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Peridotites and basalts reveal broad congruence between two independent records of mantle f_{O2} despite local redox heterogeneity

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ABSTRACT

The oxygen fugacity (f_{O2}) of the oceanic upper mantle has fundamental implications for the production of magmas and evolution of the Earth's interior and exterior. Mid-ocean ridge basalts and peridotites sample the oceanic upper mantle, and retain a record of oxygen fugacity. While f_{O2} has been calculated for mid-ocean ridge basalts worldwide (>200 locations), ridge peridotites have been comparatively less well studied (33 samples from 11 locations), and never in the same geographic location as basalts.

In order to determine whether peridotites and basalts from mid-ocean ridges record congruent information about the f_{O2} of the Earth's interior, we analyzed 31 basalts and 41 peridotites from the Oblique Segment of the Southwest Indian Ridge. By measuring basalts and peridotites from the same ridge segment, we can compare samples with maximally similar petrogenetic histories. We project the composition and oxygen fugacity of each lithology back to source conditions, and evaluate the effects of factors such as subsolidus diffusion in peridotites and fractional crystallization in basalts.

We find that, on average, basalts and peridotites from the Oblique Segment both reflect a source mantle very near the quartz–fayalite–magnetite (QFM) buffer. However, peridotites record a significantly wider range of values (nearly 3 orders of magnitude in f_{O2}), with a single dredge recording a range in f_{O2} greater than that previously reported for mid-ocean ridge peridotites worldwide. This suggests that mantle f_{O2} may be heterogeneous on relatively short length scales, and that this heterogeneity may be obscured within aggregated basalt melts. We further suggest that the global peridotite f_{O2} dataset may not provide a representative sample of average basalt-source mantle. Our study motivates further investigation of the f_{O2} recorded by ridge peridotites, as peridotites record information about the f_{O2} of the Earth's interior that cannot be gleaned from analysis of basalts alone.

1. Introduction

The oxygen fugacity (f_{O2}) of the oceanic upper mantle plays an important role in the production of melts and fluids beneath mid-ocean ridges. Oxygen fugacity affects the speciation of fluids (e.g., O'Neill and Wall, 1987; Wood et al., 1990; Frost and McCammon, 2008), the stability of many mineral phases such as oxides, sulfates/sulfides, and carbon-bearing minerals, which in turn affect the position of the mantle solidus (e.g., Dasgupta and Hirschmann, 2006; Stagno et al., 2013), and the partitioning behavior of multivalent elements such as Fe, Cr, V, C, and S (e.g., Wood et al., 1990; Canil, 1997; Frost and McCammon, 2008; Gaillard et al., 2015). In addition, uncertainty in the oxygen fugacity of sub-ridge mantle can have large implications for the calculation of important ridge parameters such as primary magma composition and the thickness of the oceanic crust (e.g., Herzberg and Asimow, 2015; Putirka, 2016). Precise constraints on the absolute value and variability of mantle f_{O2} are particularly important because small variations affect our interpretation of mantle velocity anomalies (e.g., Dalton et al., 2014), mantle potential temperature (e.g. Herzberg and Asimow, 2015), phase equilibria (e.g., Dasgupta and Hirschmann, 2006), and gas speciation (e.g., Gaillard et al., 2011).

To investigate the oxygen fugacity of sub-ridge mantle, geoscientists have primarily used two distinct proxies—the oxygen

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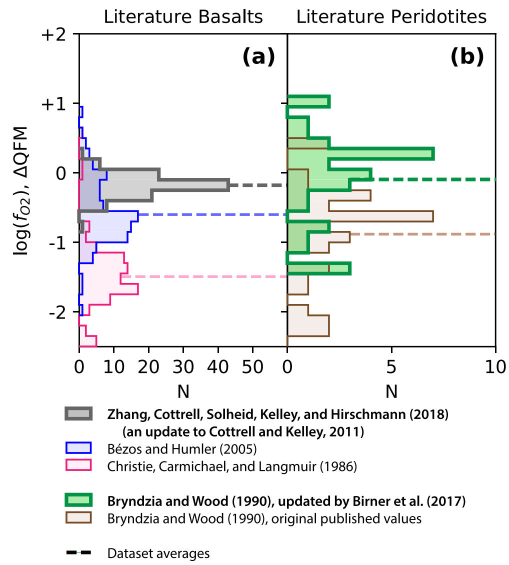

Fig. 1. Literature oxygen fugacity data, showing the evolution of f_{O_2} averages for both lithologies. Histograms with thick borders represent the most up-to-date estimates for f_{O_2}, while darker shades show where histograms overlap. **(a)** Global mid-ocean ridge basalt oxygen fugacity, from Zhang et al. (2018—an update of the Cottrell and Kelley, 2011, dataset), compared to the earlier works of Christie et al. (1986) and Bézos and Humler (2005). **(b)** Global mid-ocean ridge peridotite oxygen fugacity, revised by Birner et al. (2017) from the dataset of Bryndzia and Wood (1990), compared to the original published values of Bryndzia and Wood (1990). The revised values were calculated using the method of Davis et al. (2017) and additionally use a lower pressure and temperature of equilibration, as described in Appendix B.

fugacity recorded by mid-ocean ridge basalts (MORB) and the oxygen fugacity recorded by ridge peridotites. These two lithologies are petrogenetically related, as MORBs are produced via partial melting of peridotites at depth (e.g., Kushiro, 1968; Stolper, 1980; Kinzler and Grove, 1992). As a result, peridotites and basalts both provide a window into the oxygen fugacity of the Earth's upper mantle. Despite the applicability of these lithologies to the study of f_{O_2}, many aspects of oceanic upper mantle f_{O_2} remain poorly constrained. In particular, little is known about the magnitude and length scales of heterogeneity in f_{O_2} beneath ridges (e.g., Cottrell and Kelley, 2013), and little work has been done to compare current estimates for the oxygen fugacity of the upper mantle as implied by the different proxies.

The oxygen fugacity of mid-ocean ridge basalts has received significant attention. The seminal work of Christie et al. (1986) used wet chemistry to determine $Fe^{3+}/\Sigma Fe$ ratios in basaltic glass, and concluded that MORBs record f_{O_2} values between 1 and 2 log units more reduced than the quartz–fayalite–magnetite (QFM) buffer ($Fe^{3+}/\Sigma Fe = 0.07 \pm 0.01$, QFM -1.20 ± 0.44, $n = 87$, Fig. 1a). This estimate was revised upward to $Fe^{3+}/\Sigma Fe = 0.12 \pm 0.02$ ($n = 104$) by Bézos and Humler (2005), based on determinations of $Fe^{3+}/\Sigma Fe$ using a different wet-chemical method. Their revised estimate put the f_{O_2} recorded by MORB at QFM -0.41 ± 0.43, about 0.8 log units more oxidized than the Christie et al. (1986) estimate [Fig. 1a]. This estimate was revised upwards again by Cottrell and Kelley (2011), who used micro X-ray Absorption Near Edge Structure (μ-XANES) spectroscopy to measure the $Fe^{3+}/\Sigma Fe$ ratio in MORB glasses. The μ-XANES technique has the advantage of ensuring that only glass is analyzed, as opposed to bulk techniques such as wet chemistry that may incorporate olivine phenocrysts and thus overestimate the ferrous iron present in the basalt. Cottrell and Kelley (2011) used room temperature Mössbauer spectroscopy to calibrate the standards used for XANES, but a recent recalibration accounts for the effects of recoilless fraction (Zhang et al., 2018). The Cottrell and Kelley (2011) result has thus been revised, putting the f_{O_2} of MORB at QFM -0.18 ± 0.16 ($Fe^{3+}/\Sigma Fe = 0.143 \pm 0.008$, $n = 103$; Fig. 1a).

All four studies (Christie et al., 1986; Bézos and Humler, 2005; Cottrell and Kelley, 2011; Zhang et al., 2018) agree that MORB records relatively homogeneous oxygen fugacity globally ($1\sigma < 0.5$ log units). Each study analyzed over 75 basalts, together representing over 200 distinct locations from the ridges in Earth's three major ocean basins [Fig. 2a]. While studies such as Cottrell and Kelley (2013) have found evidence of systematic variation in redox between ridges, these changes are small compared to changes in basalt redox seen within and amongst subduction zones and back arc basins (Carmichael, 1991; Kelley and Cottrell, 2009; Brounce et al., 2014).

In contrast to the f_{O_2} of MORB, the oxygen fugacity recorded by ridge peridotites has received less attention. Seminal work by Bryndzia and Wood (1990) used spinel oxybarometry, based on phase equilibrium between olivine, orthopyroxene, and spinel, to calculate the oxygen fugacity of 35 peridotite samples from 12 ridge and transform fault locations. Of these, Bryndzia and Wood excluded the anomalously oxidized St. Paul's Rocks from their discussion of typical ridge f_{O_2}, as these peridotites are unusual, subaerially exposed, amphibole-bearing mylonites. They determined an average f_{O_2} of QFM -0.88 ± 0.70 [Fig. 1b] from the remaining 33 peridotites, >90% of which are from transform faults [Fig. 2b]. Notably, when compared to the Zhang et al. (2018) estimate for MORB f_{O_2}, the Bryndzia and Wood peridotites record 4 times more variability (Fig. 1), despite the much sparser global coverage for peridotite analyses [Fig. 2b]. At the time of publication, Bryndzia and Wood noted the agreement between the f_{O_2} recorded by global MORB in the Christie et al. (1986) study, and the f_{O_2} recorded by their 11 peridotite locations using spinel oxybarometry. However, as more recent studies have upwardly revised the f_{O_2} recorded by basalts, and the number of basalts with f_{O_2} constraints has greatly expanded, the need arises to further expand and investigate the peridotite dataset (Frost and McCammon, 2008; Davis and Cottrell, in press).

In theory, basaltic melts and peridotite residues, in equilibrium, should record the same f_{O_2}. Although different proxies must be employed to calculate f_{O_2} for each lithology, experimental work by Davis and Cottrell (in press) has demonstrated the congruence of these two methods. By equilibrating olivine + orthopyroxene + spinel + basaltic melt at 1 atmosphere, Davis and Cottrell (in press) showed that both XANES (Cottrell et al., 2009) and spinel oxybarometry (Davis et al., 2017) return f_{O_2} values consistent with the known f_{O_2} of the furnace. We can therefore eliminate the possibility of a systematic offset between these two f_{O_2} proxies in a melt + peridotite system at equilibrium. However, several complicating factors arise when assessing f_{O_2} congruence between natural basalts and peridotites. Using the Bryndzia and Wood (1990) dataset in conjunction with the global MORB f_{O_2} dataset to assess the degree of agreement between these two f_{O_2} proxies is problematic because there is essentially no overlap between the peridotite and basalt locations [Fig. 2]. While basalts can be sampled at almost all ridge segments worldwide, peridotites are exposed primarily at slow and ultraslow ridges, where crustal production is limited due to the thick conductive cooling lid (e.g., Cannat, 1996; Dick et al., 2003; Montési et al., 2011). As a result, the global MORB f_{O_2} dataset extends across all three major ocean basins [Fig. 2a], whereas the peridotite dataset of Bryndzia and Wood (1990) is confined primarily to the Indian Ocean basin [Fig. 2b]. Thus the basalt average may not reflect the peridotite average due to this sampling bias. In addition, the limited number of peridotite samples from each location makes the length scale of mantle heterogeneity unclear. Finally, the seminal work of Bryndzia and Wood (1990) does not consider how the f_{O_2} recorded by peri-