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## Oxygen Fugacity Across Tectonic Settings

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### ABSTRACT

Experiment and observation have established the centrality of oxygen fugacity ( $fO_2$ ) to determining the course of igneous differentiation, and so the development and application of oxybarometers have proliferated for more than half a century. The compositions of mineral, melt, and vapor phases determine the  $fO_2$  that rocks record, and the activity models that underpin calculation of  $fO_2$  from phase compositions have evolved over time. Likewise, analytical method development has made new sample categories available to oxybarometric interrogation. Here we compile published analytical data from lithologies that constrain  $fO_2$  ( $n=860$  volcanic rocks – lavas and tephra – and  $n=326$  mantle lithologies – the majority peridotites) from ridges, back-arc basins, forearcs, arcs, and plumes. Because calculated  $fO_2$  varies with choice of activity model, we recalculate  $fO_2$  for each dataset from compositional data, applying the same set of activity models and methodologies for each data type. Additionally, we compile trace element concentrations (e.g., vanadium) which serve as an additional  $fO_2$ -proxy. The compiled data show that, on average, volcanic rocks and mantle rocks from the same tectonic setting yield similar  $fO_2$ s, but mantle lithologies span a much larger range in  $fO_2$  than volcanics. Multiple Fe-based oxybarometric methods and vanadium partitioning vary with statistical significance as a function of tectonic setting, with  $fO_2$  ridges < back arcs < arcs. Plume lithologies are more nuanced to interpret, but indicate  $fO_2$ s  $\geq$  ridges. We discuss the processes that may shift  $fO_2$  after melts and mantle lithologies physically separate from one another. We show that the effects of crystal fractionation and degassing on the  $fO_2$  of volcanics are smaller than the differences in  $fO_2$  between tectonic settings and that effects of subsolidus metamorphism on the  $fO_2$  values recorded by mantle lithologies remain poorly understood. Finally, we lay out challenges and opportunities for future inquiry.

### 3.1. INTRODUCTION

The role that oxygen fugacity ( $fO_2$ ) plays in producing the unique topography of Earth's surface, defined by high-standing continents and low-lying ocean basins, was recognized in the 1950s, when workers such as Kennedy (1955), Eugster (1957, 1959), and Osborn (1959) established the link between  $fO_2$  and the course of igneous differentiation. Crystallization under high  $fO_2$  leads to the calc-alkaline magmatic series common on the continents, while crystallization under low  $fO_2$  results in the tholeiitic magma series common in ocean basins. In order to

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connect these laboratory-based insights to natural rocks, petrologists began to develop proxies for  $fO_2$ , and to apply them in earnest. Through seminal contributions such as Eugster (1959), Haggerty (1976), Christie et al. (1986), Carmichael (1991), Wood et al. (1990), Frost and Lindsley (1992), Ballhaus (1993), Canil (1997), and innumerable others, petrologists began to quantify and map the link between tectonic environment and oxygen fugacity.

### 3.1.1. Theoretical Background

Oxygen fugacity, or  $fO_2$ , describes the potential for an element to occur in an oxidized or reduced state – that is, with a higher or lower charge. If oxygen were an ideal gas, its chemical potential ( $\mu$ ) would simply be related to its partial pressure ( $P$ ) via

$$\mu_{O_2} = \mu_{O_2}^\circ + RT \ln \frac{P}{P_0} \quad (3.1)$$

Where  $\mu_{O_2}^\circ$  is the standard state chemical potential of  $O_2$ ,  $R$  is the gas constant,  $T$  is the temperature in Kelvin, and  $P_0$  is the standard state pressure of pure  $O_2$ . Because no gas, and certainly no rock, behaves as an ideal gas, we substitute fugacity ( $f$ ) for partial pressure, which corrects pressure for non-ideality, much as chemical activity corrects concentration for non-ideality. The chemical potential of oxygen is then

$$\mu_{O_2} = \mu_{O_2}^\circ + RT \ln \frac{f_{O_2}}{f_{O_2}^\circ} = \mu_{O_2}^\circ + RT \ln f_{O_2} \quad (3.2)$$

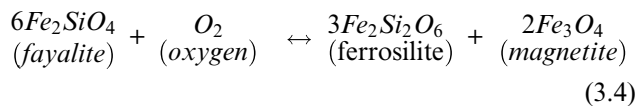
when  $f_{O_2}^\circ = 1$  (the fugacity of pure  $O_2$  at 1 bar and  $T$  of interest). In this way, we can relate the free energy of any equilibria of pure phases involving  $O_2$  to oxygen fugacity via the change in Gibbs free energy ( $\Delta G_{reaction}^\circ$ )

$$\Delta G_{reaction}^\circ = -RT \ln K_{eq} \quad (3.3)$$

where  $K_{eq}$  is the equilibrium constant. When  $P$  and  $T$  are specified, such equilibria of pure phases fix the activity of  $O_2$ , or “buffer” the  $fO_2$ .

### 3.1.2. Fe-Based Oxybarometry

Equilibria involving iron are useful because iron is the most abundant multivalent element in the solid Earth and is present in the common rock-forming minerals. For example, the oxygen fugacity of the equilibrium reaction of the pure phases fayalite goes to ferrosilite plus magnetite:



can be calculated from the free energy change of the reaction using Equation 3.3. The equilibrium constant can be written:

$$K_{eq} = \frac{(a_{Fe_2Si_2O_6}^{opx})^3 (a_{Fe_3O_4}^{spl})^2}{(a_{Fe_2SiO_4}^{olv})^6 f_{O_2}} \quad (3.5)$$

where  $a_{component}^{mineral}$  represents the activity of the end-member component (e.g., ferrosilite) within the mineral phase (e.g., orthopyroxene). In the case of pure phases, the activity is equal to unity, and so the following relationship holds true:

$$\log K_{eq} = -\log f_{O_2} = \left( \frac{6\Delta G_{Fe_2SiO_4}^\circ - 2\Delta G_{Fe_3O_4}^\circ - 3\Delta G_{Fe_2Si_2O_6}^\circ}{\ln(10)RT} \right) \quad (3.6)$$

In experimental systems, oxygen fugacity can be imposed by an invariant buffer reaction involving pure phases (activities equal to unity, for example nickel [Ni] and nickel oxide [NiO]). In natural systems, oxygen fugacity is determined by equilibria involving multi-component silicate minerals, melts, and gases; mineral phases are rarely found as pure end-member compositions. This requires us to relate mineral compositions to component activities. Accurate activity-composition models are therefore important when comparing the  $fO_2$  recorded by a single equilibrium reaction across a wide range of compositions, and even more so when comparing the  $fO_2$  recorded by different  $fO_2$  equilibria – when the accuracy, and not just the precision, of each equilibrium reaction is paramount. We relate the measured compositions of natural phases to the activities of end-member components (e.g., the activity of pure magnetite in spinel,  $a_{Fe_3O_4}^{spinel}$ ) via equations like

$$-\log f_{O_2} = \left( \frac{\Delta G_{reaction(P,T)}^\circ}{\ln(10)RT} \right) - 2\log a_{Fe_3O_4}^{spinel} - 3\log a_{Fe_2Si_2O_6}^{opx} + 6\log a_{Fe_2SiO_4}^{olivine} \quad (3.7)$$

Equation 3.7 describes the spinel oxybarometer (Ballhaus et al., 1991; O'Neill & Wall, 1987; Wood & Virgo, 1989) and its form prompts a review of several important points.

Any calculation of  $fO_2$  assumes that all phases that fix the activity of oxygen are present and in equilibrium. For example,  $fO_2$  is not constrained by the spinel oxybarometer if orthopyroxene is absent from the assemblage (unless the activity of silica can be constrained by some other means). Likewise, the composition of magnetite records  $fO_2$  only in the presence of ilmenite (Buddington & Lindsley, 1964). We can also see from the above equations that the activity of oxygen will rise with temperature such that it is convenient

to refer to a reference buffer. In this contribution we reference the quartz-fayalite-magnetite (QFM) buffer (Frost, 1991) because its pressure-dependence parallels adiabatic melt ascent (Kress and Carmichael, 1991), facilitating comparison of magmas equilibrated at different pressures and temperatures.

It also follows from the thermodynamic treatment above that the bulk rock ratio of ferric to total iron ( $\text{Fe}^{3+}/\Sigma\text{Fe} = \text{Fe}^{3+}/[\text{Fe}^{3+} + \text{Fe}^{2+}]$ ) in crystalline rocks cannot be equated to oxygen fugacity, because the former varies with mineral mode (extensive property) whereas the latter varies with component activity (intensive property). In melts (and glasses), steric effects are greatly reduced, such that melt (glass)  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios can be related to  $f\text{O}_2$ ; however, this does not mean that the  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios of melts vary systematically with  $f\text{O}_2$  independent of composition. With melts too,  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios must be related to  $f\text{O}_2$  after considering composition because oxide components in the melt can stabilize or destabilize  $\text{Fe}^{3+}$  relative to  $\text{Fe}^{2+}$  at given  $f\text{O}_2$  (e.g., Borisov et al., 2018; Kress & Carmichael, 1991; O'Neill et al., 2018).

Based on iron's role in both setting and monitoring  $f\text{O}_2$  (Frost, 1991; D. J. Frost & McCammon, 2008), prior Fe-based compilations of  $f\text{O}_2$  as a function of tectonic setting have relied on either spinel oxybarometry (e.g., Ballhaus, 1993; Wood et al., 1990), magnetite-ilmenite equilibria (e.g., Frost & Lindsley, 1992), or bulk rock and/or sediment  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios (e.g., Carmichael, 1991; Lecuyer & Ricard, 1999). In this chapter, we do not compile  $f\text{O}_2$  calculated for bulk "glass"  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios because in most cases the metadata provided in publications are absent or insufficient to ensure that the samples have not suffered post-eruptive oxidation or are free of phenocrysts, both of which have been shown to compromise the fidelity of  $f\text{O}_2$  proxies (Bezous & Humler, 2005; Brounce et al., 2017; Cottrell & Kelley, 2011; Grocke et al., 2016; Stolper & Bucholz, 2019; Bezous et al., 2021). Further, while very convenient for generating large datasets and informing box models (e.g., Brounce et al., 2019; Canil & Fellows, 2017; Evans, this volume; Evans & Tomkins, 2011; Evans et al., 2012; Lecuyer & Ricard, 1999; Stolper & Bucholz, 2019), applications of bulk "glass" or whole rock  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios are limited because the  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios of crystalline rocks and mixtures (like cumulates and sediments) cannot be directly equated to  $f\text{O}_2$  – as detailed above.

### 3.1.3. Trace-Element Oxybarometry

In addition to iron, the periodic table offers us a wealth of elements that undergo valence state changes in response to changes in  $f\text{O}_2$ . The theory that underpins trace element

oxybarometry is that  $f\text{O}_2$ -driven valence state changes will result in changes to mineral-melt partition coefficients. Thus, the concentration of a multivalent trace element in melt should reflect the residual mineralogy, the melt composition, and the pressure, temperature, and oxygen fugacity of the system during melting. In this way, the power of redox-sensitive minor and trace element partitioning can be harnessed to monitor the  $f\text{O}_2$  of geologically relevant lithologies, and can offer advantages over Fe. Trace element concentrations offer advantages because they are (i) relatively straightforward to measure and (ii) should be less susceptible than formal valence state to modification after the melt separates from the residue. A wide range of redox-sensitive elements (e.g., Ti, V, Cr, Ce, Eu, U, Mo, W, Re) are discussed separately by Mallmann et al. (2021) within this volume, and we refer the interested reader to that chapter. Several trace elements, however, have been employed to infer the  $f\text{O}_2$  of basalt source rocks (the mantle) as a function of tectonic setting (e.g., Bali et al., 2012; Bucholz & Kelemen, 2019; Canil, 1997; Laubier et al., 2014; Lee et al., 2005; Lee et al., 2010; Lee et al., 2012; Mallmann & O'Neill, 2009; Mallmann & O'Neill, 2013; Shervais, 1982). A review of all of these studies and proxies is beyond the scope of this chapter; however, we will discuss vanadium (V) – the most widely applied of these proxies. Vanadium valence can be  $\text{V}^{2+}$ ,  $\text{V}^{3+}$ ,  $\text{V}^{4+}$ , or  $\text{V}^{5+}$  in geologically relevant systems. The incompatibility of  $\text{V}^{3+}$  in mantle minerals is similar to many other trivalent elements, such as the rare earth elements, Sc, Y, and Ga, while  $\text{V}^{4+}$  and  $\text{V}^{5+}$  are more highly incompatible. Therefore, with all other parameters equal, melting peridotite at higher  $f\text{O}_2$  should result in systematically higher melt V concentrations relative to other trivalent trace elements (Canil, 1997; Lee et al., 2003, 2005).

### 3.1.4. Other Oxybarometers

We emphasize that there are many additional, and very valuable, proxies for  $f\text{O}_2$  that are not yet widely applied to volcanics from arc, ocean island, and mid-ocean ridge settings, but may be in the future, such as stable isotope proxies (Dauphas et al., 2009; Nebel et al., 2015; Williams et al., 2005). Similarly, microprobe peak energies (e.g., Carroll & Rutherford, 1988) and S X-ray Absorption Near Edge Structure spectra (e.g., Fleet et al., 2005) can determine sulfur oxidation state, but analyses from both techniques can be compromised by beam damage during analysis (e.g., Klimm et al., 2012; Rowe et al., 2007; Wilke et al., 2008), leaving only a handful of vetted analyses. For these, we point the interested reader to other chapters in this volume that describe some of these approaches in detail.

### 3.2. SAMPLE SELECTION, METHODOLOGY, AND DESIGN OF THIS STUDY

We can envision many valid approaches for compiling  $fO_2$  determinations from the literature. In this contribution, we focus on the oxybarometric approach and apply oxybarometers that have all been cross-calibrated at 1 atmosphere under controlled atmosphere conditions at known  $fO_2$ . We compile published compositions from Earth's ridges, back arcs, forearcs, arcs, and plumes and recalculate the  $fO_2$  values recorded by these volcanics (lavas and tephra) and mantle lithologies (mostly peridotites). We have opted to include samples wherein the original publications provide sufficient information to recalculate  $fO_2$  (e.g., microprobe analyses) such that we may apply a single set of activity models and methodologies to all of the compositional data collected in disparate studies. This is essential, because the  $fO_2$  calculated from a given composition may vary by up to a log unit depending on the activity model employed (e.g., Birner et al., 2017; Herd, 2008; Wood, 1990). Further, many publications do not report the formulation of the reference buffer (for example, QFM from O'Neill [1987] vs Frost [1991] vs Myers & Eugster [1983]), such that reported  $fO_2$ s may not be comparable.

We describe our methods, including chosen activity models, in detail in our methods appendix. In brief, we include widely applied oxybarometric techniques that have documented intra-technique consistency, and which require minimal metadata: magnetite-ilmenite pairs, spinel-oxybarometry, and glass spectroscopy. For example, Davis and Cottrell (2018) show that both the spinel oxybarometric method of Wood and Virgo (1989) and the  $Fe^{3+}/Fe^{2+}$  activity model of Kress and Carmichael (1991) return the experimentally imposed  $fO_2$  of gas-mixing experiments containing spinel, olivine, and orthopyroxene in basaltic andesite liquid. Likewise,  $Fe^{3+}/\Sigma Fe$  ratios of glasses converted to  $fO_2$  via the Kress and Carmichael (1991) algorithm are consistent with magnetite-ilmenite oxybarometry using the activity model of Ghiorso and Evans (2008) (Crabtree & Lange, 2011; Waters & Lange, 2016). Table 3.1 summarizes the oxybarometric methods we apply and the studies we include. A more detailed discussion of alternative parameterizations for  $fO_2$  can be found in the methods appendix. The compiled dataset can be downloaded as a data library (Cottrell et al., 2021). The dataset is unique in that we aggregate  $fO_2$  data from different studies, different authors, and with different proxies, but we reprocess and quality check the data to facilitate global comparisons. This exercise also identifies which regions and tectonic settings lack direct  $fO_2$  constraints (Figure 3.1).

We first present the Fe-proxy-based  $fO_2$ s recorded by rocks from each tectonic setting (ridge, back arc, arc,

and plume). We discuss the processes that may perturb these proxies and the extent to which the  $fO_2$  recorded by rock samples is representative of the mantle source. We then compare Fe-based proxies to the inferences that can be drawn from magmatic V concentrations across tectonic settings. Like all elements, the V concentrations of basaltic liquids change as fractional crystallization proceeds, necessitating the normalization of V concentration to another trace element. Although many studies normalize V concentrations to Scandium (Sc), Mallmann and O'Neill (2009) and Laubier et al. (2014) critically evaluate candidate trivalent cations and conclude that the V/Sc ratio does not remain constant as fractionation proceeds. V/Sc begins to rise as MgO falls below 8 wt.%, making this ratio unsuitable to evaluate primitive arc basalts (Laubier et al., 2014). Following Laubier et al. (2014) we choose Yb for normalization because it remains constant during crystallization of typical basalts down to < 6 wt.% MgO. We use the compilation of Gale et al. (2013a) for MORB and BABB chemistry, which ensures that samples derive from on-axis locations and that trace element analyses are of high quality. We use the compilation of Turner and Langmuir (2015) for arc basalt chemistry, which ensures that samples derive from arc-front volcanoes and, again, that trace element analyses are of high quality. Following Laubier et al. (2014), we filter these compilations for 6 wt.% < MgO < 12 wt.% to ensure that we are evaluating compositions that represent liquids (not cumulates) and that magnetite has not yet begun to crystallize (V is compatible in magnetite). We only evaluate compositions with Dy/Yb < 2 to avoid residual garnet in the source (Laubier et al., 2014). With these filters in place, we compile trace element data for 1294 MORB and 225 BABB, as well as 317 basalts from 37 arc-front volcanoes. We did not include plume-derived basalts in this comparison because the residual garnet in plume sources complicates interpretation of V/Yb. Yb (and Sc) are highly compatible in garnet, and the relationship between V/Yb (or V/Sc) and  $fO_2$  is poorly defined (Canil, 2002; Davis et al., 2013; Lee et al., 2005).

### 3.3. RESULTS

Calculated  $fO_2$  for each sample in this study is available in the data library associated with this publication (Cottrell et al., 2021).

#### 3.3.1. Fe-Based Oxybarometry

**Mid-Ocean Ridges.** Mid-ocean ridges sample Earth's convecting mantle and represent the majority of volcanism on the planet. Both melts and mantle

**Table 3.1** Results and Method Summary.

Tectonic setting	$\delta Q_{FM}$ (s)	Lithology	n	Method	Activity-composition models and other method notes	Method error in $fO_2$ in log units	Notes	Data included
mid-ocean ridge	-0.17 (0.15)	basalt pillow glass	160	XANES	At 1atm. Kress & Carmichael, 1991; parameterization of $fO_2$ as a function of composition	0.27	Fe oxidation state determined using the Mössbauer calibration of Zhang et al., 2018	Cottrell & Kelley, 2011; Le Voyer et al., 2015 (except the 6 analyses of hydrothermally altered dredge 16D); Birner et al., 2018
mid-ocean ridge	0.19 (0.36)	basalt pillow glass	42	XANES	At 1atm. O'Neill et al., 2018; parameterization of $fO_2$ as a function of composition	0.52	Fe oxidation state determined using the Mössbauer calibration of Berry et al., 2018	O'Neill et al., 2018
mid-ocean ridge	0.16 (-)	lava	1	mag-ilm pairs	$fO_2$ at T recorded and 1 atm. Ghiorso & Evans 2008	0.25**	passes Bacon & Hirschmann, 1988, test for equilibrium	Mazzullo & Bence, 1976
mid-ocean ridge	0.31 (0.73)	peridotite	72	sp-oxybarometry	$fO_2$ at T and 0.6GPa. Mattioli & Wood, 1988; and Wood & Virgo, 1989; with $aFe_3O_4$ from Sack & Ghiorso, 1991a, 1991b; <a href="http://melts.ofm-research.org/CalcForms/index.html">http://melts.ofm-research.org/CalcForms/index.html</a> ; Temperature from spinel-olivine Fe-Mg exchange thermometer of Li et al., 1995	Between about +0.6/-1.0 and $\pm 0.2$ depending on spinel $Fe^{3+}/\Sigma Fe$ ratio of spinel (see Methods Appendix and Davis et al., 2017)***	see Davis et al., 2017; and Birner et al. 2017; for discussions of a-X model choices	Bryndzia & Wood, 1990; Birner et al., 2018
back arc basin spreading center	0.22 (0.30)	submarine lava	37	XANES	at 1atm and 1200°C. Kress & Carmichael, 1991	0.27		Kelley & Cottrell, 2009; Brounce et al., 2014
arc front	0.96 (0.39)	basalt glass in olivine-hosted inclusions, basalt pillow glass	119	XANES	at 1atm and 1200°C. Kress & Carmichael, 1991	0.27		Bonnin-Mosbah, 2001; Kelley & Cottrell, 2009; Kelley & Cottrell, 2012; Brounce et al., 2014; Brounce et al., 2016 (data from Gaetani et al., 2012, excluded from average due to oxidative beam damage)
arc front	1.28 (0.64)	volcanics (lavas and tephra)	114	mag-ilm pairs	$fO_2$ at T recorded and 1 atm. Ghiorso & Evans, 2008	0.25**	passes Bacon & Hirschmann, 1988, test for equilibrium	Carmichael, 1967; Luhr & Carmichael, 1980; Wallace & Carmichael, 1994; Rutherford & Devine, 1996; Mandeville et al., 1996; Luhr, 2000; Coombs & Gardner, 2001; Devine et al., 2003; Costa et al., 2004; Grove et al., 2005; Larsen, 2006; Toothill et al., 2007; Izbekov et al., 2002; Browne et al., 2010; Baggerman & Debari, 2011; Crabtree & Lange, 2011; Stelten & Cooper, 2012; Arce et al., 2013; Waters & Lange, 2013; Howe et al., 2014; Frey & Lange, 2011; Muir et al., 2014; Waters et al., 2015; Grocke et al., 2016; Crabtree & Waters, 2017; Waters & Frey, 2018
arc front	0.96 (0.81)	peridotite xenoliths	47	sp-oxybarometry	$fO_2$ at T and 0.6GPa. Mattioli & Wood, 1988; and Wood & Virgo, 1989; with $aFe_3O_4$ from Sack & Ghiorso, 1991a, 1991b; <a href="http://melts.ofm-research.org/CalcForms/index.html">http://melts.ofm-research.org/CalcForms/index.html</a> ; Temperature from spinel-olivine Fe-Mg exchange thermometer of Li et al., 1995	Between about +0.6/-1.0 and $\pm 0.2$ depending on spinel $Fe^{3+}/\Sigma Fe$ ratio of spinel (see Methods Appendix and Davis et al., 2017)***	see Davis et al., 2017; and Birner et al., 2017; for discussions of a-X model choices	Wood & Virgo, 1989; Canil, 1990; Brandon & Draper, 1996; Parkinson et al., 2003; Bénard et al., 2018

(continued overleaf)

**Table 3.1** (Continued)

Tectonic setting	$\delta QFM$ (s)	Lithology	n	Method	Activity-composition models and other method notes	Method error in $fO_2$ in log units	Notes	Data included
forearc	0.22 (0.75)	trench wall peridotite and peridotite xenoliths	64	sp-oxybarometry	$fO_2$ at T and 0.6 GPa. Mattioli & Wood, 1988; and Wood & Virgo, 1989; with $aFe_3O_4$ from Sack & Ghiorso, 1991a, 1991b; <a href="http://melts.ofm-research.org/CalcForms/index.html">http://melts.ofm-research.org/CalcForms/index.html</a> ; Temperature from spinel-olivine Fe-Mg exchange thermometer of Li et al., 1995	Between about +0.6/-1.0 and $\pm 0.2$ depending on spinel $Fe^{3+}/\Sigma Fe$ ratio of spinel (see Methods Appendix and Davis et al., 2017)***	see Davis et al., 2017; and Birner et al., 2017; for discussions of a-X model choices	Parkinson & Pearce, 1998; Pearce et al., 2000; Birner et al., 2017
plume	0.10* (0.71)	basalt pillow glass	334	XANES	at 1 atm and 1200°C. Kress & Carmichael, 1991	0.59	Studies using the standard glasses of Cottrell et al., 2009, are recalculated using the $Fe^{3+}/Fe^{2+}$ ratios reported by Zhang et al., 2018	Brounce et al., 2017; Moussallam et al., 2014; Helz et al., 2017; Moussallam et al., 2016; Shorttle et al., 2015; Hartley et al., 2017; Moussallam et al., 2019
plume	-0.25 (0.55)	lavas	47	mag-ilm pairs	$fO_2$ at T recorded and 1 atm. Ghiorso & Evans, 2008	0.25**	passes Bacon & Hirschmann, 1988, test for equilibrium	Carmichael, 1967a,b; Anderson & Wright, 1972; Wolfe et al., 1997; Hasse et al., 1997; Gunnarsson et al., 1998; Beier et al., 2006; Genske et al., 2012; Portnyagin et al., 2012
plume	0.82 (1.40) at 0.6 GPa and 0.10 (1.42) at 2.5 GPa	peridotite and pyroxenite xenoliths	143	sp-oxybarometry	$fO_2$ at T and 0.6 GPa. Mattioli & Wood, 1988; and Wood & Virgo, 1989; with $aFe_3O_4$ from Sack & Ghiorso, 1991a, 1991b; <a href="http://melts.ofm-research.org/CalcForms/index.html">http://melts.ofm-research.org/CalcForms/index.html</a> ; Temperature from spinel-olivine Fe-Mg exchange thermometer of Li et al., 1995	Between about +1.2/-2.0 and $\pm 0.4$ depending on spinel $Fe^{3+}/\Sigma Fe$ ratio of spinel (see Methods Appendix and Davis et al., 2017)***	see Davis et al., 2017; and Birner et al. 2017; for discussions of a-X model choices	Abu El-Rus et al., 2006; Bonadiman et al., 2005; Davis et al., 2017; Grégoire et al., 2000; Hauri & Hart, 1994; Kyser et al., 1981; Neumann, 1991; Neumann et al., 1995; Neumann et al., 2002; Ryabchikov et al. 1995; Sen, 1987; Sen, 1988; Sen & Leeman, 1991; Sen & Presnall, 1986; Tracy, 1980; Wasilewski et al., 2017; Wulff-Pedersen et al. 1996

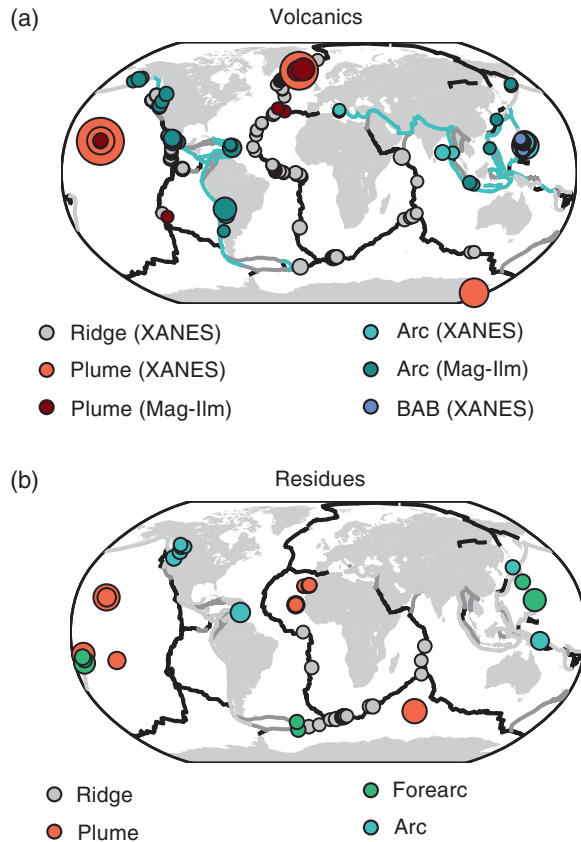
Note: \*Authors of these studies infer higher  $fO_2$  for primitive, near primary, melts based on these data: Mauna Kea >QFM 0.6 (Brounce et al., 2017); Kilauea QFM +0.4 to 0.7 (Helz et al., 2017, Moussallam et al., 2016); Iceland ~QFM + 0.4 (Shorttle et al., 2015; Hartley et al., 2017); Erebus ~QFM + 1.4 (Moussallam et al., 2014); Canary Islands ~QFM + 1.0 (Moussallam et al., 2019)

Note: \*\*Magnetite-ilmenite oxygen barometry errors reflect the average residual of model calculations and the calibration dataset: (Chiroso & Evans [2008] oxygen barometer-derived  $fO_2$  – known  $fO_2$  from calibration dataset), presented in supplemental material of Waters & Lange (2016)

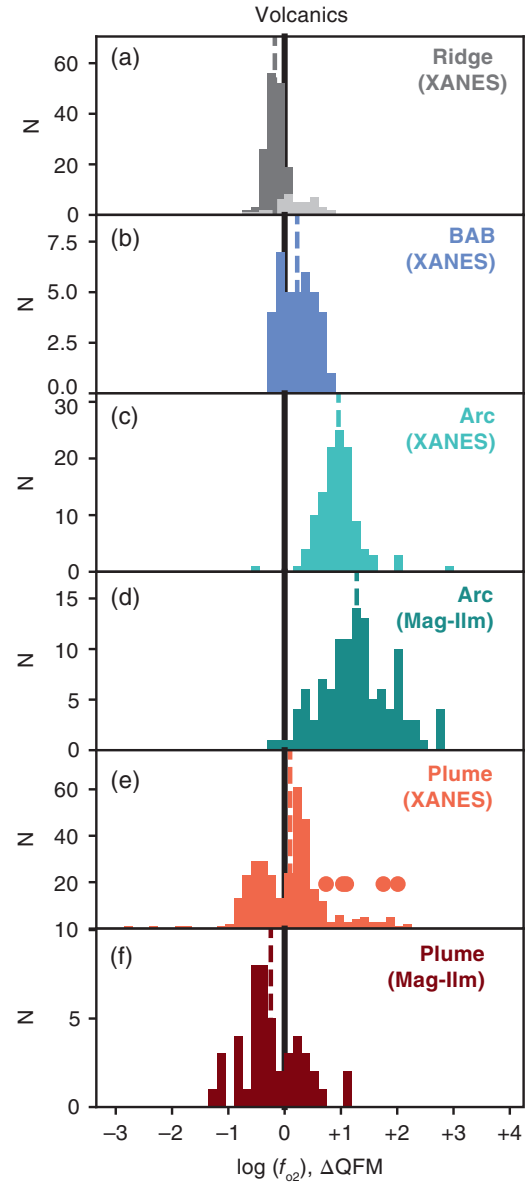
Note: \*\*\*Uncertainty in  $fO_2$  calculated from spinel oxybarometry is asymmetrical and decreases in magnitude as  $Fe^{3+}/\Sigma Fe$  ratio of spinel increases. Spinels that have  $Fe^{3+}/\Sigma Fe = 0.05$  have an uncertainty in log  $fO_2$  at the high end listed and those with  $Fe^{3+}/\Sigma Fe \geq 0.4$  at the low end. Hotspot residues, except four from Davis et al. (2017), are samples with spinel  $Fe^{3+}/\Sigma Fe$  ratios determined without Mössbauer correction standards, which roughly doubles uncertainty compared to corrected analyses (Davis et al., 2017).

lithologies offer opportunities for oxybarometry. We begin with the volcanics.

Early estimates based on wet chemistry and magnetite–ilmenite pairs indicated that mid-ocean ridge basalts (MORBs) record  $fO_2$ s similar to QFM (Carmichael & Ghiorso, 1986; Haggerty, 1976). However, upon reexamining data from the literature compiled by Haggerty (1976), we found only one sample with multiple pairs of magnetite and ilmenite in equilibrium at magmatic temperatures according to Bacon and Hirschmann (1988), and that sample (15.6m cooling unit from DSDP Leg34: site 319A) records QFM+0.16 ( $\pm 0.1$ ) at 1232 ( $\pm 37$ )°C (Mazzullo & Bence, 1976). Subsequent wet chemical work found that MORBs record  $fO_2$ s low enough to suggest graphite is a stable phase in the MORB source (i.e.,  $\sim$ QFM-1, Christie et al., 1986), but more recent wet-chemical work and Fe K-edge XANES analyses have revised average MORB  $fO_2$  estimates back upwards to QFM (Bezoz & Humler, 2005; Cottrell & Kelley, 2011; O'Neill et al., 2018; Zhang et al., 2018). Five recent studies determine  $Fe^{3+}/\Sigma Fe$  ratios spectroscopically by XANES to determine the  $fO_2$  of average MORB



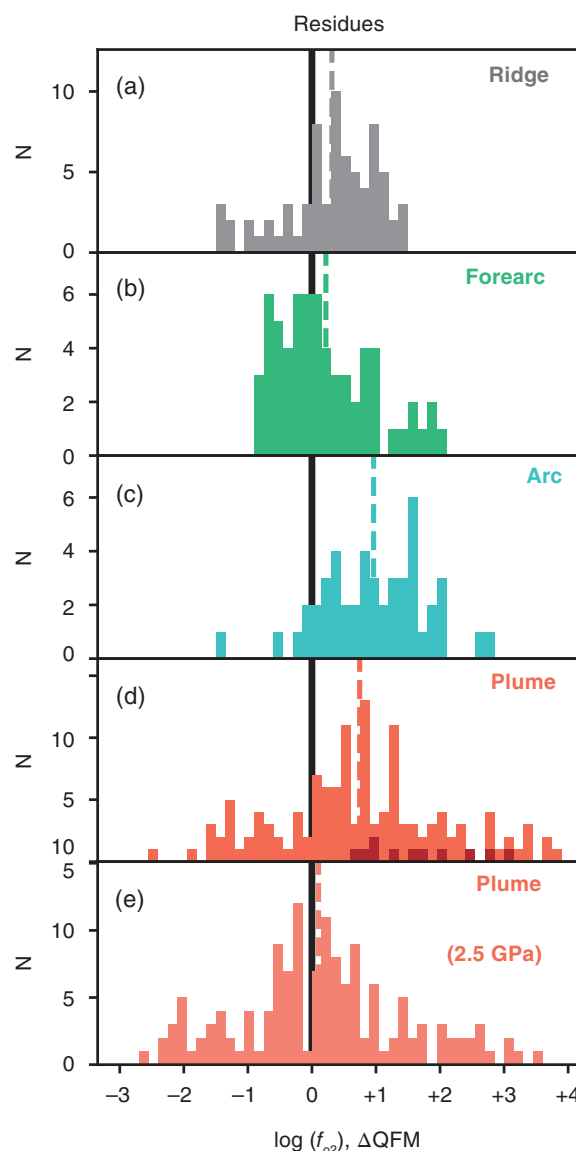
**Figure 3.1** Locations of samples compiled in this study as a function of tectonic setting, lithology, and methodology. Symbol size scales linearly with the number of samples at a given locality.



**Figure 3.2** Distribution of  $fO_2$  recorded by volcanics globally in different tectonic settings and by multiple methods of oxybarometry. We have recalculated the  $fO_2$  recorded by each sample based on the reported chemical analyses except for the separate light gray dataset in panel (a), which are the observations as reported by O'Neill et al. (2018). The O'Neill et al. (2018) dataset was collected using a different set of primary standards, as described in our methods appendix. Vertical, dashed lines reflect calculated average values of  $fO_2$ . Note that volcanics in (e) include plume-affected ridge segments, which cause them to record bimodal  $fO_2$ ; the  $fO_2$ s inferred for primitive plume magmas are higher than the average and we represent each plume's primitive magma  $fO_2$  as a filled orange circle (as reported by those authors). See Table 3.1 and text for details.

(Fig. 3.1, Fig. 3.2a) (Birner et al., 2018; Cottrell & Kelley, 2011; Le Voyer et al., 2015; O'Neill et al., 2018; Zhang et al., 2018). Determinations for 166 MORB glasses that use the calibration of Zhang et al. (2018) find a narrow distribution around QFM  $-0.17 \pm 0.15$  (all uncertainty is 1 standard deviation [ $\sigma$ ] unless otherwise noted). Determinations for 42 MORB using the calibration of Berry et al. (2018) by O'Neill et al. (2018) return a mean of QFM  $+0.19 \pm 0.36$ . It is notable that O'Neill et al. (2018)'s corresponding  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios for average MORB are *lower* by  $\sim 0.04$  than those from the global survey of Zhang et al. (2018), despite their equation to higher  $f\text{O}_2$ . The difference stems from O'Neill et al. (2018)'s application of a new compositional parameterization of  $f\text{O}_2$ , which we choose not to apply in this study (see Methods Appendix for a description and assessment of parameterizations). The important point for our purpose here is that, regardless of the value of the  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratio of natural MORB, the Fe-XANES spectra of natural MORB glasses resemble the spectra of experimental MORB-composition glasses equilibrated at  $f\text{O}_2$  similar to the QFM buffer (see Methods Appendix, Fig. S1), and there is general agreement among all recent spectroscopic studies that MORB glasses record QFM. The  $f\text{O}_2$ s recorded by average MORBs (7.58 wt.% MgO, Gale et al., 2013b) will be maxima with respect to the  $f\text{O}_2$  of the mantle from which they derive, because  $\text{Fe}^{3+}$  is moderately incompatible during low-pressure fractional crystallization and average MORBs are not primary melts of the mantle ( $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios increase by 0.03 as MgO falls from 10 to 5 wt.%; Cottrell & Kelley, 2011).

Oxybarometry of mid-ocean ridge peridotites has only been investigated in two studies (Birner et al., 2018 and Bryndzia & Wood, 1990) and in a handful of localities (Fig. 3.1). Global ridge peridotites record  $f\text{O}_2 = \text{QFM} + 0.31 (\pm 0.73)$ , but we note that more than half of these data derive from a single ridge segment (Fig. 3.1, Fig. 3.3a). Birner et al. (2018) found that  $n=41$  peridotites dredged from the Southwest Indian Ridge (SWIR) record QFM  $+0.61 (\pm 0.63)$  at 0.6 GPa and the closure temperature of olivine-spinel exchange. This is significantly higher than the  $f\text{O}_2$  recorded by basalts on the same segment ( $p\text{-value} < 0.01$ ); however, the discrepancy disappears once the peridotites' conditions of last equilibration with basalt are considered (Birner et al., 2018). The method of projecting peridotite  $f\text{O}_2$  to the PTX conditions of last equilibration with basalt considers three sub-solidus reactions that may alter the  $f\text{O}_2$  recorded by the rock: Mg-Fe exchange between olivine and spinel, Al-Cr exchange between spinel and orthopyroxene, and a Tschermak reaction that produces spinel at the expense of olivine and Al-rich orthopyroxene during cooling. Although a dearth of knowledge as to ferric iron partitioning behavior between spinel and pyroxenes during cooling leads to



**Figure 3.3** Distribution of  $f\text{O}_2$  recorded by mantle lithologies (peridotites and olivine-orthopyroxene-spinel-bearing pyroxenites) globally in different tectonic settings. We have recalculated the  $f\text{O}_2$  recorded by each sample at 0.6 GPa (2.5 GPa in [e]) and temperature recorded by spinel-olivine thermometry using the methodology of Birner et al. (2018) and Davis et al. (2017) based on the reported chemical analyses. All samples are peridotites except for (d) where the overlain histogram in red are pyroxenites. We caution against overinterpreting the wide range of xenolith  $f\text{O}_2$ s recovered at plumes due to (i) the near absence of samples from this setting characterized using Mössbauer-characterized spinel standards or Mössbauer spectroscopy; (ii) uncertainty in the barometry and metamorphic history of these samples (which will alter the  $f\text{O}_2$  they record); and (iii) limited data by which we may judge the extent to which these lithospheric xenoliths record ridge versus plume  $f\text{O}_2$ .



significant uncertainty in the magnitude of projection ( $\pm 0.5$  log units, Birner et al., 2018), the direction of the model is to decrease recorded peridotite  $fO_2$  values when projecting back to high temperature-pressure source conditions. This projection thus brings peridotite  $fO_2$  values into closer agreement with basalt  $fO_2$  values, suggesting that  $fO_2$  values recorded by peridotites, without these corrections, may systematically overestimate the redox conditions of MORB-source mantle (Birner et al., 2018).

We highlight that peridotites along SWIR record five times greater range in  $fO_2$  when compared to basalts dredged from the same segment. On the global scale, Bryndzia and Wood (1990) investigated the  $fO_2$  of 35 ridge peridotites from 12 localities. When filtered to exclude four samples from two anomalous locations (the sub-aerial St. Paul's Rocks and the tectonically complex Mid-Cayman Rise), and recalculated according to the methods presented here, this sample set records  $fO_2$  of QFM  $-0.08 \pm 0.68$  and spans a range of nearly 2.5 orders of magnitude in  $fO_2$  (Birner et al., 2018). When comparing Fig. 3.2a and 3.3a, we observe that global mid-ocean ridge volcanics display low variance relative to ridge peridotites. These limited data suggest that basalts may homogenize kilometer-scale redox heterogeneity in the upper mantle (Birner et al., 2018). Globally, ridge peridotites calculated at 0.6 GPa and the temperature of olivine-spinel closure record average  $fO_2$ s about half a log unit higher than basalts calculated at 1 bar and 1200 °C. Because we have not attempted here to account for subsolidus processes in the peridotites globally, comparisons between the two distributions should not be overinterpreted. A more comprehensive global peridotite dataset is required to evaluate the response of mantle residues to melt extraction and subsolidus re-equilibration.

**Arcs and Back Arcs.** Subduction influences the composition of mantle melts and arc volcanics, generating continental crust in the process (e.g., Elliott et al., 1997; Gill, 1981; Grove et al., 2012; Kelemen et al., 2003; Kelemen et al., 2007; Osborn, 1959; Plank & Langmuir, 1988; Stolper & Newman, 1994; Turner & Langmuir, 2015; Zimmer et al., 2010). Both melts and mantle lithologies offer opportunities for oxybarometry. We begin with the volcanics.

Seminal contributions by Carmichael (1991) and Frost and Lindsley (1992) surveyed the  $fO_2$ s recorded by arc rocks using wet-chemistry and magnetite-ilmenite pairs, respectively, and found that arc rocks record  $fO_2$ s up to several orders of magnitude higher than MORBs. Our compilation of 5 XANES spectroscopic studies ( $n=119$  samples, Figure 3.2c) of olivine-hosted melt inclusions and submarine pillow glasses shows that arc basalts record, on average, QFM  $+0.96 (\pm 0.39)$ . One set of outliers from Cerro Negro record QFM  $+4.75 (\pm 0.40)$  (Gaetani et al., 2012), but spectra from these hydrous samples have

suffered from radiation-induced beam damage (Cottrell et al., 2018, Gaetani, pers. comm.) and are not included in our statistical analysis. Nearly 90% of samples with XANES measurements erupted through the thin crust ( $\sim 25$  km, Takahashi et al., 2007) of the active Mariana arc front (Fig. 3.1a), and thus there is significant location bias in this dataset.

Globally, magnetite-ilmenite pairs, from 114 arc lavas sampling 11 different arcs, record QFM  $+1.28 (\pm 0.64)$  (Figure 3.2d; see methods appendix and the online data library associated with this contribution, Cottrell et al., 2021, for citations). These samples contain Fe-Ti oxides with compositions that record a range of temperatures (700–1085 °C), span a wide range of compositions (basaltic andesite to rhyolite) but are predominantly dacitic, and erupt through crust ranging from 25 to 66 km thick.

The mean  $fO_2$  recorded by olivine-hosted melt inclusions and submarine arc-front glasses ( $\Delta QFM = 0.96 \pm 0.39$ ,  $n=119$ ) is slightly lower than that recorded by magnetite-ilmenite pairs ( $\Delta QFM = 1.28 \pm 0.64$ ,  $n=114$ ) at the 95% confidence level ( $t_{\text{statistic}} = 4.6$ ,  $t_{\text{critical}} = 2.0$ , degrees of freedom [DF] = 186,  $p\text{-value} < 0.001$ ). (When we compare distribution means in this contribution, we will always apply a two-sample student's t-test with  $\alpha = 0.05$  [Krzywinski & Altman, 2013] for samples of unequal variance.) We caution that the datasets are not directly comparable because of the limited geographic distribution of the melt inclusion and submarine glass dataset; because there are no samples in common between the two distributions; and because the melt inclusions may reflect magma compositions that precede magnetite and ilmenite saturation. Thus, to first order, our global result is not inconsistent with the results of Waters and Lange (2016) and Crabtree and Lange (2011) who found congruence when they compared magnetite-ilmenite oxybarometry to wet-chemical titration on the same suite of very fresh aphyric lavas.

A more direct comparison can be made between the olivine-hosted melt inclusions and submarine glasses erupted along the active Mariana Arc, and back arc basin (BAB) glasses erupted at depth along the associated back arc spreading center: the Mariana Trough. Both datasets apply the same method (XANES) to arrive at  $fO_2$  estimates, and both sample suites comprise basaltic to basaltic andesite glasses representing similar stages of differentiation in thin crust (similar MgO). The Mariana arc front samples record  $fO_2$ s that are on average 0.73 log units higher than the Mariana trough samples (Mariana arc: QFM  $+0.95 \pm 0.36$  for  $n = 107$  vs Mariana trough: QFM  $+0.22 \pm 0.30$  for  $n=37$ , respectively) (Brounce et al., 2014; Kelley & Cottrell, 2009).

Another direct comparison can be made between submarine basalts in ridge (MORB) and BAB tectonic settings. Here we find that BAB from the Mariana trough ( $n=37$ ) record significantly higher  $fO_2$ s than MORB

globally ( $n=160$ ) by 0.4 log units ( $t_{\text{statistic}} = 7.8$ ,  $t_{\text{critical}} = 2.0$ , degrees of freedom  $[df] = 41$ ,  $p\text{-value} \ll 0.001$ ). This comparison is particularly germane for inferring the effect of subduction on mantle  $f\text{O}_2$  because submarine back-arc ridges and mid-ocean ridges are tectonically similar and differences in their melt chemistry can be largely attributed to the influence of subduction (Stolper & Newman, 1994). As indices of subduction influence in Mariana trough lavas go from negligible to significant (e.g., as  $\text{H}_2\text{O}$  contents and the ratios of fluid mobile to fluid immobile incompatible trace elements increase),  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios (and  $f\text{O}_2$ s) also increase (Brounce et al., 2014; Kelley & Cottrell, 2009, 2012). In the Marianas, volcanics erupted over the course of the arc's maturation also record increasing  $f\text{O}_2$  with increasing subduction influence. Modern arc tholeiites record similar  $f\text{O}_2$ s to the boninites that erupted during the early stages of slab influence on the mantle wedge; and both lithologies are more oxidized than the forearc basalts that tapped the mantle prior to slab influence (Brounce et al., 2021; Brounce et al., 2015). The volatile and trace element signals of subduction appear intimately tied to elevated  $f\text{O}_2$ s in space and in time.

Mantle lithologies recovered from arc settings comprise primarily forearc and arc peridotites. Forearc peridotites are exposed on trench walls and may sample ancient lithospheric mantle (Parkinson & Pearce, 1998), mantle wedge metamorphosed by the subducting slab (Fryer et al., 1985), or processes associated with subduction initiation (Birner et al., 2017). In comparison, arc peridotites rapidly ascend to the surface as xenoliths encased within their basaltic hosts at arc front volcanoes. The mean  $f\text{O}_2$  recorded by forearc peridotites is statistically indistinguishable from the mean  $f\text{O}_2$  recorded by ridge peridotites ( $t_{\text{statistic}} = 0.73$ ,  $t_{\text{critical}} = 2$ ,  $df = 131$ ,  $p\text{-value} = 0.47$ ) (Fig. 3.3). As discussed by Birner et al. (2017), this result contrasts with Parkinson and Pearce (1998)'s study of forearc peridotites from the Izu-Bonin subduction zone, primarily because we apply the spinel activity model of Sack and Ghiorso (1991) instead of Nell and Wood (1991). Yet, consistent with Parkinson and Pearce (1998), Birner et al. (2017) show that peridotites that have interacted with slab-influenced melts do yield elevated  $f\text{O}_2$ . This influence is additionally evident in the distribution of  $f\text{O}_2$  recorded by arc xenoliths from five studies (Table 3.1), which lies significantly higher, by 0.65 log units, than ridge peridotites ( $t_{\text{stat}} = 4.4$ ,  $t_{\text{crit}} = 2.0$ ,  $df = 90$ ,  $p\text{-value} \ll 0.001$ ) or forearc peridotites. Another unique characteristic of sub-arc peridotites is the extended range of melt extraction they record. Spinel Cr#, commonly taken as a proxy for melt extraction, extends to much higher values ( $> 60$ ) in sub-arc peridotites than in ridge peridotites. This extended range of melt extraction may provide an opportunity to investigate the relationship between extent of melting and  $f\text{O}_2$ . For

example, Benard et al. (2018b) found a weak positive correlation ( $p\text{-value} > 0.06$ ) between  $f\text{O}_2$  and modal orthopyroxene, which they interpreted as evidence of  $f\text{O}_2$  falling with melt extraction; however, the positive correlation between spinel Cr# and  $f\text{O}_2$  in these same samples suggests the relationship between  $f\text{O}_2$  and melt extraction may be more complicated. No correlation exists between  $f\text{O}_2$  and orthopyroxene mode or spinel Cr# in the Tonga peridotites of Birner et al. (2017). More work is needed to better constrain the effects on  $f\text{O}_2$  of extracting melt from the mantle.

**Plumes.** Mantle plumes are thermal upwellings that impinge on the lithosphere (French & Romanowicz, 2015; Montelli et al., 2006; Sleep, 1992). Capable of generating low degree mantle melts that more ably sample mantle heterogeneity, mantle plumes can produce ocean island basalts (OIB) (Dasgupta et al.; McKenzie & Onions, 1983; Stracke et al., 2005) and xenoliths wrenched from the lithospheric mantle (Frey & Roden, 1987). Both melts and xenoliths at ocean islands offer opportunities for oxybarometry; however, it remains challenging to interpret the relationship between lithospheric mantle peridotites and OIB. We begin with the volcanics.

Melt inclusions and submarine basalts erupting at and around the mantle plumes of Hawaii, Erebus, Iceland, and the Canary Islands record, on average, QFM +0.1 (7 XANES spectroscopic studies with  $n = 334$  samples; Table 3.1, Fig. 3.2e). The Fe- XANES-based  $f\text{O}_2$  in this case is higher than the record of magnetite-ilmenite pairs ( $n=47$ ) by 0.35 log units ( $t_{\text{statistic}} = 3.8$ ,  $t_{\text{critical}} = 2$ ,  $df = 69$ ,  $p\text{-value} = 0.003$ ); however, we emphasize that these datasets have no samples in common. There is no meaningful difference between the  $f\text{O}_2$ s recorded by OIBs and MORBs. In the case of OIB volcanics, most XANES studies have either interrogated a geographic gradient in  $f\text{O}_2$  (e.g., Shorttle et al., 2015) or the effect of differentiation (crystallization and degassing) on  $f\text{O}_2$  (e.g. Brounce et al., 2017; Helz et al., 2017; Moussallam et al., 2016; Moussallam et al., 2014). We therefore observe a bimodal distribution of  $f\text{O}_2$  recorded by plume-affected glasses (Fig. 3.2e). Glasses erupted along mid-ocean ridges that approach plumes, and glasses affected by degassing, record lower  $f\text{O}_2$ , while primitive and relatively undegassed melt inclusions record higher  $f\text{O}_2$  (Fig. 3.2e, and see discussion). The authors of the detailed studies that have interrogated the  $f\text{O}_2$  of plumes and plume-affected ridges have inferred plume mantle source  $f\text{O}_2$ s anywhere from 0.4 to 2 log units higher than the average  $f\text{O}_2$  recorded by the volcanics (filled circles in Figure 3.2e). In all cases, the authors have suggested that the mantle sources of these OIBs are more oxidized than those of MORB, and that this may be due to incorporation of recycled components (e.g. Brounce et al., 2017; Moussallam

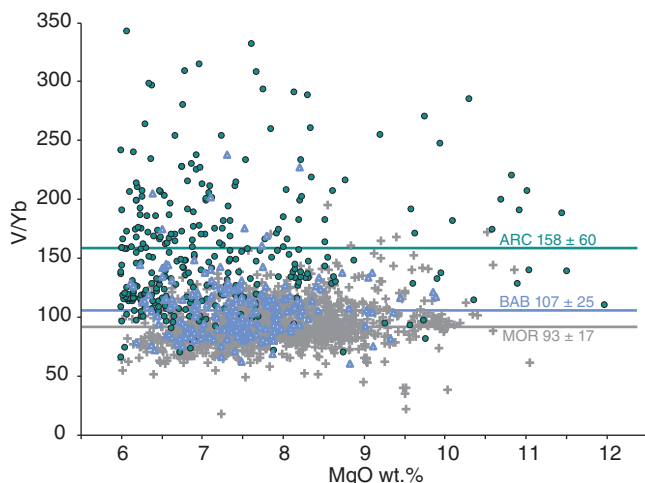
et al., 2019; Helz et al., 2017; Moussallam et al., 2016; Moussallam et al., 2014; Shorttle et al., 2015). Investigators have drawn such inferences by projecting the glass  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios along compositional trends (e.g., to more primitive, less degassed, and more enriched compositions) or geographic trends (e.g., along a ridge toward a plume). We discuss some of these projections in greater detail in Section 3.4.1.1.

We have additionally compiled data from 13 studies to calculate the  $f\text{O}_2$  of 143 ocean island xenoliths. Unlike all of the ridge peridotites and most of the arc peridotites, none of the published spinel compositions, save for Davis et al. (2017), were obtained using spinel standards with  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios independently characterized. Without using standards to correct spinel  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios, uncertainties in  $\log f\text{O}_2$  are roughly double those of samples calculated from corrected spinel  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios (Davis et al., 2017, see Methods Appendix and Table 3.1). Despite, or because of, this limitation, we see that ocean island xenoliths record a wide range of  $f\text{O}_2$ , from QFM  $-2$  to nearly QFM  $+4$  with a mean equal to QFM  $+0.82$  ( $\pm 1.40$ ). This is a much broader range, extending to lower  $f\text{O}_2$ , than compiled by Ballhaus (1993); the mean is within error of that compiled by Mallmann and O'Neill (2007), though again the variance is greater in the present compilation. Of the 143 xenoliths compiled here, 11 were identified by the original authors as pyroxenites (Sen, 1987; Tracy, 1980) which record a more oxidized mean  $f\text{O}_2$  of QFM  $+1.44$  ( $\pm 0.63$ ) than the whole set of OIB xenoliths (see red histogram overlain on Fig. 3.3d). The range of  $f\text{O}_2$  recorded by OIB lavas falls within the range recorded by ocean island xenoliths; however, we cannot draw a genetic relationship between all lithospheric mantle xenoliths and the mantle melts that exhume them at plumes (compare Fig. 3.2e to 3.3d). Presumably, many of these xenoliths represent lithospheric mantle that has experienced limited chemical interaction with plume-derived melts. Others are likely products of melt-rock reaction between lithospheric peridotite and plume-generated melts. The pyroxenite xenoliths were especially likely to have been derived in this way (e.g., Sen & Leeman, 1991), but it is unclear how many of the peridotites were also influenced by plume-sourced melts. There is another caveat; we do not know the equilibration pressure at the closure temperature of these plume xenoliths. At ridges, we can reasonably infer pressure from peridotite thermometry because geothermal gradients are reasonably well-characterized. That is not the case in plume settings, where thermal gradients are radial as well as vertical (e.g., Farnetani & Hofmann, 2010). In Figure 3.3e we demonstrate how equilibration at 2.5 GPa, instead of 0.6 GPa, would shift  $f\text{O}_2$  down by two thirds of a log unit. This illustrates our community's need for better peridotite mineral barometry.

We venture that a more appropriate comparison might be drawn between peridotitic ocean island xenoliths and ridge peridotites. Both may initiate as residues of melting at ridges, with the former transiting and cooling prior to interacting with a mantle plume. The range of  $f\text{O}_2$ s recorded by ocean island xenoliths encompasses the range of ridge peridotites but skews to higher  $f\text{O}_2$ s by 0.37 log units if we hold pressure constant at 0.6 GPa ( $t_{\text{stat}} = 2.6$ ,  $t_{\text{crit}} = 2.0$ ,  $\text{df} = 211$ ,  $p\text{-value} = 0.01$ ). Notably, spinel-olivine Fe-Mg exchange (Li et al., 1995) records higher temperatures in the ocean island xenoliths than in the ridge peridotites. This difference in temperature could be the result of heating of the oceanic lithosphere beneath oceanic islands by the plume (Ballhaus, 1993), or it could result from exhumation of these xenoliths from greater depths than the depth of last equilibration experienced by ridge peridotites. In the former case, temperature-dependent exchange reactions suggest that a mantle parcel preserving a record of hotter conditions should record lower  $f\text{O}_2$  than a parcel at the same pressure that records cooler conditions (Birner et al., 2018). Consideration of these subsolidus reactions would thus predict ocean island xenoliths to be more reduced than ridge peridotites, in contrast to what we observe. If this interpretation is correct, then the difference in  $f\text{O}_2$  between ridge peridotites and OIB xenolith source mantle prior to plume heating is even greater than the 0.6 GPa plots in Figure 3.3 suggest, perhaps driven by the interaction of some of these xenoliths with oxidized plume melts. In the latter case, changes in  $f\text{O}_2$  due to changes in pressure would additionally have to be accounted for to make a direct comparison between ridge peridotites and OIB xenoliths. If no changes in mineral composition or mode are considered, the lower average  $f\text{O}_2$  calculated assuming a higher pressure of equilibration (Fig. 3.3) suggests that if OIB xenoliths do generally sample deeper portions of the lithosphere than ridge peridotite, then average  $f\text{O}_2$  of the two are comparable. While exchange reactions and modal changes during ascension and cooling may complicate this relationship, at this time, the data do not suggest that xenoliths recovered from plumes significantly differ in their  $f\text{O}_2$  compared to peridotites recovered in the ridge setting. Constraints on pressure and effects of temperature on the  $f\text{O}_2$  recorded by peridotites below their solidus remain poorly understood, and further work is needed to clarify the  $f\text{O}_2$  signature of xenoliths entrained within plume lavas.

### 3.3.2. V/Yb Concentrations

V/Yb ratios range from 17–195 in MORB, 60–238 for BABB, and 65–422 in arcs (excluding one arc basalt with a ratio of  $> 800$ ). We find average V/Yb concentrations in each tectonic setting that are all statistically distinct ( $p\text{-values} \lll 0.001$ ) with V/Yb of MORB ( $93 \pm 17$ )



**Figure 3.4** V/Yb ratios of ridge (gray “+” symbols, Gale et al., 2013), back-arc (blue triangles, Gale et al., 2013), and arc lavas (teal circles, Turner & Langmuir, 2015) as a function of weight percent MgO. We filtered each published data compilation for 6 wt.% < MgO < 12 wt.% and for Dy/Yb < 2 (Laubier et al., 2014). See text for details.

< BABB ( $107 \pm 25$ ) < arcs ( $158 \pm 60$ ). We illustrate this in Figure 3.4 with a plot of V/Yb ratios against MgO concentrations in ridge, back-arc, and arc settings. Translating trace element ratios measured in glass (magmatic liquid) to the oxygen fugacity of the source rock (residue) depends on having accurate, composition-dependent, mineral-melt partition coefficients, an accurate knowledge of the source composition, and an accurate melting model (e.g., Canil, 1997; Lee et al., 2003; Lee et al., 2005; Mallmann & O’Neill, 2009; Mallmann et al., 2019). Mallmann and O’Neill (2013), Nicklas et al. (2019), Mallmann et al. (2019), Bucholz and Kelemen (2019), and others have discussed the difficulty in translating V/Sc ratios or olivine-melt partition coefficients into source  $fO_2$ s. For example, the  $fO_2$  of modern MORB, or Archean mantle, based on V partitioning is up to a log unit *higher* than that implied by modern MORB  $Fe^{3+}/\Sigma Fe$  ratios (Mallmann and O’Neill, 2013; Nicklas et al., 2019). For these reasons, we do not calculate  $fO_2$  for each tectonic setting based on the V/Yb ratio, but simply infer the relative oxygen fugacity of each tectonic setting based on the premise that basalt V/Yb will rise with the  $fO_2$  of the mantle source that generated the basalt. Under these assumptions, it is clear that  $fO_2$  ridges <  $fO_2$  back arcs <  $fO_2$  arcs.

### 3.4. DISCUSSION

Our compilation and reprocessing of analytical data from the literature yields a synoptic picture of the  $fO_2$ s recorded by volcanic and mantle rocks across tectonic

settings. Some three decades have passed since the seminal compilations from last century (e.g., Ballhaus et al., 1991; Carmichael, 1991; Christie et al., 1986; Frost & Lindsley, 1992; Wood et al., 1990). The volume of data and geographic coverage have increased tremendously and the analytical techniques and activity models have evolved; however, a key finding from those studies remains robust today. Volcanic and mantle rocks from arc settings record significantly higher  $fO_2$  than those from ridges. Recycling of oceanic crust and lithosphere back into the Earth at subduction zones generates arc volcanics and related mantle lithologies that record higher  $fO_2$  relative to those recovered from ridges. Additional work, particularly in forearc and back-arc settings, support this observation by showing that  $fO_2$  becomes elevated in proportion to the rock’s subduction affinity (Benard et al., 2018; Birner et al., 2017; Brounce et al., 2014; Brounce et al., 2021; Brounce et al., 2015; Kelley & Cottrell, 2009, 2012; Parkinson & Arculus, 1999). This remains true for the back-arc basin basalts erupted at pressures > 200 bar and through a comparable crustal column to normal MORB. Moreover, in both the ridge and arc settings, melts (lavas and tephra) and mantle (peridotites and pyroxenites) both record an offset in oxygen fugacity of similar magnitude between the two settings. While these observations are robust, the mechanism by which subduction generates more oxidized lavas and associated mantle lithologies remains a matter of debate and is beyond the scope of this contribution to review (e.g., Andreani et al., 2013; Benard et al., 2018; Canil & Fellows, 2017; Carmichael, 1991; Chin et al., 2018; Debret et al., 2014; Evans, this volume; Farner & Lee, 2017; Foden et al., 2018; Gaillard et al., 2015; Kelley & Cottrell, 2009; Lecuyer & Ricard, 1999; Lee et al., 2005; Mungall, 2002; Nebel et al., 2015; Parkinson & Arculus, 1999; Tang et al., 2018; Tollan & Hermann, 2019; Williams et al., 2004; Wood et al., 1990).

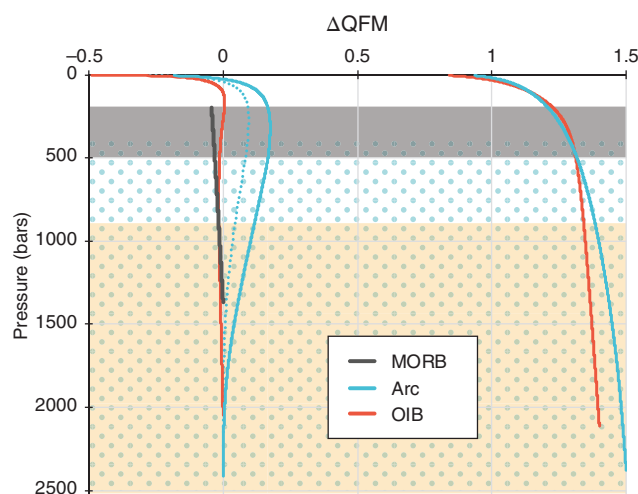
#### 3.4.1. Linking the $fO_2$ of Volcanics and Mantle Lithologies

Linking magmatic  $fO_2$  to melt residue  $fO_2$  and, ultimately, to the  $fO_2$  of the subsolidus convecting mantle presents a grand challenge to the fields of petrology, experimental petrology, and modeling. When the mantle first begins to melt at infinitesimally small melt fractions, the composition of residual silicate phases will not change significantly, and the  $fO_2$  of the unmelted, solid mantle source will impose  $fO_2$  on low degree partial melts (whether silicate melts or carbonated silicate melts), and set the melt’s  $Fe^{3+}/\Sigma Fe$  ratio. However, at some point during adiabatic ascent, the melt fraction will grow to an extent that the composition of the solid phases are themselves modified, and the  $fO_2$  of the assemblage

(solid + melt) changes. Examples of anticipated changes during melting that could affect  $f\text{O}_2$  include the exhaustion of reduced carbon or sulfur phases from the solid assemblage (Lee et al., 2012; Stagno et al., 2013), and an increase of the  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratio of spinel resulting from  $\text{Al}/\text{Fe}^{3+}$  exchange with the melt that favors concentrating  $\text{Fe}^{3+}$  in the spinel (Ballhaus et al., 1991; Davis & Cottrell, 2018). At this point, the  $f\text{O}_2$  of the mantle will change in ways that experiments and models have not yet elucidated. Indeed, experiments that investigate  $f\text{O}_2$  as a variable in the context of partially melting the mantle are nascent (Ballhaus et al., 1991; Davis & Cottrell, 2018; Sorbadere et al., 2018), and stand as a challenge for the future (see Section 3.5). However, once melt and residue separate, melt  $f\text{O}_2$  changes little relative to the QFM buffer during volatile-undersaturated adiabatic ascent (Kress & Carmichael, 1991). Thus, at ridges, near primary basaltic melts should serve as accurate proxies for average mantle source conditions (e.g., Carmichael, 1991); however, such accuracy may not extend to mantle rocks, and volcanic rocks from other settings.

Once melts become volatile saturated or begin to undergo assimilation-fractional crystallization processes within the crust, the relationship between mantle source and magmatic  $f\text{O}_2$  may become more tenuous. Here we briefly review processes that may modify melt  $f\text{O}_2$  signal from source to surface: degassing and crystal fractionation within thick crust.

**Degassing.** Observational studies that have investigated the relationship between degassing and magmatic  $f\text{O}_2$  have thus far observed reduction of melt  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios in response to degassing. For example, numerous XANES studies on natural glasses have captured the potential for sulfur degassing to reduce melt  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios (Brounce et al., 2014; Brounce et al., 2017; Hartley et al., 2017; Helz et al., 2017; Kelley & Cottrell, 2012; Moussallam et al., 2016; Moussallam et al., 2014; Moussallam et al., Shorttle et al., 2015). In order to gain further insight into the effect of C–O–H–S degassing on magmatic  $f\text{O}_2$ , we present results from the gas-melt equilibrium model D-Compress of Burgisser et al. (2015) (see Methods Appendix). Detailed explanations of how D-Compress treats  $f\text{O}_2$  during degassing can be found in Burgisser et al. (2015), Moussallam et al. (2016), and Brounce et al. (2017). A general feature of the model output is a prediction of modest changes in  $f\text{O}_2$  ( $< 0.2$  log units), both positive and negative, as degassing proceeds until pressures fall below  $\sim 250$  bar, at which point  $f\text{O}_2$  falls sharply in all tectonic settings (Fig. 3.5). D-Compress therefore predicts that the  $f\text{O}_2$  of MORB is negligibly affected by degassing (Fig. 3.5, gray line) owing to the fact that MORBs erupt at pressures greater than 200 bar and the dominant degassing volatile is, which has limited



**Figure 3.5** Progressive degassing of a C–O–H–S vapor in ridge, arc, and plume settings using the gas-melt equilibrium model D-Compress of Burgisser et al. (2015). For the model run shown by the dashed blue curve, we have set the solubility of  $\text{H}_2$  in silicate melt to zero; this assumption creates no resolvable difference for any of the other curves shown. For DCompress model details, see the Methods Appendix. Model runs marked OIB, Arc, and MORB are intended to mimic the degassing trajectories of typical magmas from each setting (see methods appendix for details). The OIB and arc scenarios were each run at QFM and near QFM +1.5 to demonstrate the impact of initial  $f\text{O}_2$  on degassing trajectory. Orange shaded field shows estimated entrapment pressures for olivine-hosted melt inclusions in OIB based on water and  $\text{CO}_2$  concentrations (Tucker et al., 2019). Teal stippled field shows minimum estimated entrapment pressures for olivine-hosted melt inclusions considering water concentrations alone (Plank et al., 2013), which will underestimate typical entrapment pressures. Gray shaded field shows eruption pressures for MORB, which are constrained by ridge depth.

power to shift magmatic  $f\text{O}_2$  so long as the MORB source is more oxidized than graphite saturation (Cottrell and Kelley, 2011). Degassing- $f\text{O}_2$  pathways at arcs and sub-aerial plume volcanoes have greater potential to shift  $f\text{O}_2$  because lavas and tephra can degas to 1 atmosphere total pressure. However, melt inclusions may be trapped at nearly any point along the degassing pathway, which may spare some arc and plume sample sets from recording strong modification. Typical water contents of arc melt inclusions yield a conservative estimate of entrapment pressures of 400–3000 bar (Plank et al., 2013). At these entrapment pressures, arc magmas with typical volatile concentrations may be slightly more or less oxidized, but within  $\sim 0.2$  log units of their source, depending on their initial  $f\text{O}_2$  (Fig. 3.5). The fact that arc melt inclusions become progressively reduced during degassing (e.g., Helz et al., 2017; Kelley & Cottrell, 2012; Moussallam et al., 2014; Moussallam et al., 2019) strongly indicates that

the arc source is significantly more oxidized than MORB (compare teal arc degassing pathways initiated at QFM vs QFM +1.5 in Figure 3.5).

The much higher ratios of sulfur to water in undegassed OIB magmas lead to a larger magnitude of reduction as degassing proceeds in OIB settings compared to arc settings, because the reducing effects of degassing ~2000 ppm S are not as strongly offset by the slightly oxidizing effects of degassing H<sub>2</sub>O, as is the case for H<sub>2</sub>O-rich arc magmas (Fig. 3.5, orange lines). The model predictions in Fig. 3.5 that link degassing to reduction are consistent with observations of natural glass and melt inclusion suites, as reviewed above, and implies that the  $fO_2$  recorded by plume-source glasses is typically a minimum (Brounce et al., 2017; Helz et al., 2017; Moussallam et al., 2019). Corroborating evidence is found when we compare the more primitive and less degassed plume glasses (orange circles, Fig. 3.2e) to magnetite–ilmenite oxybarometry in plume lavas (Fig. 3.2f). The latter record lower  $fO_2$  on average, and we speculate that this may reflect magnetite and ilmenite crystallization further along the liquid line of descent, after significant degassing. Further, if fractional crystallization acts to oxidize iron in typical plume lavas, its effect is either counterbalanced by degassing or is not on display here as we compare these two proxies. The caveat is that these are global compilations; Fig. 3.2e and 3.2f do not have samples in common, and we need targeted studies to untangle these competing effects.

If we look to the mantle for further insights about plume  $fO_2$ , we find additional evidence that plumes may be oxidized, but the story remains nuanced. Pyroxenite xenoliths from OIB localities have been interpreted as the products of extensive refertilization of the lithosphere by plume-derived melts (Sen & Leeman, 1991). The relatively oxidized  $fO_2$  recorded by these pyroxenite xenoliths provides further evidence that OIB source regions are more oxidized than the MORB source (Figure 3.3d). The opportunity to investigate the Fe<sup>3+</sup>/ΣFe ratios of submarine and melt inclusion suites from arcs and plumes holds great future promise for reconstructing primitive melt compositions from partially degassed samples.

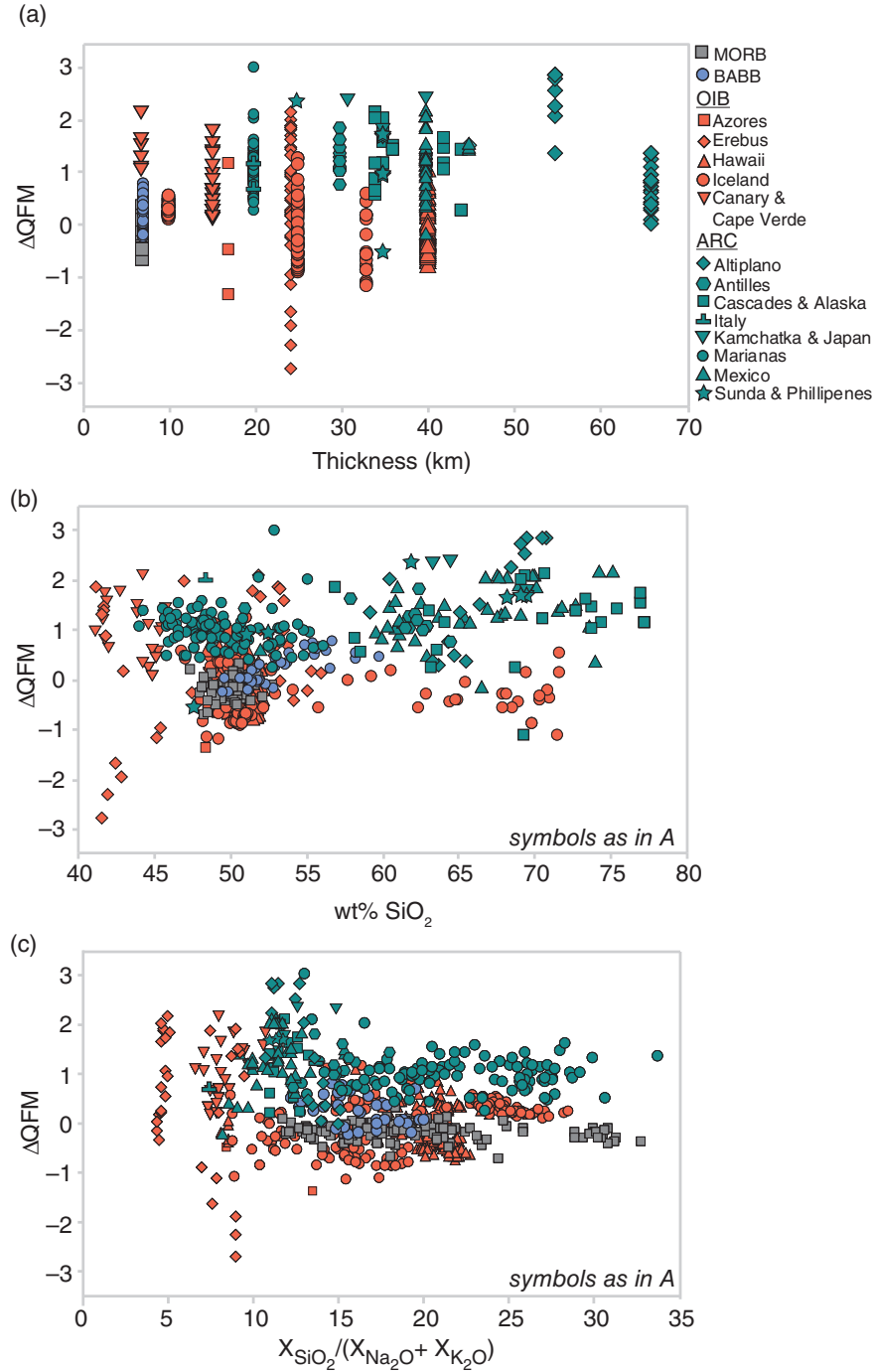
**Crystal Fractionation.** Cottrell and Kelley (2011) and numerous studies since (Birner et al., 2018; O'Neill et al., 2018; Shorttle et al., 2015), have shown how Fe<sup>3+</sup>/ΣFe ratios increase during low-pressure crystal fractionation by a few percent, and that the  $fO_2$  of MORB glass spans a smaller range of  $fO_2$  (e.g., Fig. 3.2a) than indicated by wet-chemistry. However, extensive crystal fractionation and crustal assimilation are commonly observed in magmas that transit thick arc crust, and this has been invoked to shift magmatic  $fO_2$  away from its mantle source (e.g., Chin et al., 2018; Grocke et al., 2016; Lee et al., 2005; Tang et al., 2018).

The dearth of  $fO_2$  studies on the rare basalts and olivine-hosted melt inclusions that transit the continental crust poses a challenge to the community. Insights can be gleaned, however, from extensive analytical work on magnetite–ilmenite pairs in more evolved arc rocks. In the arc crust, we observe that magnetite–ilmenite only precipitate once primary magmas have fractionated significant quantities of olivine and clinopyroxene (which remove Fe<sup>2+</sup> from the melt), and magnetite–ilmenite pairs in arc lavas record slightly higher  $fO_2$ s than primitive arc glasses, in accordance with this expectation (see Results, Table 3.1, and Fig. 3.2). Within the BABB suite, silica and  $fO_2$  do covary, although this relationship is demonstrably unrelated to crystal fractionation (Brounce et al., 2014). SiO<sub>2</sub> and  $fO_2$  covary because of two independent phenomena: melting more hydrous mantle yields primary magmas with higher SiO<sub>2</sub> concentrations (Kushiro, 1972) and melting mantle with more subduction influence yields primary magmas with higher  $fO_2$ s and also more water (Kelley & Cottrell, 2009).

Figure 3.6 shows all of the volcanic data we have compiled as a function of both crustal thickness (from 7 to nearly 70 kilometers), SiO<sub>2</sub> concentration (a proxy for crystal fractionation, ranging from ~45 to > 75 wt.%), and SiO<sub>2</sub>/Alkali ratios. We observe that magmas record  $fO_2$ s in excess of ~QFM +1 only when the crust is thicker than that found in the ridge setting. However, from volcanics erupted through ~25 km of oceanic crust to volcanics erupted through nearly 70 km of continental crust, we observe no global correlation between crustal thickness and  $fO_2$ . Neither do we observe a correlation between  $fO_2$  and silica content or SiO<sub>2</sub>/alkalis, within or among arcs. Figure 3.6 demonstrates that, to first order and on average, there is no simple relationship amongst the variables of crustal thickness, differentiation, and oxygen fugacity. Thus, while the relative influence of slab characteristics, the mantle wedge, and differentiation within the overlying crust on the geochemistry of arcs in the broadest sense remains an active area of research (Chin et al., 2018; Farner & Lee, 2017; Lee et al., 2013; Tang et al., 2018; Turner & Langmuir, 2015; Turner et al., 2016), thick crust and crystal fractionation are not necessary for the generation of oxidized magmas.

**Inferences about Mantle  $fO_2$  as a Function of Tectonic Setting.** From the analysis above, we may conclude that neither degassing nor crystal fractionation can generate the increases we observe in Fe<sup>3+</sup>/ΣFe ratios as we move from the mid-ocean ridge, to the back-arc, to the arc-front environment. The inability of these processes to greatly alter  $fO_2$  is evidenced by the fact that magnetite–ilmenite oxybarometry on volcanics, and spinel–oxybarometry on the source mantle itself, also record increasing  $fO_2$  as we





**Figure 3.6** Magmatic oxygen fugacity as recorded by volcanics for samples in our compilation as a function of the crustal thickness (a) and SiO<sub>2</sub> (b), and the molar ratio of SiO<sub>2</sub>/Na<sub>2</sub>O+K<sub>2</sub>O (c). We combine oxygen fugacities derived from melt inclusions with those from magnetite-ilmenite pairs for each tectonic setting in each panel; we do not distinguish results based on method. Crustal thickness taken from (Behn & Grove, 2015; Calvert et al., 2008; Chulick et al., 2013; Darbyshire et al., 2000; Das & Nolet, 1998; Ferrari et al., 2012; Finotello et al., 2011; Janiszewski et al., 2013; Levin et al., 2002; Manalo et al., 2015; McGlashan et al., 2008; Nicolich et al., 2000; Saiga et al., 2010; Sevilla et al., 2010; Spieker et al., 2018; Syuhada et al., 2016; Takahashi et al., 2007; Veenstra et al., 2006; Watts & ten Brink, 1989).

move from the ridge, to the back-arc, to the subduction-influenced forearc, to the arc-front setting. We conclude from this evidence that the mantle source itself must become oxidized as the influence of subduction increases. Indeed, *in situ* work by Kelley and Cottrell (2009) and numerous studies since (Brounce et al., 2014; Brounce et al., 2021; Brounce et al., 2015; Kelley & Cottrell, 2012), have linked the  $fO_2$  recorded by submarine glasses and olivine-hosted melt inclusions to enrichment in slab-derived fluid-mobile incompatible trace elements. However, it is critical to consider other lines of evidence, such as trace element proxies, that have been argued to be more robust proxies for mantle  $fO_2$  (e.g., Lee et al., 2005).

We compare our Fe-based oxybarometry results to those obtained from trace element partitioning. Several studies based on V/Sc, V/Y, V/Ti, V/Ga, Zn/Fe ratios, or Cu concentrations have concluded that the  $fO_2$  recorded by arc volcanics are statistically indistinguishable from those recorded by MORB (Lee et al., 2005; Lee et al., 2010; Lee et al., 2012; Mallmann & O'Neill, 2013); this study, and others, have reached the opposite conclusion (Bucholz & Kelemen, 2019; Laubier et al., 2014; Shervais, 1982). It is beyond the scope of this contribution to translate the V/Yb ratios we have compiled into  $fO_2$ ; however, the conclusion that V/Yb of MORB < BABB < arc basalts is robust (Figure 3.4). This implies that subduction-modified mantle is more oxidized than the MORB source mantle, consistent with Fe-based oxybarometry, for reasons that remain debated (e.g., Andreani et al., 2013; Benard et al., 2018; Canil & Fellows, 2017; Carmichael, 1991; Chin et al., 2018; Debret et al., 2014; Evans, this volume; Farner & Lee, 2017; Foden et al., 2018; Gaillard et al., 2015; Kelley & Cottrell, 2009; Lecuyer & Ricard, 1999; Lee et al., 2005; Mungall, 2002; Nebel et al., 2015; Parkinson & Arculus, 1999; Tang et al., 2018; Tollan & Hermann, 2019; Williams et al., 2004; Wood et al., 1990).

### 3.5. CONCLUSIONS AND FUTURE DIRECTIONS

Oxygen fugacity varies as a function of tectonic setting. We have shown that all estimators of magmatic  $fO_2$  (XANES, magnetite-ilmenite pairs) and mantle source  $fO_2$  (spinel oxybarometry, V/Yb ratio) show independently that the  $fO_2$  of ridges < back-arcs < arcs. Inferences about plume  $fO_2$  are strongly model dependent, and our study indicates that plume  $fO_2$ s range widely, but on average are similar to or higher than mid-ocean ridges. We also strongly conclude that mantle lithologies record a much greater range in  $fO_2$  than volcanics.

The process of subduction generates elevated  $fO_2$  in both melts and mantle lithologies, though the mechanism and locus of this shift remains debated. The extent to which arc rocks are oxidized relative to MORB does not correlate with crustal thickness or indices of crystal fractionation. Degassing may oxidize or reduce magmas to small extents (< 0.2 log units) so long as melts are captured at pressures > 500 bar, and the tendency for shallow degassing (< 200 bar) to reduce magmas appears universal across all tectonic settings. Plate recycling may also enable plumes to achieve their elevated  $fO_2$  relative to mid-ocean ridges; however, when attempting to project back to near-primary compositions, the  $fO_2$  of plume lithologies is uncertain. This is because plume volcanics have thus far only constrained  $fO_2$  minima, and because plume xenoliths derive from lithospheric mantle that was generated at distal mid-ocean ridges that have subsequently metamorphosed and are variably overprinted by the passage of transiting plume-derived melts.

Several additional challenges confront a more complete understanding of oxygen fugacity as a function of tectonic setting. Geographic coverage of  $fO_2$  estimates remains poor, with peridotites from ridges, volcanic rocks and xenoliths from plumes, and primitive volcanic rocks from arcs especially so. Further sampling of primitive melts and mantle lithologies from diverse tectonic environments is needed in order to illuminate the geodynamic and compositional origins of variable  $fO_2$  across tectonic settings. Analytical challenges must still be overcome. Some of the most promising samples for the elucidation of redox processes – melt inclusions – are difficult to prepare and susceptible to radiation beam damage (Cottrell et al., 2018). Experiments and models are needed to gain insights into processes that may shift the  $fO_2$ s recorded by melts and residues during partial melting of the source and after melt and residue separate. Additional observations of natural samples and new experiments and models are required to ultimately connect the  $fO_2$  recorded by partial melts, peridotites and pyroxenites, and the  $fO_2$  of the solid convecting mantle.

### ACKNOWLEDGMENTS

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## METHODS APPENDIX

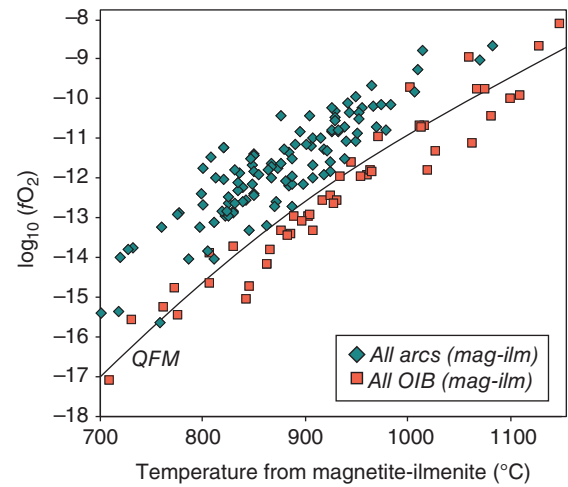
## OXYGEN FUGACITY CALCULATIONS

## Volcanics

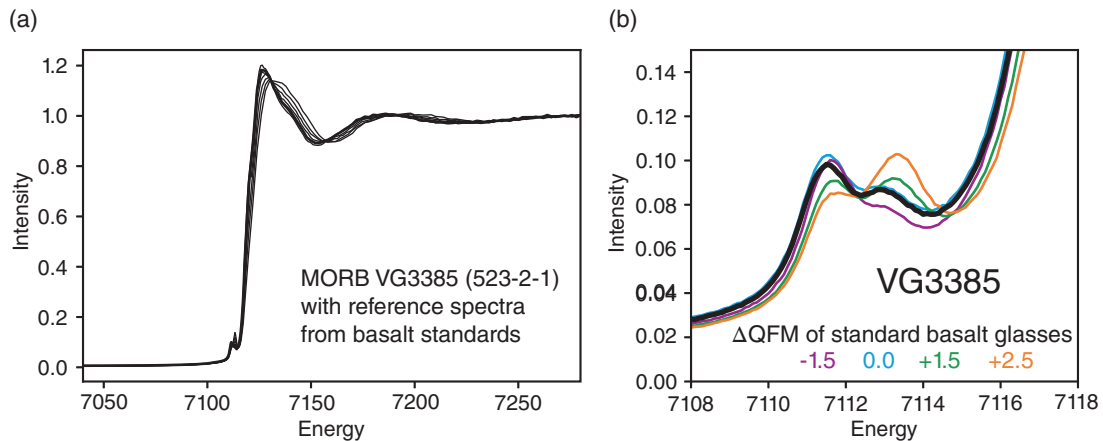
*a. Magnetite-Ilmenite Pairs*

For arc and ocean island volcanics, we collected previously reported compositions of magnetite and ilmenite from 28 studies (Arce et al., 2013; Baggerman & DeBari, 2011; Beier et al., 2006; Browne et al., 2010; Carmichael, 1967, 1964; Coombs & Gardner, 2001; Costa et al., 2004; Crabtree & Lange, 2011; Crabtree & Waters, 2017; Devine et al., 2003; Ferrari et al., 2012; Frey and Lange, 2011; Genske et al., 2012; Grocke et al., 2017; Grove et al., 2005; Gunnarsson et al., 1998; Howe et al., 2014; Izbekov et al., 2002; Larsen, 2006; Muir et al., 2014; Portnyagin et al., 2012; Stelten & Cooper, 2012; Toothill et al., 2007; Wallace & Carmichael, 1994; Waters et al., 2015; Wolfe et al., 1997; Wright, 1972). We applied the equilibrium criteria of Bacon & Hirschman (1988) to all collected oxide compositions and only use those that pass for calculations of temperature and oxygen fugacity. (Equilibrium between ilmenite and magnetite is assessed based on comparison Mn and Mg partitioning between ilmenite and magnetite pairs with a dataset of magnetite-ilmenite pairs from natural volcanics inferred to be at equilibrium). Oxide compositions were input into the model of Ghiorso and Evans (2008) to obtain temperatures and oxygen fugacities. Ghiorso and Evans (2008) report their error for the parameterization of their model in terms of the residual energies (kJ) associated with the exchange and

redox equilibria between magnetite and ilmenite. We evaluate the uncertainty of the model of Ghiorso & Evans (2008) by comparing modeled values of temperature and oxygen fugacity for experimentally grown iron oxide pairs with the reported experimental conditions (see Fig. 10 from Ghiorso & Evans, 2008). We find the uncertainty in oxygen fugacity and temperatures associated with model of Ghiorso and Evans (2008) is  $\pm 0.25$  log units and  $\pm 45^\circ\text{C}$ , respectively. All temperatures and oxygen fugacities obtained from magnetite-ilmenite pairs are shown in Figure A1.



**Figure A1** Temperatures and values of  $f\text{O}_2$  from the model of Ghiorso and Evans (2008) and all magnetite-ilmenite pairs and used in this study.



**Figure A2** XANES spectra of MORB glass VG3385 with spectra of mid-ocean ridge basalt equilibrated over a range of  $f\text{O}_2$ , modified from Fig. 1 of Cottrell and Kelley (2011). The spectra of published MORB glasses fall between basalts equilibrated at furnace  $f\text{O}_2$ s of QFM-0.71 to QFM +0.87. XANES spectroscopy strongly indicates a narrow distribution of MORB  $f\text{O}_2$  around QFM, regardless of the corresponding  $\text{Fe}^{3+}/\Sigma\text{Fe}$  of the glasses.

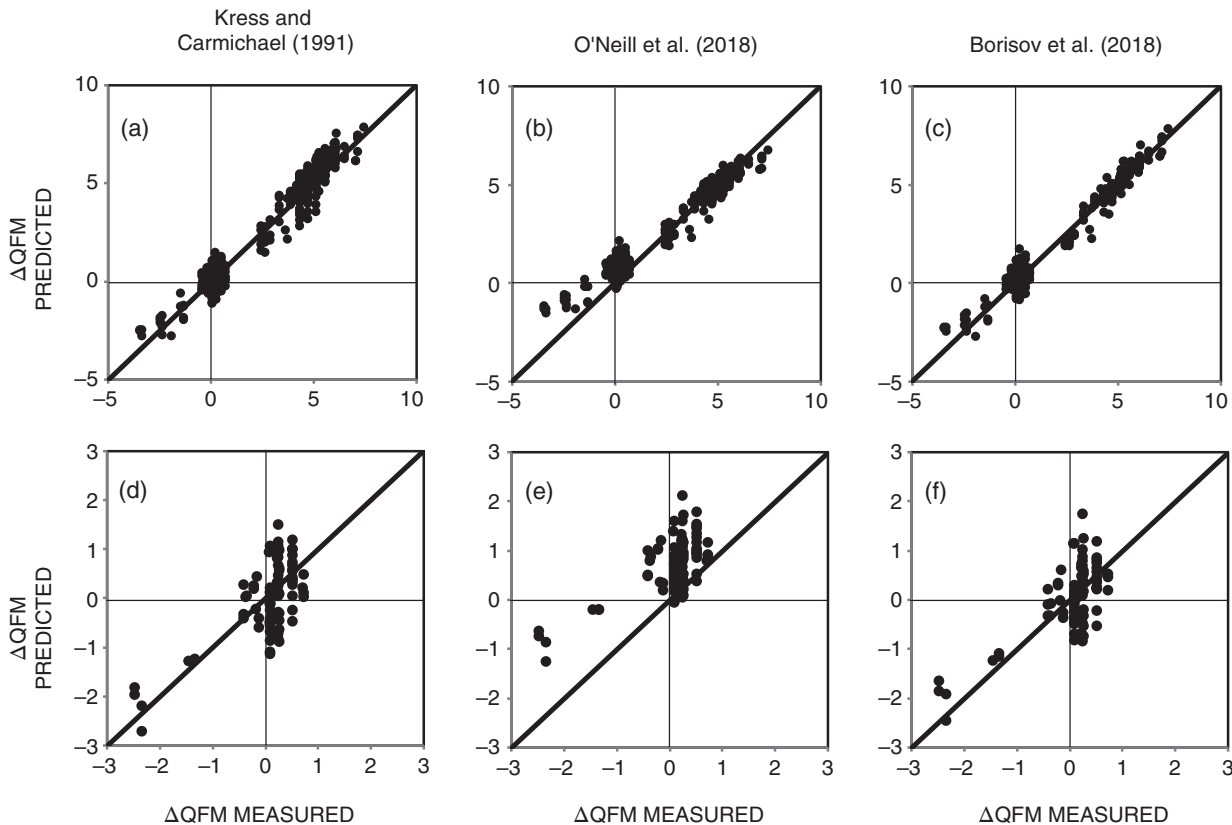
*b. Fe<sup>3+</sup>/ΣFe ratios from XANES*

We calculate magmatic  $fO_2$ s from measured  $Fe^{3+}/\Sigma Fe$  ratios using Kress and Carmichael (1991) and referenced to the QFM oxygen buffer of Frost (1991) at one atmosphere and 1200 °C, using the major element compositions reported by each study. For studies that quantify  $Fe^{3+}/\Sigma Fe$  ratios using the standard glasses of Cottrell et al. (2009; see Table 3.1), we have recalculated those  $Fe^{3+}/\Sigma Fe$  ratios according to a revision of the

Mössbauer-determined  $Fe^{3+}/\Sigma Fe$  ratios of those standard glasses (Zhang et al., 2018). Oliver Shorttle (pers. comm.) provided us with his revised  $Fe^{3+}/\Sigma Fe$  ratios based on the Zhang et al. (2018) update.

*c. Application of Kress and Carmichael (1991)*

A subset of the data we compiled for this review reports glass  $Fe^{3+}/\Sigma Fe$  ratios. Unlike mineral equilibria, we must relate glass  $Fe^{3+}/\Sigma Fe$  ratios to  $fO_2$  via an empirical model



**Figure A3** The measured experimental furnace  $fO_2$  in log units relative to the QFM buffer for Borisov et al. (2018)'s recent compilation of 435 controlled-atmosphere experiments vs the  $fO_2$  predicted by three  $fO_2$  parameterizations (i.e. calculated  $fO_2$  from the inputs of  $Fe^{3+}/\Sigma Fe$  ratio, T, and major element composition). (a–c) Furnace  $fO_2$  predicted by each parameterization for 435 compositions from QFM -3.3 to +7.3, and (d–f) for 98 “terrestrial” compositions (see Table A1) in the Earth-relevant  $fO_2$  range of QFM -3 to +3. Panels (a) and (d) use the parameterization of Kress and Carmichael (1991); panels (b) and (e) use the parameterization of O'Neill et al. (2018); panels (c) and (f) use the parameterization of Borisov et al. (2018).

**Table A1** Major element criteria for “terrestrial” lavas between QFM -3 and QFM +4.1 and “MORB-like” lavas between QFM -2 and QFM +2

	SiO <sub>2</sub>	TiO <sub>2</sub>	FeO	Na <sub>2</sub> O	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	MnO	P <sub>2</sub> O <sub>5</sub>
“terrestrial” N=98	42–78	0–4	0.1–18	1–6	11–23	0.1–15	1–14	0–6	0–0.5	0–2
MORB-like N=33	45–55	0.5–4	6–16	1.5–4	12–18	8–14	4–12	0–3	0–0.4	0–1

Major element ranges equal or exceed (Basaltic Volcanism Study Project, 1981) and (Ewart, 1979)

that accounts for composition. Several studies parameterize the relationship between  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratio and  $f\text{O}_2$  and a detailed comparison can be found in Borisov et al. (2018). For this compilation, we investigated those of Borisov et al. (2018), O'Neill et al. (2018), and Kress and Carmichael (1991). [During preparation of this manuscript, a typo in O'Neill et al. (2018) came to light; the coefficient for  $\text{P}_2\text{O}_5$  in Eqn. 9b in the text of O'Neill et al. (2018) should be  $-0.018$  not  $-0.18$  as written. We use the correct equation here.]

The Borisov et al. (2018) and Kress and Carmichael (1991) models are both empirical parameterizations of hundreds of wet-chemical determinations of  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios of glasses of diverse compositions equilibrated in controlled-atmosphere experiments. O'Neill et al. (2018) heavily weights (“anchors”) their calibration with the Mössbauer determinations of  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios of basalts (one basalt composition from Berry et al. (2018), two basalt compositions from Cottrell et al. (2009), but with the  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios “corrected” to be consistent with Berry et al. (2018), one low-Fe basalt composition from Jayasuriya et al. (2004), and one high-Fe sherggote from Richter et al. (2013), but without that study’s correction for recoilless fraction). They then derive the compositional terms from approximately the same database of wet-chemical results used in the Borisov et al. (2018) and Kress and Carmichael (1991) models, though O'Neill et al. (2018) uses only compositions with  $< 60$  wt.%  $\text{SiO}_2$ . Not included was the Mössbauer study of Zhang et al. (2018), which determined recoilless fraction using cryogenic Mössbauer. Correction for recoilless fraction reduces the  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios of Cottrell et al. (2009) by a few percent absolute, though this decrease is not equivalent to the “correction” applied by O'Neill et al. (2018). The Mössbauer studies of Zhang et al. (2018) and Berry et al. (2018) obtain fundamentally different results. We prefer the Mössbauer treatment of Zhang et al. (2018) because the methods applied in Berry et al. (2018) depend on assumptions we believe are flawed, including that highly reduced basalt is free of ferric iron (even under the most reducing conditions,  $\text{Fe}^0$  coexists with substantial  $\text{Fe}^{3+}$  (Allen & Snow, 1955; Bowen & Schairer, 1932); that hyperfine parameters remain constant as  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratio varies (there is ample evidence to the contrary, e.g., Mysen, 2006); and that center shifts  $> 0.6$ , at low quadrupole splitting, should be assigned to ferrous iron (this assertion is unsupported, see Zhang et al., 2018 for a discussion). Of course, when exploring the accuracy of a technique, it is advantageous to cross-calibrate. We note that the calibration of Zhang et al. (2018) yields an  $f\text{O}_2$ - $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratio relationship that is the same within uncertainty as Kress and Carmichael (1991) model and Borisov et al. (2018) model, based on independent wet-chemical measurements (see also

Partzsch et al., 2004), and spinel oxybarometry (Davis & Cottrell, 2018). Debate on these points must play out in the peer-reviewed literature and so for the purpose of this compilation, we take a different, agnostic, approach.

For our assessment, we take advantage of the fact that electrochemical sensors, the devices that monitor the  $f\text{O}_2$  within gas-mixing furnaces, are accurate to better than  $\pm 0.1$  log units in  $f\text{O}_2$  and yield oxybarometric results consistent with independent calorimetric data, even accounting for potential interlaboratory biases due to poor calibration of the furnace hotspot (O'Neill & Pownceby, 1993). Taking advantage of this precision and accuracy, we use Borisov et al. (2018)’s recent compilation of 435 controlled-atmosphere experiments to assess the parameterizations; the same experimental database that provides the compositional terms in all three parameterizations. The 435 experiments have wet-chemical determinations of  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios, and so are independent of the aforementioned debate concerning Mössbauer spectroscopy. We calculated the furnace  $f\text{O}_2$  predicted by each parameterization for 435 compositions from QFM  $-3.3$  to  $+7.3$ , and for 98 “terrestrial” compositions (Table A1) in the Earth-relevant  $f\text{O}_2$  range of QFM  $-3$  to  $+4.1$ .

Because our inputs are the experimental temperatures, reported major elements, and reported wet-chemical determinations of  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios of the experiments, this analysis makes no assumptions about the accuracy of the data that underlie O'Neill et al. (2018), Borisov et al. (2018), or Kress and Carmichael (1991). This analysis only asks how well the three parameterizations predict the known furnace  $f\text{O}_2$  of those 435 experiments given their independently-determined compositions. For the indicated terrestrial range, O'Neill et al. (2018)’s parameterization returns furnace  $f\text{O}_2$ s that are, on average,  $0.56$  ( $\pm 0.55$ ) log units higher than measured, Kress and Carmichael (1991)’s returns furnace  $f\text{O}_2$ s that are  $0.09$  ( $\pm 0.58$ ) lower than measured, and Borisov et al., (2018)’s returns  $0.05$  ( $\pm 0.52$ ) lower than measured. Standard errors on the estimates are reported in Table A2. We could therefore move forward confidently with either Kress and Carmichael (1991) or Borisov et al. (2018) but use the former simply because we had completed our analysis before Borisov et al. (2018) was published. Table A2 reports the standard error of each parameterization for the entire compilation and compositional subsets as defined in Table A1. Our analysis assumes that there is no systematic inaccuracy amongst the wet-chemical studies compiled by Borisov et al., (2018). O'Neill et al. (2018) raise the possibility that some wet-chemical determinations could be erroneous, and cite four suspect studies. Of these four, only two are included in the compilation of Borisov et al. (2018), and of these, 80% are from the study of Thornber et al. (1980). We therefore assessed whether

**Table A2** Standard error ( $\sigma_{\text{est}}$ ) of three  $f\text{O}_2$  parameterizations.

reference	n=435	n=98	n=33
	(all expts compiled by [Borisov et al., 2018])	("terrestrial" lavas)	("MORB-like" lavas)
Kress & Carmichael, 1991	0.56	0.59	0.53
Hugh St C. O'Neill et al., 2018	0.58	0.79	0.8
Borisov et al., 2018	0.38	0.53	0.49

inclusion/exclusion of the Thornber et al. (1980) data would significantly impact our analysis. It does not. For example, excluding data from Thornber et al. (1980) from the terrestrial data set ( $n = 55$  without Thornber) causes the standard error of O'Neill et al. (2018) parameterization to degrade to 0.84, while the standard error of Kress and Carmichael (1991) stays constant and that of Borisov et al. (2018) improves to 0.50.

**c. Vanadium oxybarometry using  $\text{VIYb}$  ratios.**

All method details provided in the main text.

## Mantle Lithologies

We calculated the oxygen fugacity of mantle lithology (peridotites and olivine-orthopyroxene-spinel bearing pyroxenites) by spinel oxybarometry, following the procedures of Davis et al. (2017). This method uses phase equilibrium between olivine, orthopyroxene, and spinel to constrain the oxygen fugacity of the system.

Calculated oxygen fugacity values are highly dependent on mineral activity models. We have thus recalculated all literature data to use a single set of activity models. For olivine and orthopyroxene, we use the activity models cited in Wood and Virgo (1989). For spinel, we use the activity model developed by Sack and Ghiorso (1991a, b). This spinel activity model better reproduces the experimental data of Wood (1990) than do other commonly used spinel activity models such as those of Mattioli and Wood (1988) and Nell and Wood (1991) (see Davis et al., 2017, for further discussion). Additionally, the Sack and Ghiorso (1991a,b) model is more applicable to spinels at high Cr#, such as the arc and forearc peridotites reported in this work (see Birner et al., 2017, for further discussion).

The activity of magnetite in spinel is itself highly dependent on accurate determination of the ferric iron content within the spinel phase. The studies included in this compilation determine ferric iron content in spinel using either Mössbauer spectroscopy or electron probe microanalysis (EPMA). In the case of EPMA, ferric iron content cannot be determined directly and is instead calculated using stoichiometric constraints. The preferred method of determining ferric iron content in this manner involves correcting the values based on a set of calibration spinels, with ferric iron contents independently

determined by Mössbauer, run at the beginning and end of each EPMA session (e.g., Wood & Virgo, 1989; Davis et al., 2017). For peridotites from ridges, arcs, and forearcs compiled in this study, we have only included data in which the  $\text{Fe}^{3+}/\sum\text{Fe}$  ratio of spinel was determined via Mössbauer or corrected EPMA. In the case of xenoliths from OIB localities, we have chosen to additionally include a number of studies in which this correction was not applied, due to the paucity of measurements using spinel standards for correction. Uncertainty in  $f\text{O}_2$  increases when uncorrected EPMA analyses of spinels are used to calculate  $f\text{O}_2$ , but the degree to which that uncertainty increases is dependent on the  $\text{Fe}^{3+}/\sum\text{Fe}$  ratio of the spinel. Uncertainty in  $f\text{O}_2$  is greater for spinels with lower  $\text{Fe}^{3+}/\sum\text{Fe}$  ratios and lesser for spinels with higher  $\text{Fe}^{3+}/\sum\text{Fe}$  ratios (Ballhaus et al. 1991; Davis et al. 2017). For example,  $f\text{O}_2$  calculated from corrected EPMA analyses of spinels with  $\text{Fe}^{3+}/\sum\text{Fe} = 0.10$  has an  $f\text{O}_2$  uncertainty of about  $+0.3/-0.4$  log units, whereas the uncertainty roughly doubles for uncorrected spinel analyses. At  $\text{Fe}^{3+}/\sum\text{Fe} > 0.35$ ,  $f\text{O}_2$  uncertainty is only about 0.1 log units for corrected EPMA analyses, and doubles to about 0.2 log units when the analyses are uncorrected. Therefore, the potential effects of including uncorrected analyses on the distribution of  $f\text{O}_2$  recorded by peridotites from an oxidized setting is likely to be small.

The calculation of oxygen fugacity also depends highly on assumptions about the temperature and pressure of equilibration. In order to maintain consistency between datasets, we calculate the  $f\text{O}_2$  values of all mantle lithologies at 0.6 GPa and the temperature recorded by spinel-olivine thermometry. Justification for this choice can be found in Birner et al. (2017) for forearc/arc peridotites and Birner et al. (2018) for mid-ocean ridge peridotites. Although we choose these values to maintain consistency, there is no rigorous method available to estimate pressure recorded by spinel peridotite xenoliths and no thermal model that can be easily applied to plume-influenced lithosphere that would allow recorded temperature to be related to a depth along a geotherm. OIB xenoliths could potentially have been exhumed from any depth within the spinel stability field. Assuming a maximum pressure of 2.5 GPa, the choice to calculate  $f\text{O}_2$  at 0.6 GPa may lead to an overestimation of  $f\text{O}_2$  relative to QFM by as much as 0.6 to 0.8 log units. This difference

in  $fO_2$  relative to QFM is owing to the differences in  $\Delta V$  of the QFM reaction and the reaction underlying the spinel oxybarometer (fayalite-ferrosilite-magnetite).

**Modeling in DCompress.** We modeled the change in magmatic  $fO_2$  with progressive degassing of a C-O-H-S vapor using the gas-melt equilibrium model of Burgisser et al. (2015). This thermodynamic model computes C, H, O, and S concentrations and speciation in coexisting gas and silicate melt as functions of pressure, temperature, melt composition, and  $fO_2$ , based on experimental calibrations of melt solubility and homogeneous equilibrium in the gas phase for H<sub>2</sub>, H<sub>2</sub>O, CO, CO<sub>2</sub>, SO<sub>2</sub>, H<sub>2</sub>S, and S<sub>2</sub> species. The melt does not change in major element composition during degassing (i.e., there is no crystallization) and it is not permitted to precipitate separate sulfide or carbon phases.

We followed the methodology of Brounce et al. (2017) to compute the degassing trajectories, except that we used the DCompress default solubility models for C-O-H-S species. We used the default basalt composition and non-temperature dependent solubility relationships of H<sub>2</sub>, H<sub>2</sub>O, CO<sub>2</sub>, H<sub>2</sub>S, and SO<sub>2</sub>. We also executed model runs wherein we set the solubility of H<sub>2</sub> in the silicate melt to zero in order to demonstrate how uncertainty in the speciation of H-species in silicate melts (e.g., finite solubility [Hirschmann et al., 2012; Mysen et al., 2011] vs no solubility [Newcombe et al., 2017]) propagates into uncertainty in degassing trajectories, particularly those at relatively low  $fO_2$ . Among these simulations, only the scenario of an arc magma decompressing at QFM = 0 (i.e., H<sub>2</sub>O-rich magma in equilibrium with a gas phase containing non-negligible amounts of H<sub>2</sub>) was sensitive to this assumption (Fig. 3.5). All calculations are calculated as equilibrium (i.e., batch) isothermal decompression, at 1100 °C. The calculations intended to simulate MORB degassing were started at QFM and 1385 bar, with concentrations of volatiles similar to those calculated for globally representative primary MORB melts (Le Voyer et al., 2018) containing 0.2 wt.% H<sub>2</sub>O, 1100 ppm CO<sub>2</sub>, and 1425 ppm S. Increasing CO<sub>2</sub> to several thousand ppm has no effect on the trajectories shown. The calculations intended to simulate OIB degassing were started at QFM +1.4 and 2115 bar, with concentrations of volatiles similar to those expected for undegassed Erebus melts (Mousallam et al., 2014) containing 1.5 wt.% H<sub>2</sub>O, 1710 ppm CO<sub>2</sub>, and 2430 ppm S. The calculations intended to simulate arc degassing were started at QFM +1.5 and 2380 bar, with concentrations of volatiles similar to those observed in melt inclusions from Agrigan volcano, containing 4.5 wt.% H<sub>2</sub>O, 800 ppm CO<sub>2</sub>, and 2050 ppm S (e.g., Kelley & Cottrell, 2012). Melt chemistry (including  $fO_2$ ) and gas phase compositions were calculated in 1 bar increments and stopped at 5 bars (total pressure).

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