 ± 0.18, considering the large uncertainties of that model when the phases have high Mg# as do the experiments in our study. With these values, we can use Eq. 1 to calculate $X_{Fe^{3+}}^{pyx}$ for both opx and cpx in each experiment with coexisting olivine. Resulting Fe$^{3+}$/ΣFe ratios vary from 0.03 ± 0.03 to 0.29 ± 0.04 in opx and 0.07 ± 0.05 to 0.43 ± 0.06 in cpx (Supplementary Table S13).

**Fe$_2$O$_3$ partition coefficients**

We use our measurements of Fe$^{3+}$/ΣFe ratios in glass and spinel and our calculated Fe$_2$O$_3$ concentrations in pyroxenes to estimate Fe$_2$O$_3$ partition coefficients between minerals and melt and intermineral partition coefficients. We find that $D_{Fe^{3+}/melt}^{melt}$ increases as a function of the Fe$_2$O$_3$ concentration in the spinel (Fig. 6). As is required for the analysis above,
Fe$_2$O$_3$ concentrations in pyroxenes and melts are well-fit by a line through the origin. From the slope of these lines, we calculate average $D^{\text{opx}}_{\text{melt}}/\text{Fe}_2\text{O}_3 = 0.63 \pm 0.10$ and $D^{\text{cpx}}_{\text{melt}}/\text{Fe}_2\text{O}_3 = 0.78 \pm 0.30$ (Fig. 7). Mineral-melt partition coefficients calculated from each individual experiment are given in Supplementary Table S14.

Discussion

Comparisons with previous experiments

Spinel-melt partitioning of Fe$_2$O$_3$

There are several other experimental data sets we can compare to our measurements of $D^{\text{spl}}_{\text{Fe}_2\text{O}_3}$. Mallmann and O’Neill (2009) performed experiments at 0.1 MPa and 1 GPa over a large range of $f_{O_2}$ and fit functions for the partition coefficients of Fe$^{2+}$ and Fe$^{3+}$ between spinel and melt by assuming that functionally all Fe was Fe$^{2+}$ in the most reduced experiments and Fe$^{3+}$ in the most oxidized. Davis and Cottrell (2018) performed 0.1 MPa experiments and measured Fe$^{3+}$/ΣFe ratios in glasses and spinels also equilibrated with olivine and opx. Sorbadere et al. (2018) presented $D^{\text{spl}}_{\text{Fe}_2\text{O}_3}$ from a suite of 1.5 GPa piston cylinder experiments performed in graphite, Re, and AuPd capsules. Sorbadere et al. (2018) applied several methods to estimate $f_{O_2}$ and, in contrast to this study, reported that the various methods disagreed by 1–7 log units within individual experiments; however, we recalculated $f_{O_2}$ from their reported spinel, olivine, and opx analyses and found that the $f_{O_2}$ they reported by spinel-olivine-opx oxybarometry is miscalculated, resulting in values of $f_{O_2}$ too low by 2–3 log units in their Re1 and AuPd1 experiments. We plot the erroneous $f_{O_2}$ reported by Sorbadere et al. (2018) and our recalculated values against their measured spinel Fe$^{3+}$/ΣFe ratios in Supplementary Figure S2. For the purpose of comparing their results to ours, we have recalculated $D^{\text{spl}}_{\text{Fe}_2\text{O}_3}$ for the Sorbadere et al. (2018) experiments using $f_{O_2}$ calculated from their spinel, olivine, and opx data following the same method we use for calculating $f_{O_2}$ in our own experiments. We provide more details about recalculating the Sorbadere et al. (2018) data in the Supplement, and versions of our figures that include the reported partition coefficients of Sorbadere et al. (2018) can be found as Supplementary Figures S3 and S4.

Piston cylinder experiments in this study and 0.1 MPa experiments of Davis and Cottrell (2018) both show increasing $D^{\text{spl}}_{\text{Fe}_2\text{O}_3}$ with increasing Fe$_2$O$_3$ concentrations in the spinel, but the two trends are offset with the new experiments at lower $D^{\text{spl}}_{\text{Fe}_2\text{O}_3}$ at a given spinel Fe$_2$O$_3$ concentration (Fig. 6). Recalculated 1.5 GPa experiments from Sorbadere et al. (2018) plot along the same trend as our 1.5 GPa experiments. We can demonstrate that these two trends in
$D_{\text{Fe}_2\text{O}_3}^{\text{spl/melt}}$ are effects of Fe$_2$O$_3$ concentration independent of $f_{\text{O}_2}$ by comparing experiments at similar $f_{\text{O}_2}$ but with different spinel Fe$_2$O$_3$ concentrations. Experiments PC109 (QFM + 1.51 ± 0.48) and PC231 (QFM + 1.66 ± 0.43) record similar $f_{\text{O}_2}$ but have different spinel Fe$_2$O$_3$ concentrations (3.57 ± 0.30 wt% in PC109 and 8.99 ± 0.30 wt% in PC231) and values of $D_{\text{Fe}_2\text{O}_3}^{\text{spl/melt}}$ (2.53 ± 0.22 in PC109 and 3.51 ± 0.16 in PC231). These experiments crystallized spinel with different Fe$_2$O$_3$ concentrations at similar $f_{\text{O}_2}$, because PC109 experienced greater Fe-loss than PC231. Fe-loss decreases the Fe$_2$O$_3$ concentration of the spinel and, consequently, the activity of magnetite. Nonetheless, high $f_{\text{O}_2}$ in the solid assemblage is maintained, because Fe-loss also leads to an increase in the forsterite content of the olivine, which has significant leverage in the $f_{\text{O}_2}$ calculation with higher forsterite contents corresponding to higher $f_{\text{O}_2}$.

The increase in $D_{\text{Fe}_2\text{O}_3}^{\text{spl/melt}}$ with increasing spinel Fe$_2$O$_3$ concentrations is clear in Fig. 6, but the reason for the offset between the 0.1 MPa and 1.5 GPa trends is not obvious. There are three major differences between the two sets of experiments that define these trends. The Davis and Cottrell (2018) experiments: (1) were performed at lower pressure (0.1 MPa v. 1.5 GPa), (2) were performed at lower temperature (1225 °C v. 1350–1400 °C), and (3) have spinels with greater Cr# (0.61–0.68 v. 0.09–0.33). We performed the 0.1 MPa experiments presented here to attempt to isolate some of these variables. Our new 0.1 MPa experiments are at the same pressure as the experiments we presented in Davis and Cottrell (2018) and also have similar Cr# = 0.61–0.67. The experiments are hotter than the experiments in Davis and Cottrell (2018), allowing us to test the effect of temperature at constant pressure and spinel composition (although, by necessity, there are still differences in the glass compositions). These two experiments show a trend of decreasing $D_{\text{Fe}_2\text{O}_3}^{\text{spl/melt}}$ with increasing temperature from the 1225 °C experiments of Davis and Cottrell (2018) to the 1400 °C and 0.1 MPa experiment of this study (Fig. 8b).

We can further demonstrate that temperature is likely an important variable for $D_{\text{Fe}_2\text{O}_3}^{\text{spl/melt}}$ using the experiments of Mallmann and O’Neill (2009). Their partition coefficients are fit to data from both 0.1 MPa and 1 GPa experiments, and there is no indication in their results that this pressure interval is important to $D_{\text{Fe}_2\text{O}_3}^{\text{spl/melt}}$. The Mallmann and O’Neill (2009) experiments were performed at 1300 °C, which is intermediate to the temperatures of experiments of Davis and Cottrell (2018) and the 1.5 GPa experiments of this study. The Cr# of the Mallmann and O’Neill (2009) spinels bracket the other available data. The Mallmann and O’Neill (2009) spinels show only a small difference in $D_{\text{Fe}_2\text{O}_3}^{\text{spl/melt}}$ over a large range of spinel Cr# (Fig. 8a). This effect is not strong enough to explain the large difference in average $D_{\text{Fe}_2\text{O}_3}^{\text{spl/melt}}$ between the experiments of Davis and Cottrell (2018) and this study. If we instead focus on the $D_{\text{Fe}_2\text{O}_3}^{\text{spl/melt}}$ relationship to temperature, we see that the experiments of Mallmann and O’Neill (2009) have similar average $D_{\text{Fe}_2\text{O}_3}^{\text{spl/melt}}$ to piston cylinder experiments in this study. The experiments in this study are 50–100 °C hotter; however, the effects of temperature are obscured in Fig. 8b, because the data plotted there span a large range of spinel Fe$_2$O$_3$ concentrations, which
we have already shown has a strong effect on $D_{\text{Fe}_2 \text{O}_3}^{\text{pl/melt}}$. After correcting for the effect of spinel Fe$_2$O$_3$, the temperature effect on $D_{\text{Fe}_2 \text{O}_3}^{\text{pl/melt}}$ becomes clearer (Fig. 8c). We note that the Sorbadere et al. (2018) experiments alone do not show a trend between $D_{\text{Fe}_2 \text{O}_3}^{\text{pl/melt}}$ and temperature after correcting for spinel Fe$_2$O$_3$; however, there are two reasons why such a trend might be obscured in the Sorbadere et al. (2018) data. First, because we calculated Fe$_2$O$_3$ in the glasses of these experiments from spinel oxbyrometry, uncertainties in $D_{\text{Fe}_2 \text{O}_3}^{\text{pl/melt}}$ are likely minor, we do not yet have sufficient data to determine whether spinel Al$_2$O$_3$ and Cr$_2$O$_3$ concentrations can have a significant effect on $D_{\text{Fe}_2 \text{O}_3}^{\text{pl/melt}}$ at extreme compositions like those in the most oxidized Sorbadere et al. (2018) spinels.

We modeled the effects of temperature and spinel Fe$_2$O$_3$ concentration on $D_{\text{Fe}_2 \text{O}_3}^{\text{pl/melt}}$ empirically using the piston cylinder experiments from this study and experiments from Davis and Cottrell (2018). We excluded the Mallmann and O’Neill (2009) partition coefficients, the Sorbadere et al. (2018) partition coefficients, and our new 0.1 MPa partition coefficients from fitting so we could use those experiments for validation. We performed a multiple linear regression to fit coefficients $a$, $b$, and $c$ from the following function:

$$D_{\text{Fe}_2 \text{O}_3}^{\text{pl/melt}} = a \frac{10000}{T} + b + c \ln(C_{\text{Fe}_2 \text{O}_3}^{\text{pl}}),$$

(2)

where $T$ is temperature in Kelvin and $C_{\text{Fe}_2 \text{O}_3}^{\text{pl}}$ is wt.% of Fe$_2$O$_3$ in spinel. Fits are $a = 0.87 \pm 0.07$, $b = -4.6 \pm 0.4$, and $c = 0.24 \pm 0.02$. The Mallmann and O’Neill (2009) partition coefficients, the recalculated Sorbadere et al. (2018) partition coefficients, and our 0.1 MPa partition coefficients are well-fit by the model (Fig. 8d) despite there being no model dependence on Cr or Al concentrations. Although, all the Mallmann and O’Neill (2009) experiments have low total Fe concentrations, there is a significant difference in total Fe between the high-Al and high-Cr groups, and it may be that the differences in $D_{\text{Fe}_2 \text{O}_3}^{\text{pl/melt}}$ between these groups are driven by differences in spinel Fe$_2$O$_3$ concentration rather than Cr#. Additional experiments at varying spinel Cr#s are needed to better constrain the effects of other spinel compositional components on $D_{\text{Fe}_2 \text{O}_3}^{\text{pl/melt}}$, but we are confident that Eq. 2 can be used to model $D_{\text{Fe}_2 \text{O}_3}^{\text{pl/melt}}$ under similar conditions to the experiments of this study, such as those that are pertinent to MORB generation.

**Pyroxene-melt partitioning of Fe$_2$O$_3$**

We compare our $D_{\text{Fe}_2 \text{O}_3}^{\text{opx/melt}}$ and $D_{\text{Fe}_2 \text{O}_3}^{\text{px/melt}}$ to data from the literature (McCanta et al. 2004; Mallmann and O’Neill 2009; Rudra and Hirschmann 2019) in Fig. 9. In our experiments, there is no correlation between $D_{\text{Fe}_2 \text{O}_3}^{\text{opx/melt}}$ or $D_{\text{Fe}_2 \text{O}_3}^{\text{px/melt}}$ and $f_O$. There is no compelling evidence to suggest anything other than constant partition coefficients for both $D_{\text{Fe}_2 \text{O}_3}^{\text{opx/melt}}$ and $D_{\text{Fe}_2 \text{O}_3}^{\text{px/melt}}$ over the compositional range of our experiments and $f_O$ between about QFM-3 and QFM + 3 (Fig. 9).

**Comparing intermineral Fe$_2$O$_3$ partitioning to Mössbauer measurements of minerals in peridotite xenoliths**

We also compare Fe$_2$O$_3$ concentrations and intermineral partition coefficients to Mössbauer spectroscopy measurements of Fe$_2$O$_3$ concentrations in minerals from spinel peridotite xenoliths (Dyar et al. 1989, 1992; McGuire et al. 1991; Luth and Canil 1993; Canil and O’Neill 1996; Woodland et al. 2006), which are more abundant than experiment measurements. Fe$^{3+}$/ΣFe ratios in our experimental opx are higher than in the natural pyroxenes at a given $f_O$, while Fe$^{3+}$/ΣFe ratios in our experimental cpx agree well with the natural data (Supplementary Figure S5a and b). Consequently, our experiments predict a slightly higher opx-cpx intermineral partition coefficient than the natural data (Supplementary Figure S5c).
Woodland et al. (2006) investigated spinel-cpx intermineral partitioning of Fe$_2$O$_3$ in xenoliths and found $D_{\text{Fe}_2\text{O}_3}^{\text{spl/cpx}}$ increases with increasing spinel Cr/(Cr + Al + Fe$^{3+}$) ratio. We do not observe a correlation between $D_{\text{Fe}_2\text{O}_3}^{\text{spl/cpx}}$ and spinel Cr/(Cr + Al + Fe$^{3+}$) ratio in our experiments (Supplementary Figure S6a). $D_{\text{Fe}_2\text{O}_3}^{\text{spl/cpx}}$ in the xenolith data is also negatively correlated with cpx Al$_2$O$_3$ concentration ($R^2=0.40$, $p$ value <0.0001; Fig. 10). $D_{\text{Fe}_2\text{O}_3}^{\text{spl/cpx}}$ in our experiments is consistent with the relationship between $D_{\text{Fe}_2\text{O}_3}^{\text{spl/cpx}}$ and cpx Al$_2$O$_3$ concentration in the xenoliths, falling to the Al$_2$O$_3$-rich side of the trend (Fig. 10).

**Implications for Fe$_2$O$_3$ systematics in MORB lavas and MORB-source mantle**

Fe$_2$O$_3$ and Na$_2$O in MORB corrected for crystal fractionation to a common MgO of 8 wt% (Fe$_2$O$_3$(8) and Na$_2$O(8)) are negatively correlated, which is opposite the expected trend if Fe$_2$O$_3$ could be treated simply as an incompatible element with a static partition coefficient (Bézos and Humler 2005; Cottrell and Kelley 2011). Fe$^{3+}$/ΣFe ratios of MORB corrected for crystal fractionation do not correlate with Na$_2$O(8), so that even as $T_p$ and mean $F$ of melting in the MORB source increase there is little change in the $f_{O_2}$ of the melting region, similar to conclusions drawn from previous experimental studies of $f_{O_2}$ and peridotite partial melting (Davis and Cottrell 2018; Sorbadere et al. 2018). But what is the mechanism that allows $f_{O_2}$ and melt Fe$^{3+}$/ΣFe ratios to remain stable as melts are extracted? The negative correlation of FeO(8) with Na$_2$O(8) and with depth to the ridge axis have been attributed to variations in $T_p$ (Klein and Langmuir 1987); that Fe$_2$O$_3$(8) is similarly correlated with Na$_2$O(8), and indeed with FeO(8), may indicate that temperature controls Fe$_2$O$_3$ concentrations in primary MORB as well.

Cottrell and Kelley (2011) explored this idea with a forward melting model that used the mineral/melt partition coefficients of Mallmann and O’Neill, (2009) and compared their model to MORB data. They found that those partition coefficients could produce melts with Fe$_2$O$_3$(8) and Na$_2$O(8) concentrations similar to the average of the MORB array if the MORB-source mantle contained 0.37 wt% Fe$_2$O$_3$. Furthermore, they suggested the negative correlation between Fe$_2$O$_3$(8) and Na$_2$O(8) can be accounted for if the bulk partition coefficient for Fe$_2$O$_3$ varied strongly as a function of temperature; however, insufficient data were available to test the magnitude of a temperature effect on bulk $D_{\text{Fe}_2\text{O}_3}$. With our new Fe$_2$O$_3$ partition coefficients and our temperature-dependent equation for $D_{\text{Fe}_2\text{O}_3}^{\text{melt}}$ (Eq. 2), we can revisit this modeling approach. We note that using partition coefficients for Fe$_2$O$_3$ is a fraught approach. Using a single bulk partition coefficient for Fe$_2$O$_3$ and treating it as a trace element is certainly problematic; rigorous modeling of partial melting in the mantle requires maintaining redox equilibrium between residues and instantaneous partial melts. Thermodynamic models, such as the model of Jennings and Holland (2015), can treat mantle melting in this way, but it is not trivial for us to introduce our new findings about Fe$_2$O$_3$ partitioning into that framework. Additionally, conditions of redox equilibrium between melt and residue are not maintained even in some of the most complex, popular, and successful thermodynamic models. For example, we have previously demonstrated that the MELTS family of models (Ghiorso and Sack 1995; Asimow and Ghiorso 1998; Ghiorso et al. 2002) generates residues and liquids that are far from redox equilibrium (Davis and Cottrell 2018). Ultimately, the amount of Fe$_2$O$_3$ that enters mantle partial melts will still be governed by mineral–melt partition coefficients, assuming the absence of other significant redox couples (i.e., all the carbon is already oxidized). The following treatment works as a first approach to testing whether temperature-driven changes to Fe$_2$O$_3$ partitioning are strong enough to account for variations observed in MORB and to estimate bulk Fe$_2$O$_3$ in the MORB source; although, we hope to see our experimental results incorporated into thermodynamic models in the future.

We modeled Fe$_2$O$_3$ and Na$_2$O concentrations of primary MORB melts by calculating bulk partition coefficients for Fe$_2$O$_3$ and Na$_2$O assuming modal mineralogy of Depleted MORB Mantle (DMM) from Workman and Hart (2005). We used average values of $D_{\text{Fe}_2\text{O}_3}^{\text{melt}}$ and $D_{\text{Na}_2\text{O}}^{\text{melt}}$ from our experiments, calculated $D_{\text{Fe}_2\text{O}_3}^{\text{melt}}$ from Eq. 2, and used $D_{\text{Na}_2\text{O}}^{\text{melt}}$ from Mallmann and O’Neill, (2009). We calculated $D_{\text{Na}_2\text{O}}^{\text{melt}}$ from Eq. 16 of Blundy et al. (1995) and calculated $D_{\text{Fe}_2\text{O}_3}^{\text{melt}}$ relative to $D_{\text{Na}_2\text{O}}^{\text{melt}}$ from the intermineral partition coefficient...
Na₂O between opx and cpx from 1 and 1.5 GPa partial melting experiments (Supplementary Fig S7). Accumulated near-fractional melting calculations in pMELTS (Ghiorso et al. 2002) suggest that the 1380 °C average temperature of our experiments is similar to the mean temperature of isentropic melting of mantle with a potential temperature (T_P) of 1400 °C. We calculated accumulated fractional melts at various melt fractions and source Fe₂O₃ concentrations and corrected those melts for crystal fractionation for comparison to MORB glasses at 8 wt% MgO. We estimate 1σ uncertainties on model Fe₂O₃(8) at about 0.15 wt% and on model Na₂O(8) at about 0.05 wt.% for each point along each of the modeled T_P curves. Additional details can be found in the Supplement.

For T_P = 1400 °C and range of F = 12–20%, we found that a source Fe₂O₃ concentration of 0.48 ± 0.03 wt% gave the best fit to the MORB data (Fig. 11), which corresponds to a bulk D_{Fe₂O₃} = 0.368 ± 0.057 and a source Fe³⁺/ΣFe ratio of 0.053 ± 0.003. To model the effect of varying T_P, we also performed calculations at T_P = 1320 °C and T_P = 1440 °C, approximately spanning the range of T_P suggested by Dalton et al. (2014). Because Eq. 2 has a temperature dependence, we can see the effect of the T dependence of D_{spl/melt} by changing the input temperature of the model (for T_P = 1320 °C bulk D_{Fe₂O₃} = 0.387 ± 0.057 and for T_P = 1440 bulk D_{Fe₂O₃} = 0.358 ± 0.057) and shifting the range of F upward for higher T_P and downward for lower T_P. Dashed curves in Fig. 11 show that the T dependence of D_{spl/melt} alone captures 41% of the MORB data.

Temperature may have an even larger effect if pyroxene/melt partition coefficients are also sensitive to temperature. Although we do not have sufficient experimental data to test for the effect of temperature on pyroxene/melt partitioning, we can estimate the temperature effect through intermineral partitioning between spinel and pyroxenes. We calculated the model again allowing D_{spl/melt} and D_{spl/cpx} to change by fixing the values of D_{cpx/spl} and D_{cpx/cpx} for the same range of potential temperatures and melt fractions, consideration of the pyroxene partition coefficients’ temperature dependence causes the model curves to extend to both higher and lower Fe₂O₃(8) at a given value of Na₂O(8) such that the model curves bound 83% of the MORB glasses and capture the entire MORB data array within error when bulk mantle Fe₂O₃ = 0.48 ± 0.03 wt% (Fig. 11). When pyroxene-melt partition coefficients are allowed to change in this way bulk D_{Fe₂O₃} for T_P = 1400 remains = 0.368 ± 0.057, but bulk D_{Fe₂O₃} changes more strongly with temperature (for T_P = 1320 °C bulk D_{Fe₂O₃} = 0.457 ± 0.057 and for T_P = 1440 bulk D_{Fe₂O₃} = 0.314 ± 0.057). That these model curves span the MORB data suggests that changes in the bulk partition coefficient with T_P are plausible drivers of MORB Fe₂O₃-Na₂O systematics, and that the ferric iron content of the mantle may be higher than previously thought.

The best-fit source Fe₂O₃ concentration of 0.48 ± 0.03 wt% is considerably greater than past estimates. Based on correlations between MgO and Fe₂O₃ in reconstructed whole rock compositions of continental xenoliths, Canil et al. (1994) estimated that Primitive Upper Mantle has 0.3 wt.% Fe₂O₃ (although we note that this estimate would increase slightly if Canil et al. (1994) had allowed for scant ferric iron in olivine, consistent with Mallmann and O’Neill (2009)). O’Neill et al. (2018) estimated a MORB source with Fe₂O₃ = 0.21 ± 0.06 wt% from their measurements of Fe³⁺/ΣFe ratios of MORB glasses and using partition coefficients from Mallmann and O’Neill (2009). Shorttle et al. (2015) used Fe³⁺/ΣFe ratios of glasses from Reykjanes Ridge and the Mallmann and O’Neill (2009) partition coefficients to

Fig. 11 MORB glass Fe₂O₃(8) and Na₂O(8) and forward-model melting curves are modified from Cottrell and Kelley (2011) using MORB data from Zhang et al. (2018), new data from this study, and a new modeling approach (described in the text). We corrected natural MORB glass compositions for crystal fractionation. We first corrected MORB with MgO > 8.5 wt% to MgO = 8.5 wt% by subtracting equilibrium olivine (K_{Fe²⁺/Mg} = 0.3) and assuming perfect incompatibility of Na₂O and Fe₂O₃. We then further corrected those compositions and the MORB glasses with MgO ≤ 8.5 wt% to MgO = 8 wt% using the equation of Klein and Langmuir (1987) Na₂O(8) = Na₂O + 0.373*MgO – 2.98 and the equation Fe₂O₃(8) = Fe₂O₃ – 0.2391*(8-MgO). In the Fe₂O₃(8) equation, −0.2391 is the slope of all the MORB glasses with MgO ≤ 8.5 wt% from Cottrell and Kelley (2011) with Fe³⁺/ΣFe ratios recalculated according to Zhang et al. (2018) in MgO-Fe₂O₃ space. The solid black curve is for a source with bulk Fe₂O₃ = 0.48 wt%, T_P = 1400 °C, and for various melt fractions explored at 1% increments as indicated by tick marks on the model curves. Dashed curves show the effect of changing T_P from 1400 °C (red) or 1320 °C (blue) when D_{spl/melt} and melt fraction are the only model inputs that change as a function of temperature. Dark red (T_P=1440 °C) and blue (1320 °C) curves show the effect of temperature for a source with bulk Fe₂O₃ = 0.48 wt% when D_{spl/melt} and D_{cpx/spl} have a temperature dependence, achieved by holding intermineral partitioning of Fe₂O₃ constant. We estimated model output uncertainty by propagating uncertainties in the mineral–melt partition coefficients through the model calculation. Model error (1σ) on Fe₂O₃(8) is approximately 0.15 wt% and on Na₂O(8) is approximately 0.05 wt%
estimate a MORB source with Fe₂O₃ = 0.2–0.45 wt%, which just overlaps our estimate at the high end. If our model results accurately reflect Fe₂O₃ concentrations in the MORB source, then it requires the convecting upper mantle to be significantly more oxidized than peridotites in the continental lithosphere after a similar amount of melt extraction. This difference is great enough that we consider potential flaws in our analysis that may explain the disparity.

Our method of estimating true olivine-pyroxene \( K_{D}^{Fe-Mg} \) may be leading to an overestimation of Fe₂O₃ concentrations in the pyroxenes. Instead of estimating true \( K_{D}^{Fe-Mg} \) as described above, if we set true \( K_{D}^{Fe-Mg} \) equal to \( K_{D}^{Fe-Mg}_{melt} \) of experiment PC216 performed in graphite, then we can test the conservative assumption that the pyroxenes in those experiments have zero Fe₂O₃. When we recalculate pyroxene Fe₂O₃ concentrations in this way, the new partition coefficients are \( D_{FeO/melt}^{pyrox} = 0.57 \pm 0.06 \) and \( D_{FeO/melt}^{pyrox} = 0.67 \pm 0.11 \), and the best fit to the MORB array is for source Fe₂O₃ = 0.45 ± 0.03 wt%. The pyroxene Fe₂O₃ concentrations in our experiments cannot be lower than this, and resulting partition coefficients still require considerably more MORB-source Fe₂O₃ than estimates of other workers.

We may be predicting too great a MORB-source Fe₂O₃ concentration if Fe₂O₃ in the MORB glasses has been overestimated. Berry et al. (2018) present an alternative method for interpreting Mössbauer spectra of silicate glasses that leads to a XANES calibration that is incompatible with the XANES calibration used by Cottrell et al. (2009), Cottrell and Kelley (2011), and Zhang et al. (2018), which we used to determine Fe³⁺/ΣFe ratios in the glasses presented here. Although all these studies agree that MORB glasses record a fO₂ near QFM (Cottrell and Kelley 2011; O’Neill et al. 2018; Zhang et al. 2018), they disagree about what the Fe³⁺/ΣFe ratio of basalt is as a function of fO₂. If the XANES calibration of Cottrell et al. (2009) modified by Zhang et al. (2018) leads to overestimates of Fe₂O₃ in silicate glasses, as suggested by Berry et al. (2018), then the ferric iron content in our experimental melts is lower and ferric iron is more compatible in spinel and pyroxene than we report here. At first blush, this would seem to lead to an even higher estimate for mantle ferric iron contents; however, the Fe³⁺/ΣFe ratios in the MORB glasses would also be overestimated (0.14 ± 0.01 from Zhang et al. (2018) vs 0.10 ± 0.02 from Berry et al. (2018) such that our model would still overestimate Fe₂O₃ of the MORB source. To explore this further, we applied the correction factor supplied by Berry et al. (2018) to our experiments from this study and from the 0.1 MPa study of Davis and Cottrell (2018). The systematic effects of composition and temperature we have described no longer hold, and there is no longer any systematic relationship that explains the variations in \( D_{FeO/melt}^{pyrox} \) from Davis and Cottrell (2018), Sorbadere et al. (2018), Mallmann and O’Neill (2009), and this study (see Supplementary Figure S8). The modeling we describe above would no longer be valid (see Supplement). Ultimately, interpretation of partitioning in our experiments requires that we choose which method of interpreting the glass Mössbauer spectra is correct, and we choose to follow the Zhang et al. (2018) calibration for the reasons given within Zhang et al. (2018), Cottrell et al. (2021), Borisov et al. (2018), and as further described in the Supplementary text.

Our study may incorrectly ascribe the differences in spinel/melt partitioning between experiments in this study and those from Davis and Cottrell (2018) to temperature when they might instead be a compositional effect. Although the experiments of Mallmann and O’Neill (2009) do not support this interpretation, and our 0.1 MPa experiments demonstrate the temperature effect isolated from changes in spinel composition, future experiments are needed to confirm our results.

**Implications of and supporting evidence for a more oxidized MORB-source mantle**

Now let us consider the implications if our modeled MORB source with 0.48 ± 0.03 wt% Fe₂O₃ is correct (corresponding to mantle Fe³⁺/ΣFe ratio = 0.053 ± 0.003). It requires that the MORB-source mantle be considerably more oxidized than similarly fertile sub-continental peridotites (Canil et al. 1994). There is already some evidence for this in the xenolith record. Ballhaus (1993) showed that spinel xenoliths from oceanic island basalts (OIB), representing the oceanic lithosphere, are 1–2 log units more oxidized than continental xenoliths with similar spinel Cr# and recording similar temperatures. Cratonic lithospheric mantle in particular has been isolated from mantle convection since its formation, but has been altered since emplacement by transiting melts and fluids (e.g., Menzies et al. 1987). Cratonic lithospheric mantle may have begun just as oxidized as we envision for the modern MORB source and was later reduced by metasomatic fluids. Luth and Stachel (2014) describe just such a scenario and suggest that light rare earth element signatures of cratonic peridotites require concentrations of reducing metasomatic agents sufficient to reset the fO₂ of the cratonic lithospheric mantle.

A MORB-source more oxidized than implied by continental xenoliths also would bring measured fO₂ of MORB and model estimates of mantle fO₂ into agreement. Several different methods of modeling fO₂ in the mantle find that for a bulk mantle Fe³⁺/ΣFe ratio of 0.03 (Canil et al. 1994) the shallow mantle should record fO₂ of about QFM-1, which is in agreement with the continental xenolith record (e.g., Frost and McCammon 2008) but about one log unit more reduced than recorded by average MORB (Cottrell and Kelley 2011; O’Neill et al. 2018; Zhang et al. 2018). Jennings and Holland
(2015) and Stolper et al. (2020) used a THERMOCALC-based model, and Stolper et al. (2020) also used pMELTS, to calculate phase equilibria for a peridotite bulk composition with fixed Fe\(^{3+}/\Sigma Fe\) ratio = 0.03 at upper mantle pressures and temperatures. Jennings and Holland (2015) allowed melting to occur and Stolper et al. (2020) suppressed melt formation, but both found that \(f_{o2}\) is lower in the spinel peridotite stability field than in the shallower part of the garnet peridotite stability field. Each predict that spinel-field \(f_{o2}\) is in the range QFM-2 to QFM-1. The implications of Jennings and Holland (2015) and Stolper et al. (2020) is that mantle with continental lithosphere-like Fe\(_2\)O\(_3\) concentrations are more reduced at the depths of MORB generation than QFM, which is the \(f_{o2}\) of the MORB source inferred from MORB themselves (Fig. 1; Cottrell and Kelley 2011; O’Neill et al. 2018). It is possible that the process of melt generation itself could lead to oxidation of peridotite as Fe\(_2\)O\(_3\) is redistributed among the residual phases and the melt. In both a mass balance model and in pMELTS, Gaetani (2016) found that batch melting of peridotite along an adiabatic ascent path leads to oxidation of the residue and melt system by potentially more than a log unit \(f_{o2}\). However, Gaetani’s model does not allow for changes to the subsolidus modal mineralogy with temperature, only with pressure. The model does not include temperature effects such as decreasing spinel mode with increasing temperature (Canil and O’Neill 1996) that might counteract the decrease in \(f_{o2}\) his model predicts with isobaric heating. The thermodynamic model of Jennings and Holland (2015), which does allow for T-driven variations in mode shows much less variation in \(f_{o2}\) along the spinel peridotite solidus than is predicted by Gaetani (2016). The model of Jennings and Holland (2015), which is also a batch melting model, also predicts slight oxidation along an adiabatic ascent path above the solidus, but only predicts 0.2–0.4 log units oxidation. Future models that can incorporate new data about Fe\(_2\)O\(_3\) partitioning may help to resolve questions of how \(f_{o2}\) evolves as melts are extracted beneath ridges.

A more oxidized MORB source has further implications for phase equilibria deeper in the upper mantle. The model of Stagno et al. (2013) predicts that for mantle with Fe\(^{3+}/\Sigma Fe\) ratio = 0.03 and bulk \(C = 30\) ppm (which can oxidize 1% of the total Fe in the mantle residue), redox melting will begin at about 150 km depth. A mantle Fe\(^{3+}/\Sigma Fe\) ratio between 0.05 and 0.06 would initiate redox melting at depths between 200 and 230 km. This is nearly identical to the range 200–250 km suggested by Dasgupta et al. (2013) that would be consistent with the depth of peak conductivity in the upper mantle (Lizarralde et al. 1995). A more oxidized MORB source than can be predicted from continental xenoliths, therefore, ties together \(f_{o2}\) estimates for MORB with thermodynamic models and geophysical evidence for deep onset of melting.

Conclusions

We performed multiple-saturation experiments at 1.5 GPa, 1350–1400 °C and \(f_{o2}\) from ~QFM-3 to QFM+3 using Pt-Fe alloy capsules graphite capsules. We also performed experiments at 0.1 MPa producing spinel–melt pairs at 1300 and 1400 °C. We measured Fe\(^{3+}/\Sigma Fe\) ratios in glasses and spinels and we estimate Fe\(_2\)O\(_3\) of opx and cpx from Mg-Fe exchange between olivine and pyroxenes. We used resulting mineral/melt partition coefficients for Fe\(_2\)O\(_3\) to model Fe\(_2\)O\(_3\) and Na\(_2\)O concentrations of mantle partial melts. Varying \(T_p\) from 1320 to 1440 °C allows the model to capture ~40% of the variation in MORB Fe\(_2\)O\(_3\)8-Na\(_2\)O(8) systematics from the temperature dependence of \(D_{Fe2O3}^{melt}\) alone. When we allow pyroxene/melt partitioning of Fe\(_2\)O\(_3\) to vary with temperature through intermineral partitioning between pyroxenes and spinel, the whole MORB data set can be fit within error for the same range of \(T_p\) and source bulk Fe\(_2\)O\(_3\) = 0.48 ± 0.03 wt%, corresponding to mantle Fe\(^{3+}/\Sigma Fe\) ratio = 0.053 ± 0.003.

This best-fit source concentration is considerably greater than the widely cited previous estimate of 0.3 wt% from the continental xenolith study of Canil et al. (1994). If our model is correct, then the convecting mantle is more oxidized than the continental lithosphere.

A MORB source at 1 GPa with \(f_{o2}\) near QFM (Cottrell and Kelley 2011; O’Neill et al. 2018; Zhang et al. 2018) is more oxidized than continental xenoliths at 1 GPa, which record QFM-1. Therefore, either the process of melting leads to significant oxidation or the MORB-source is more oxidized than the continental lithospheric mantle at the same depth. Our Fe\(_2\)O\(_3\) partitioning experiments and melting model provide support for the latter. A more oxidized MORB source may also allow for carbon-driven redox melting at depths of high conductivity in the upper mantle between 200 and 250 km (Dasgupta et al. 2013).

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