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Oxidized Mantle Sources of HIMU and EM-type Ocean Island Basalts

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Abstract:

Oxygen fugacity ($f$O$_2$) is a fundamental variable in igneous petrology with utility as a potential tracer of recycled surficial materials in the sources of mantle-derived lavas. It has been postulated that ocean island basalts (OIB) have elevated $f$O$_2$ relative to mid-ocean ridge basalts (MORB) owing to more oxidized source regions. To clarify this issue, trace-element systematics of olivine grains are reported from OIB lavas with HIMU (high-$\mu$; Mangaia, Canary Islands), enriched mantle (EM; Samoa; São Miguel, Azores Islands) and depleted MORB mantle (DMM; Pico, Azores) Sr-Nd-Pb-Os isotopic signatures, to constrain the $f$O$_2$ of each magmatic system. Despite sampling distinct mantle reservoirs based on radiogenic isotope systematics, these OIB suites show similar $f$O$_2$, ranging from +1.5 to +2.9 ΔFMQ, with an average of 2.0 ± 0.7 ΔFMQ, significantly higher than MORB at +0.6 ± 0.2 ΔFMQ using the same oxybarometer. OIBs show no correlation between $f$O$_2$ and bulk rock isotopic ratios or parental magma compositions. The lack of correlations with isotopic signatures likely results from radiogenic isotope signatures being hosted in volumetrically minor trace element enriched mantle lithologies, while $f$O$_2$ reflects the volumetrically dominant mantle component. Higher $f$O$_2$ in OIB relative to MORB implies a uniformly oxidizing plume source mantle that may be the result of either a common oxidized oceanic crust-rich reservoir parental to all modern plume lavas, or preservation of un-degassed and oxidized mantle domains formed early in Earth history.

Introduction

Oxygen fugacity ($f$O$_2$) is an intensive variable in igneous petrology that controls the geochemical behavior of redox-sensitive elements such as Fe, V, Cr, S, C and H. It is defined as
the chemical potential of molecular oxygen (O$_2$) in equilibrium with an igneous system and, like all equilibria, oxygen fugacity depends on temperature and pressure. It is therefore normally discussed in igneous petrology relative to mineral redox buffers, with the most common being the fayalite-magnetite-quartz, or FMQ buffer (Lindsley, 1991). Oxygen fugacity varies significantly in natural Earth systems by ~nine orders of magnitude, from the reduced metallic core to an atmosphere that contains ~20% molecular O$_2$. Igneous systems also show large variations in $f_{O_2}$, with arc basalts and alkaline continental basalts showing systematically higher $f_{O_2}$ relative to plume and ridge basalts (Carmichael, 1991; Brounce et al. 2014). Oxygen fugacity in arc basalts is elevated by ~+1 to +5 log units $\Delta$FMQ above ambient mantle, although it is currently debated whether the high value of arc basalts results from subduction-related metasomatism of their mantle source, or from differentiation and degassing processes (Lee et al. 2005; Kelley and Cottrell, 2009; Brounce et al. 2014; Tang et al. 2018).

Oxygen fugacity is traditionally constrained in volcanic rocks using the Fe$^{3+}/\Sigma$Fe ratio of volcanic glasses coupled with the experimental formulation of Kress and Carmichael (1991). The Fe$^{3+}/\Sigma$Fe ratio of volcanic glasses is determined in several ways, including wet chemistry and Mössbauer spectroscopy. X-ray Absorbance Near-Edge Spectroscopy (XANES) has recently allowed for high spatial resolution coupled with relatively fast sample throughput (Cottrell et al. 2011; 2013; Moussallam et al. 2014; 2016; 2019; Brounce et al. 2014). However, XANES qualitative analyses of hydrous glasses and melt inclusions can be compromised by beam damage (Cottrell et al. 2018). Additionally, it has been shown that Fe$^{3+}/\Sigma$Fe ratio of melts can change on the order of minutes by interaction with atmospheric oxygen (Helz et al. 2017). Due to these challenges and issues, as well as the low preservation potential of pristine volcanic glasses,
alternative methods of determining magmatic $fO_2$, such as V/Sc and Zn/Fe ratios in bulk rocks (Lee et al. 2005; 2010), as well as the partitioning of V into olivine (Canil, 1997; Mallmann and O’Neill, 2009; 2013; Nicklas et al. 2018; 2019; 2021), have been developed. The oxidation state of vanadium in magmas varies from $V^{+3}$ to $V^{+5}$; the former being much more compatible in olivine, regardless of temperature, pressure and melt composition (Canil, 1997; Wang et al. 2019). The most important advantage of Vanadium-in-olivine oxybarometry over XANES Fe oxybarometry, is the possibility to obtain $fO_2$ values of the melt at the first crystallization of primitive olivine, in many cases prior to any magmatic degassing. In contrast, XANES measures the $fO_2$ as glass quenches, after the melt might have been modified by degassing and or assimilation processes. Additionally, V-in-olivine oxybarometry values are relatively hard to reset, as V diffusion in olivine is fairly slow with a diffusion coefficient on the order of $10^{-14}$ m$^2$/s (Chakraborty, 2010). This method can give erroneous results however, if the measured olivines are xenocrysts and did not crystallize from the rock in which they are found. Vanadium-in-olivine oxybarometry can be readily applied to primitive olivine-phyric lavas from a variety of settings.

In contrast to arc basalts, the $fO_2$ of ocean island basalts (OIB) has only recently received significant attention. It has been postulated, based on XANES measurements in glassy melt inclusions, that Hawaiian basalts are oxidized relative to mid-ocean ridge basalts (MORB), although degassing of sulfur has led to substantial modification of their observed $fO_2$ (Moussallam et al. 2016; Brounce et al. 2017). A similar argument for degassing of sulfide and oxidation has also been demonstrated for intraplate alkaline lavas from Mt Erebus in Antarctica (Moussallam et al. 2014). The high values of $fO_2$ (relative to MORB) measured in spinel grains hosted in residual mantle xenoliths from Cape Verde also suggest an oxidized mantle source for
Cape Verde magmas (Ryabchikov et al. 1995). Basaltic glasses from the Reykjanes Ridge adjacent to Iceland show a positive correlation between oxygen fugacity and proxies for geochemical enrichment, suggesting that significant amounts of oxidized surficial material are present within the Iceland plume (Shorttle et al. 2015; Novella et al. 2020). The idea that OIB source mantle is uniformly oxidized was extended by Moussallam et al. (2019) using new XANES measurements of melt inclusions of Cape Verde and the Canary Islands, along with a compilation of existing data from Mt. Erebus, Hawaii and Iceland. They showed a strong correlation of \( \frac{\text{Fe}^{3+}}{\Sigma \text{Fe}} \) ratio with volatile concentrations, especially S, suggesting that undegassed OIB lavas have \( f_{\text{O}_2} \), of ~+2 log units from the FMQ buffer, substantially higher than MORB, which are close to FMQ (Berry et al. 2018). However, this XANES method only gives a minimum \( f_{\text{O}_2} \), as even the most oxidized glasses may have experienced some sulfur degassing. Vanadium-in-olivine oxybarometry offers an earlier ‘snapshot’ of the \( f_{\text{O}_2} \), of such lavas, potentially enabling a better approximation of the oxygen fugacity of OIB mantle. In order to examine the \( f_{\text{O}_2} \), of OIB, and to determine whether their source is oxidized relative to the MORB source we applied V-in-olivine oxybarometry to a diverse set of OIB lavas from several different hotspots that are considered to contain recycled crustal components.

**Samples and Methods**

Olivines from twenty OIB lava samples were selected for trace element analysis. The lavas sample OIB localities with Sr-Nd-Pb-Os isotope signatures attributed to the recycling of oceanic or continental crustal sources and come from the Canary Islands, the Azores, Samoa, and Mangaia in the Cook Islands. Critically, Mangaia lavas show the highest \( ^{206}\text{Pb}/^{204}\text{Pb} \) of any OIB
and thus represent the HIMU endmember (high-μ: high long-term $^{238}\text{U}/^{204}\text{Pb}$) (Woodhead, 1996), while Samoan lavas represent the EM2 (Enriched Mantle) isotopic endmember (Jackson et al. 2007a). The Canary Island lavas are ‘HIMU-type’ (Day et al., 2010), and samples from the same Canary Island volcanos have also been measured by Moussallam et al. (2019) by XANES. The Azores samples span a range of compositions from enriched mantle (EM)-like (eastern São Miguel; Elliot et al. 2007), to akin to MORB-like lavas (Pico; Waters et al., 2020). Background details about the samples are given in the Supplementary Information.

Vanadium-in-olivine oxybarometry relies upon the experimentally constrained relationship between $D_{\text{V,olivine/melt}}$ and $f_{\text{O}_2}$. If the concentration of V in olivine can be measured, and the V concentration of the parental melt of the olivine can be constrained, $f_{\text{O}_2}$ can be calculated. Concentrations of trace elements, including V, in the cores of primitive olivine crystals were measured using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). The analytical details can be found in the Supplementary Information. Calculation of parental magma compositions used previously published bulk rock data and the method of (Nicklas et al. 2021) and are detailed in the Supplementary Information. In short, literature bulk rock data were used with the major element composition of the analyzed olivine to calculate the MgO content of the parental magma to the olivine. The method assumes FeO in the bulk rock samples are equal to that in the parental magmas, and this assumption has at most a secondary effect on the resulting $f_{\text{O}_2}$ values. The measured composition of the olivine was then subtracted from the bulk rock concentrations until it was in equilibrium with the olivine. This calculation was done for all major elements and for V, to establish the parental magma composition. The partition coefficient was then calculated using the average olivine V concentration and the modeled parental magma
V concentration. Oxygen fugacity was then related to $D_{V^{\text{olivine/melt}}}$ using the empirical calibration of Wang et al. (2019).

Results

The average concentrations of V, Al, Ca, Ni, Co, Ga and Y in olivine cores from the studied OIB samples are listed in Table 1. Vanadium concentrations range from 3.8 ± 0.4 (2SD) ppm (in GC0901) to 6.3 ± 0.7 ppm (in MG1006). Ca concentrations in olivine range from 1017 to 2707 ppm, firmly establishing that the olivines crystallized from magmas and are not mantle xenocrysts, which are globally characterized by <700 ppm Ca (Foley et al. 2013). Calculated parental magma compositions, as well as each parental magma’s non-bonding oxygen/tetrahedrally bound oxygen (NBO/T) ratios are listed in Table 2. Parental magma MgO concentrations varied between 8.7 (in PX0802) and 17.4 wt.% (in AVON3-71-22) and parental magma V concentrations varied between 226 ppm (in PX0802) and 424 ppm (in EH10) while NBO/T ratios varied between 0.84 (in PX0802) and 1.43 (in AVON3-71-22). All parental lavas had >8 wt.% MgO, and therefore in most cases, olivine was the only accumulated phase, whereas for a few samples both olivine and clinopyroxene were accumulated phases. To examine whether clinopyroxene accumulation affected the oxybarometry calculations, we measured the concentration of V in pyroxene in LP01, EH18 and LZ0601 samples that host large clinopyroxene crystals. We show that even if the bulk rock contained 50% accumulated pyroxene, the calculated $f_{O_2}$ would change by 0.27, 0.26, 0.69 log units, respectively. Based on petrographic investigations (see Online Supplementary Materials), the maximum modal clinopyroxene content is less than
30%, and therefore pyroxene accumulation had at most a marginal effect on the calculated $f_{O_2}$ values. Information on the modeling of clinopyroxene accumulation can be found in **Table 3**.

Calculated $f_{O_2}$ of the OIB samples are listed in **Table 4**, and are relatively uniform, varying between $+1.52^{+0.36}_{-0.30}$ $\Delta$FMQ (in SM0815) and $+2.86^{+0.28}_{-0.24}$ $\Delta$FMQ (in GC0901). The four Mangaia samples all show $f_{O_2}$ values that overlap within uncertainties of each other, consistent with the close relationships of lavas in the field and suggesting a statistically identical parental magma. Calculated $f_{O_2}$ values for all OIB samples show no correlation with either modeled parental magma MgO content (**Figure 1**), olivine Mg# (**Supplemental Figure 1**) or bulk rock isotopic signatures (**Figure 2**), despite wide variation in $^{206}$Pb/$^{204}$Pb (from 19.126 to 21.640) and $^{143}$Nd/$^{144}$Nd (from 0.512766 to 0.512966). Oxygen fugacity additionally shows no correlation with parental magma $\text{Al}_2\text{O}_3$ and $\text{Na}_2\text{O}$ concentrations (**Tables 2 and 4**), making it unlikely that different partial melting degrees caused the observed variation. A grand average of all the OIB yields a value of $+1.96 \pm 0.70$, significantly more oxidized than the MORB average using the V-in-olivine method at $+0.60 \pm 0.15$ $\Delta$FMQ (Nicklas et al. 2018) and the MORB average using XANES measurements at $-0.18 \pm 0.16$ $\Delta$FMQ (Zhang et al. 2018) or $\sim +0.1$ $\Delta$FMQ (Berry et al. 2018). The OIB average calculated here is also within uncertainties of data for OIB lavas from Kilauea Iki and the Western Rift Zone of Iceland of $+1.64^{+0.19}_{-0.17}$ and $+1.38^{+0.27}_{-0.23}$ $\Delta$FMQ, respectively, calculated using an identical procedure and the olivine and whole rock data of Nicklas et al. (2019). If all the data are recalculated using higher olivine crystallization temperatures of either 1250°C or 1300°C (**Table 4**), the relative positions of the data are unaffected and the average shifts to $+1.63 \pm 0.70$ and $+1.48 \pm 0.70$ $\Delta$FMQ, respectively, still significantly higher than MORB.
Discussion

Vandium-in-olivine oxybarometry data from this study, combined with those from Hawaii and Iceland (Nicklas et al., 2019) indicate oxidized mantle sources for all OIB measured to date, consistent with the conclusions from XANES measurements (Moussallam et al., 2019). Critically, these observations show that OIB have elevated $f_{O_2}$ at +2.0 ± 0.7 (2SD) $\Delta$FMQ compared to MORB at +0.6 ± 0.2 (2SD) $\Delta$FMQ, measured using the same redox proxy, and also lack any correlation between $f_{O_2}$ and isotopic signatures or with petrological indicators of magmatic differentiation (e.g., parental magma MgO, olivine Mg#). A subset of the samples from the Canary Islands, Mangaia and Samoa have also been analyzed for O and Si stable isotopic systematics (Day et al. 2009; Pringle et al. 2016), but these signatures also show no correlation with $f_{O_2}$, although data are limited. The dichotomy between reduced MORB and oxidized Samoan OIB is also consistent with the relatively high $S^{6}/ΣS$ (0.17 ± 0.11) of Samoan lavas (Labidi et al. 2015). The lack of correlation of $f_{O_2}$ with isotopic signatures in the OIB dataset contrasts to prior observations made using MORB datasets. For example, the XANES study of Cottrell and Kelley (2013) showed that isotopically enriched MORB have resolvable lower $f_{O_2}$, which they attributed to reduced carbon amount in their source regions. This correlation could also possibly instead reflect isotopically enriched MORB being generally more volatile rich, and thus having degassed more S. Our new average OIB $f_{O_2}$ value overlaps with the range of global arc basalts (i.e., Carmichael, 1991; Kelley and Cottrell, 2009) and also coincides with that of high MgO Siberian meimichites ($\sim$+2.5 $\Delta$FMQ) estimated using V-in-olivine oxybarometry (Mungall et al. 2005).
Although the data of Moussallam et al. (2019) showed that OIB are indeed oxidized, melt inclusions XANES is perhaps not the best way of constraining OIB source region $f_O^2$ for two main reasons. Firstly, degassing has affected the measured $f_O^2$ of the samples, and thus only a minimum $f_O^2$ can be calculated. It has been argued that some modern Canary lavas are the most S-rich contemporary lavas on Earth and are thus especially susceptible to substantial modification by degassing (Taracsak et al. 2019). Secondly, several of the samples from that study showed high volatile concentrations (up to $\sim$3% H$_2$O) which can cause significant analytical problems during XANES analysis (Cottrell et al. 2018) and those authors also did not seek to correlate $f_O^2$ with isotopic evidence for recycled material in their sample set. The concordance of our average OIB $f_O^2$ with the plume $f_O^2$ inferred by Moussallam et al. (2019) is remarkable, and more V-in-olivine oxybarometry and XANES measurements of the same samples will serve to clarify the utility of these two oxybarometry methods for OIB studies.

**Crustal contamination, degassing and fractional crystallization**

The uniformly high $f_O^2$ of OIB strongly suggests that their mantle sources are oxidized relative to ambient upper mantle sampled by MORB. Oxygen fugacity can be modified, however, by several post-mantle processes, such as fractional crystallization, crustal contamination, and degassing of volatiles. Fractional crystallization can oxidize an evolving melt if the fractionating mineral assemblage preferentially incorporates Fe$^{+2}$ over Fe$^{+3}$, as olivine and clinopyroxene do (Cottrell and Kelley, 2011). Modelling has shown that fractional crystallization has a relatively minor effect on melt $f_O^2$ until the lava reaches $\sim$8 wt.% MgO (Kelley and Cottrell, 2012), lower
than the parental magma compositions of any of the OIB studied here. Additionally, OIB $fO_2$
shows no correlation with parental magma MgO content (Figure 1), indicating negligible effect
of mafic mineral fractionation on $fO_2$. More recent studies of MORB lavas show that $fO_2$ of lavas
can be affected by fractional crystallization (Shorttle et al. 2015) but also found the effect to be
minimal, only increasing Fe$^{+3}/\Sigma$Fe by 0.01 per 2.0 wt.% change in MgO content. Given the spread
in parental magma MgO content of the OIB dataset, fractional crystallization will not lead to
significant increases in $fO_2$. Due to the generally lower MgO content of MORB lavas (Figure 1) and
the fact that crystallization of olivine can only have an oxidizing effect on magma, it is unlikely
that the $fO_2$ difference between OIB and MORB is generated by fractional crystallization. The
Mangaia samples have radiogenic Pb isotope ratios, and so are likely to contain the largest AOC
contribution yet show among the lowest $fO_2$ of the OIB samples. The relatively low parental
magma MgO content to the Mangaia samples (10 wt.%) shows that the reported $fO_2$ would be
even lower if fractional crystallization had significantly affected these samples. We can therefore
rule out significant effects of fractional crystallization on $fO_2$ for our sample set.

Crustal contamination can theoretically oxidize magmas if the assimilated crust is rich in
oxidized elements such as Fe$^{+3}$. Due to the relatively low Fe content of the continental crust (and
terrigenous sediments) even ~30% continental crustal assimilation is unlikely to have significantly
affected the $fO_2$ of a mantle-derived melt (Grocke et al 2005). The studied OIB suites are all
situated on oceanic crust which is relatively Fe-rich, but not grossly more so than the OIB parental
lavas themselves, meaning that significant (>20%) quantities of assimilation would be necessary
to modify their $fO_2$. Large amounts of assimilation of oxidized altered oceanic crust from the
underlying plate would affect significantly geochemical signatures of the respective OIB (e.g.,
Jackson et al., 2007; Day et al., 2010; Waters et al., 2020), leading to correlations with $fO_2$, which are not observed (Fig. 3). In particular, while the available data are limited, no correlation is seen between O isotopes (Day et al., 2009; 2010) and $fO_2$, further demonstrating that assimilation was a minor process. Finally, although crustal assimilation has been documented in selected Azores lavas using B and Li isotopes (Genske et al. 2014), such signatures do not indicate the >20% assimilation necessary to change $fO_2$ beyond uncertainties.

It has been shown in the literature that degassing of sulfur in OIB melts can have a strong reducing effect on the $fO_2$ of a melt, with 6 moles of Fe$^{+3}$ reduced to Fe$^{+2}$ for every mole of S$^2$ degassed as SO$_2$ (Moussallam et al. 2014; 2016; 2019). Water and CO$_2$ degassing, in contrast, have negligible effects on the $fO_2$ of an evolving melt (Moussallam et al. 2014; Waters et al. 2016). Sulfur degassing is not the cause of the OIB-MORB $fO_2$ dichotomy for three reasons: first and most importantly, as V-in-olivine oxybarometry measures $fO_2$ as olivine is crystallized early in a magma’s evolution, it likely avoids much of the degassing that is observed from XANES measurements on glass. Second, S degassing has only been shown to have a reducing effect and could not oxidize OIB relative to MORB, although it is possible that the global MORB signature is underestimated, as most MORB are sulfide-saturated during eruption (Le Voyer et al. 2015). Third, our new OIB average overlaps well with the estimate for global undegassed OIB measured by XANES (Moussallam et al. 2019), which is unlikely if degassing was the root cause of the oxidized OIB signature. For these reasons, we conclude that the oxidized OIB signature is derived from a relatively oxidized OIB source mantle, consistent with the conclusions of Moussallam et al. (2019) and is not the result of later magmatic processes.
Lithologically distinct mantle sources?

It has been postulated that some OIB magmas preferentially sample olivine-free lithologies such as mantle pyroxenites as opposed to normal mantle peridotite (Sobolev et al. 2005; 2007) due to the high Ni content (and to a lesser extent low Mn and Ca) at constant Mg# in OIB olivine as opposed to MORB olivine. However, elevated Ni signatures have also been attributed to contamination by core metal (Herzberg et al. 2013), or high-pressure melting of normal mantle peridotite (Matzen et al. 2017; Gleeson and Gibson, 2019). To investigate if different mantle lithologies show different $f_{O_2}$, oxygen fugacity is plotted against average olivine Ni/MgO in Figure 3. No correlation is observed, indicating that any difference in $f_{O_2}$ between pyroxenite and peridotite in OIB sources is not resolvable in the current dataset. This conclusion only holds, however, if high Ni in olivine reflects a larger pyroxenite component (Sobolev et al. 2005), which is disputed (Matzen et al. 2017; Gleeson and Gibson, 2019). It is therefore not simple to determine if OIB lavas originate from melting of peridotite or pyroxenite. For example, it is also disputed whether the isotopically enriched-endmember in the Canary plume derives from pyroxenite or peridotite (Day et al. 2009, 2012; Gurenko et al. 2009). Pyroxenite is conventionally thought to be the result of hybridization of recycled AOC and peridotite (Sobolev et al. 2005), and therefore would likely be more Fe$^{+3}$-rich (i.e., high $f_{O_2}$) than ambient peridotite. Either pyroxenite in the sources of the studied OIB is not more oxidized than peridotite, or pyroxenite-derived melt represents a minor portion of the parental melts contributing to the studied lavas so as to be undetectable by the method use here. In either scenario, more data are necessary on pyroxenite and peridotite-derived OIB to clarify the issue. It is worth noting that
previous studies have concluded that pyroxenite is lacking in the source of Azores lavas (Sobolev et al. 2007).

Oxidized sources and crustal recycling processes

Oxygen fugacity shows no correlation with bulk-rock isotopic signatures for $^{206}\text{Pb}/^{204}\text{Pb}$, $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{187}\text{Os}/^{188}\text{Os}$ (Figure 2). This is unexpected, given that the dataset samples a wide range of geochemical compositions, including some of the most extreme HIMU signatures present in mantle-derived lavas, which are likely to host large amounts of AOC in their source regions. The Mangaia HIMU end-member likely hosts a component of subducted ~2.5 Ga AOC (e.g., Cabral et al., 2013). HIMU is characterized by high $^{206}\text{Pb}/^{204}\text{Pb}$, which results from high $^{238}\text{U}/^{204}\text{Pb}$ in a long-lived mantle source (Chauvel et al. 1992; Woodhead et al. 1996). The mantle source of HIMU lavas is thought to host ~5% AOC mixed with ambient mantle (Nebel et al. 2013). Whether the AOC is present as a separate, oxidized pyroxenite lithology or the isotopic signatures of AOC have been imparted onto normal peridotite without a separate lithology being present is unsettled (Herzberg et al. 2014).

For the purpose of our modeling, we assume that AOC isotopic signatures in the Mangaia source are accompanied by oxidized AOC Fe. AOC has a relatively high Fe$^{3+}/\Sigma$Fe of 0.22 ±0.08 but can locally reach values as high as 0.36 (Evans, 2012). Even Archean AOC is likely highly oxidized, as oxidation of AOC is largely the result of serpentinization reactions in the presence of water and has little to do with atmospheric $O_2$ content (i.e., Kasting, 2014). Assuming that ambient MORB mantle has 8.05 wt.% total FeO (McDonough and Sun, 1995) with a Fe$^{3+}/\Sigma$Fe = 0.05
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(Cottrell and Kelley, 2011) and recycled AOC has 10.43 wt.% total FeO (Gale et al. 2013) with a  

\[ \frac{Fe^{3+}}{\Sigma Fe} = 0.22 \text{ to } 0.36 \] (Evans, 2012), a mixture of 95% ambient mantle and 5% AOC has a  

\[ \frac{Fe^{3+}}{\Sigma Fe} = 0.06 \text{ to } 0.07 \]. Assuming temperature is constant and mantle spinel does not change  

in composition by addition of AOC except to increase in Fe\(^{3+}\) content, addition of 5% AOC is  

calculated using the method of Ballhaus et al. (1991) to raise the \( fO_2 \) of the HIMU source by 0.34-  

0.58 log units \( \Delta FMQ \). These differences are possibly resolvable using our method, which has  

uncertainties varying from 0.13 to 0.59 log units \( \Delta FMQ \).

The reason for the uniform OIB \( fO_2 \) signature can perhaps be attributed to the differing  

compatibilities of lithophile trace element systems and redox-sensitive elements. By far the most  

abundant redox-sensitive element in mantle and recycled crustal lithologies is Fe (Evans, 2012),  

which is a major element in both mantle and crust and shows only a moderate degree of  

incompatibility during melting events. By contrast, parent, daughter or both isotopes in the Rb-  

Sr, Sm-Nd, U-Pb, Th-Pb and Lu-Hf systems, all consist of highly incompatible elements.  

Abundances of Sr, Nd, Pb, and Hf are all highly enriched in crustal lithologies relative to the  

depleted mantle (Rudnick and Gao, 2003; Salters and Stracke, 2004), and therefore their budget  
in OIB lavas may be dominated by a volumetrically minor enriched lithology similar to the model  
of Stracke et al. (2019). For example, extreme EM2 lavas from Samoa show strong isotopic  
similarities to continental sediments, but the signature can be explained by mixing only \(~6\%  
sediment into their mantle source region (Jackson et al. 2007). Indeed, Samoan lavas studied  
here show average \( fO_2 \) that is not resolvable from the global OIB dataset.
The radiogenic components responsible for HIMU may not mix as a separate lithology with ambient mantle, but instead melt and mix with melts derived from more depleted mantle lithologies. The chalcophile nature of Pb (Hart and Gaetani, 2006) during mantle melting means that a very small volume of S-rich melt could host radiogenic Pb, dampening such a melt’s effect on $f_{O_2}$ and major element abundances. Strong variations in OIB isotopic signatures are generally only present for elements that are highly enriched in crustal lithologies, as demonstrated by the relatively muted variations in major element isotopic signatures in OIB, such as Fe and Si isotopes (Williams et al. 2014; Pringle et al. 2016). Notably, Os is highly compatible during mantle melting, and Os isotope systematics are often decoupled from lithophile isotope systems in OIB as peridotite components will control Os systematics while recycled components control lithophile isotope systematics (Day 2013). Lead isotopic signatures are also decoupled from Nd, Sr, and Hf isotopic systematics, likely because Pb is controlled by mantle sulfide as opposed to silicate phases (Hart and Gaetani, 2006). The high $f_{O_2}$ component in OIB therefore probably samples a common, volumetrically dominant plume component (i.e., depleted plume or ambient mantle component) relative to the volumetrically minor recycled components that are enriched in incompatible elements that control Nd, Sr, Hf and potentially Pb isotope systematics. This simple conceptual model leads to the lack of correlation between oxygen fugacity and long-lived radiogenic or stable isotope systematics.

**Oxidation processes in OIB mantle sources**
Although isotopic parameters show no systematic variations with oxygen fugacity between OIB samples, it is evident that the OIB probe more isotopically enriched and diverse mantle signatures and are more oxidized than MORB. The presented dataset can be used to constrain the isotopic composition of this mantle component present in OIB but not MORB. Numerous studies have proposed the existence of a common mantle component present in OIB (e.g., Hart et al. 1992; Farley et al. 1992; Stracke et al. 2005), which has been termed either “FOZO” or “PHEM”. This component is thought to be located at the intersection of all major OIB isotopic arrays and to carry a high-^{3}He/^{4}He ratio and moderately depleted Sr, Nd, and Hf isotopic signatures and unradiogenic Pb. If this component is indeed present in all the studied OIB samples, it may be volumetrically dominant enough to give all the OIB uniformly elevated \( f_{O2} \).

Selected Samoan lavas examined here have been shown to have high \( ^{3}He/^{4}He \) (Ofu-04-14 has \( ^{3}He/^{4}He \) of 25 Ra; Jackson et al. 2007b), but Canary Islands (Day & Hilton, 2011), and Mangaia lavas have lower \( ^{3}He/^{4}He \), in some cases even lower than MORB lavas (Parai et al., 2009). Azores lavas are largely MORB-like with regard to He isotopes, ranging from 7.2 to 11.1 Ra (Moriera et al. 1999; 2012; Madureira et al. 2014). It is notable that regardless of the wide variation in He isotopic signatures in the studied OIB, there seems to be no variation in their \( f_{O2} \).

If the “common” component sampled by OIB is more oxidized relative to the MORB source mantle, then a model explaining its high \( f_{O2} \) is necessary. If the common component is simply a constant amount of relatively young, recycled AOC, as suggested by Stracke et al. (2005), this could be a potential source of the MORB-OIB \( f_{O2} \) dichotomy, but this model does not explain the high-^{3}He/^{4}He signature seen in Samoan OIB, as recycled crust is predicted to have low-^{3}He/^{4}He. Alternatively, if the high-^{3}He/^{4}He common component is an early, less degassed
primordial reservoir (Class and Goldstein, 2005), its high $f_{O_2}$ may reflect a more oxidized signature for such a reservoir. The DMM likely lost some of its oxidized elements by melting events depleting it in Fe$^{+3}$ over time while the common component could have remained relatively undepleted. More extensive modeling on the effect of melting on the $f_{O_2}$ of residual mantle lithologies is needed to constrain this model. Alternatively, if the common component is hosted in the lower mantle, and formed early in Earth history, it could be oxidized due to the loss of disproportionated metallic Fe (i.e., metallic Fe formed from the reaction $3\text{Fe}^{+2} \rightarrow \text{Fe}^{0} + 2\text{Fe}^{+3}$) from the lowermost mantle during a primordial magma ocean phase (Wood et al. 2006). If the common component was oxidized shortly after core formation and preserved (unmixed with upper mantle) until the present day, it would present an oxidized signature, similar to the model for the source of the 3.55 Ga Schapenburg komatiites (Nicklas et al. 2019). The Schapenburg komatiites show isotopic evidence for early lower mantle processes as well as very high $f_{O_2}$ compared to other Archean komatiites, making it likely that their mantle source region was oxidized by loss of disproportionated Fe early in Earth history. While it may seem implausible that early-formed mantle reservoirs could still be sampled by modern plume lavas, the high-$^3\text{He}/^4\text{He}$ signatures of OIB and the recently discovered $^{182}\text{W}/^{184}\text{W}$ anomalies in OIB with high-$^3\text{He}/^4\text{He}$ (Mundl et al., 2017) suggest that primordial mantle signatures continue to be sampled in modern lavas. Regardless of whether the high $f_{O_2}$ of the common OIB component is the result of a uniform recycled source (Stracke et al., 2005) or an early-formed geochemically depleted source (Hart et al., 1992; Mundl-Petermeier et al., 2020), more OIB $f_{O_2}$ data from more plumes, including those with extreme isotopic signatures, are necessary to clarify the issue. Of particular interest is the measurement of $f_{O_2}$ in samples with $^{182}\text{W}/^{184}\text{W}$ anomalies, which are sensitive indicators of
the presence of early-formed components in mantle plume sources. The current dataset only includes one such sample, OFU-4-14, that shows a strongly negative $\mu^{182}$W anomaly of $-17.3 \pm 4.5$ (Mundl-Petermeier et al. 2020) and $^{3}\text{He}^{4}\text{He}$ ratio of 25 Ra (Jackson et al. 2007) but close to average OIB $f_{O_2}$ of $+1.78^{+0.25}_{-0.22} \Delta FMQ$.

Our new $f_{O_2}$ data support the paradigm that recycled surficial materials such as AOC and sediments are present in the sources of OIB (Hofmann, 1997), possibly leading to their high $f_{O_2}$ value. There is a strong theoretical framework to support this idea, as mass-balance calculations in subduction zones (Evans, 2012; Brounce et al. 2019) show that the majority of contemporary subducted oxidants ($\text{Fe}^{3+}, \text{S}^{8+}, \text{C}^{4+}$) are not emitted by arc volcanoes, indicating that they are brought into the deep mantle. Indeed, the global study of Evans (2012) suggested that only $\sim10\%$ of the total subducted oxidants, and almost none of the subducted $\text{Fe}^{3+}$, is emitted by global arc volcanoes. There is substantial isotopic variation found in OIB (Zindler and Hart, 1984; Hofmann, 1997) likely because of varying proportions of recycled AOC, as well as terrigenous and pelagic sediments. These different lithologies are likely to show substantially different oxygen fugacity, with AOC and terrigenous sediment being oxidized relative to the mantle, and pelagic organic-rich sediments being reduced. This study shows that the quantity and type of recycled material does not appear to impact the $f_{O2}$ of the lava. Prior to this study, no work has attempted to correlate isotopic signatures of OIB with oxygen fugacity. More data will show whether the OIB source mantle is indeed uniformly more oxidized than MORB and whether any variation is shown with isotopic signatures.
Conclusions

In order to investigate the putatively high oxygen fugacity of the mantle source regions of plume lavas relative to the depleted MORB mantle, we measured the trace element systematics of primitive olivine phenocrysts from twenty OIB samples from the Azores, Samoa, the Canary Islands and the Cook Islands. The OIB samples show a wide range of isotopic signatures, likely sampling a wide variety of recycled crustal materials. Olivine trace element systematics was used to constrain magmatic \( f_{O_2} \) in each sample using the V-in-olivine oxybarometry method. All OIB samples are similar in \( f_{O_2} \), ranging from \(+1.52^{+0.36}_{-0.30} \Delta FMQ\) to \(+2.86^{+0.28}_{-0.24} \Delta FMQ\), with an average of \(1.96 \pm 0.70 \Delta FMQ\), significantly more oxidized than the V-in-olivine oxybarometry MORB average of \(+0.60 \pm 0.15 \Delta FMQ\). Additionally, OIB \( f_{O_2} \) shows no correlation with whole rock \(^{206}Pb/^{204}Pb\), \(^{143}Nd/^{144}Nd\) and \(^{187}Os/^{188}Os\) ratios, or with parental magma MgO or inferred pyroxenite content in their source regions. Given the probable presence of oxidized altered oceanic crust in high \(^{206}Pb/^{204}Pb\) OIB, such a null result is significant. This is likely due to isotopic signatures being dominated by volumetrically small, trace element-enriched components, while \( f_{O_2} \) reflects the volumetrically dominant component of the OIB source region.

The large and consistent gap in \( f_{O_2} \) between MORB and OIB samples indicates that the volumetrically dominant plume component was oxidized relative to the depleted mantle. Two main mechanisms can explain this: either the net OIB source mantle has uniformly high amounts of recycled oceanic crust, or the OIB source reflects a primitive undegassed oxidized reservoir.

Early mantle material could have become oxidized shortly after core formation by the segregation of disproportionated Fe metal formed in the lower mantle and be preserved unmixed in the lower mantle till the present day. The presence of \(^{182}W/^{184}W\) isotope anomalies in modern
OIB lend credence to the idea that plumes may sample early formed mantle reservoirs. The new dataset presented here confirms that the modern mantle is heterogeneous with respect to $fO_2$ and that different mantle reservoirs can be accurately characterized using the V-in-olivine oxybarometry method in the future.

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Author Contributions:

RWN and JMDD designed the project. RKMH and RWN prepared and performed the analyses, data reduction and calculations. The manuscript was written by RWN and RKMH with editing from JMDD, MGJ, VZ, RA and LNW. Samples were collected by JMDD, VZ and MGJ. JMDD provided funding and technical support for the project.
**Figure Captions**

**Figure 1.** Calculated $f_{O_2}$ of the OIB samples plotted against MgO content of parental magmas. MORB $f_{O_2}$ field based on olivine-glass pairs from Nicklas et al. (2019).

**Figure 2a.** Calculated $f_{O_2}$ of the OIB samples plotted against bulk rock $^{187}$Os/$^{188}$Os ratios. **b.** Calculated $f_{O_2}$ of the OIB samples plotted against bulk rock $^{206}$Pb/$^{204}$Pb ratios. **c.** Calculated $f_{O_2}$ of the OIB samples plotted against bulk rock $^{143}$Nd/$^{144}$Nd ratios. Sources of isotope data are listed in Table 4. MORB isotopic data are from Workman and Hart (2005) and MORB $f_{O_2}$ data are from Nicklas et al. (2018). Symbols as in Fig. 1.

**Figure 3.** Average Ni/MgO, in ppm/wt. % of olivine plotted against calculated $f_{O_2}$ for each suite. Symbols as in Fig. 1.
Table 1: Average concentrations of elements (in ppm) in the cores of primitive olivine crystals from each OIB sample. Data were reduced assuming uniform Si concentrations, which are taken from the literature, and vary the least of all major elements in stochiometric olivine. N – number of olivine grains analyzed for each sample, SiO₂ – assumed silica content of the olivine in wt.%, 2s – two standard deviations of the average concentration. For full dataset including concentrations in each spot analyzed, see online supplemental datasets.

| Sample      | N  | SiO₂ | Al   | Ca   | V    | Co   | Ni    | Ga   | Y   |
|-------------|----|------|------|------|------|------|-------|------|-----|
| LP03        | 19 | 39.28| 161.4| 1677 | 4.88 | 160.3| 1503  |      |     |
| 2s          |    |      | 34.5 | 518  | 0.77 | 34.7 | 318   |      |     |
| EH10        | 20 | 38.91| 182.7| 1473 | 5.77 | 212.7| 1369  | 0.20 | 0.14|
| 2s          |    |      | 39.7 | 259  | 1.11 | 17.4 | 599   | 0.03 | 0.05|
| GOM05       | 23 | 39.70| 238.5| 1774 | 6.21 | 180.9| 1669  | 0.19 | 0.13|
| 2s          |    |      | 76.2 | 265  | 1.16 | 14.0 | 177   | 0.06 | 0.04|
| LZ0601      | 25 | 38.99| 232.7| 1756 | 6.16 | 180.4| 1653  | 0.19 | 0.13|
| 2s          |    |      | 84.5 | 283  | 1.26 | 14.0 | 202   | 0.06 | 0.04|
| GC0901      | 19 | 39.05| 161.4| 1871 | 3.80 | 179.5| 2044  | 0.17 | 0.14|
| 2s          |    |      | 22.3 | 208  | 0.43 | 11.7 | 192   | 0.04 | 0.04|
| EH18        | 24 | 38.98| 160.2| 1017 | 5.79 | 198.6| 1539  | 0.19 | 0.14|
| 2s          |    |      | 40.1 | 280  | 1.03 | 29.2 | 1186  | 0.04 | 0.08|
| LP01        | 33 | 39.05| 170.6| 1712 | 5.27 | 193.1| 1289  | 0.16 | 0.13|
| 2s          |    |      | 58.8 | 388  | 1.07 | 20.2 | 165   | 0.05 | 0.05|
| 9CTEN05     | 20 | 39.63| 203.2| 2111 | 4.87 | 187.0| 1476  | 0.16 | 0.12|
| 2s          |    |      | 27.1 | 249  | 0.53 | 18.4 | 313   | 0.02 | 0.03|
| O4PAL05     | 20 | 39.39| 201.6| 2157 | 4.03 | 157.1| 1785  | 0.14 | 0.11|
| 2s          |    |      | 47.9 | 273  | 0.44 | 11.6 | 163   | 0.03 | 0.02|
| MG01        | 24 | 39.29| 204.3| 2575 | 5.63 | 187.1| 1481  | 0.15 | 0.14|
| 2s          |    |      | 20.3 | 204  | 0.60 | 10.1 | 66    | 0.03 | 0.02|
| MG02        | 23 | 38.79| 202.4| 2707 | 5.26 | 187.5| 1523  | 0.11 | 0.15|
| 2s          |    |      | 16.5 | 242  | 0.47 | 13.7 | 107   | 0.14 | 0.03|
| MG06        | 23 | 39.36| 216.8| 2340 | 6.34 | 225.1| 1207  | 0.13 | 0.18|
| 2s          |    |      | 42.7 | 363  | 0.65 | 13.1 | 176   | 0.16 | 0.02|
| MG08        | 23 | 39.15| 215.7| 2115 | 6.28 | 206.1| 1203  | 0.12 | 0.15|
| 2s          |    |      | 23.2 | 312  | 0.91 | 19.1 | 300   | 0.18 | 0.03|
| SM0815      | 19 | 39.75| 267.4| 1968 | 5.42 | 179.2| 1334  | 0.18 | 0.12|
| 2s          |    |      | 90.4 | 508  | 0.89 | 34.4 | 611   | 0.03 | 0.03|
| PX0802      | 25 | 39.14| 192.7| 1389 | 5.51 | 161.9| 1307  | 0.17 | 0.14|
| 2s          |    |      | 40.7 | 374  | 0.79 | 17.1 | 348   | 0.04 | 0.07|
| TR0802      | 26 | 39.21| 311.8| 1805 | 5.09 | 137.2| 1949  | 0.20 | 0.11|
| 2s          |    |      | 174.0| 422  | 1.31 | 38.0 | 1146  | 0.11 | 0.05|
| T-25        | 19 | 39.54| 199.3| 2061 | 5.59 | 161.1| 2079  | 0.15 | 0.12|
| 2s          |    |      | 30.9 | 430  | 0.80 | 26.8 | 287   | 0.11 | 0.07|
| OFU04-14    | 20 | 39.61| 184.5| 1882 | 5.74 | 185.2| 1681  | 0.18 | 0.11|
Table 2: Calculated major element compositions in weight %, and V concentration in ppm of parental magmas of the studied OIB samples. NBO/T is the ratio of non-bonding oxygens to tetrahedrally bonded oxygens in the parental magmas, calculated using the procedure of Mills (1993).

| Sample        | SiO2  | TiO2  | Al2O3 | FeO   | MnO   | MgO   | CaO   | Na2O  | K2O   | P2O5  | V (ppm) | NBO/T |
|---------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|---------|-------|
| LP03          | 51.3  | 2.90  | 11.2  | 13.0  | 0.22  | 12.0  | 8.34  | 0.50  | 0.11  | 0.39  | 266     | 0.95  |
| EH10          | 41.2  | 5.92  | 10.6  | 16.0  | 0.21  | 10.7  | 11.3  | 2.52  | 0.85  | 0.76  | 424     | 1.31  |
| GOM05         | 46.0  | 3.21  | 11.0  | 12.5  | 0.19  | 13.3  | 9.27  | 2.94  | 0.84  | 0.69  | 296     | 1.20  |
| LZ0601        | 47.0  | 2.68  | 13.3  | 13.0  | 0.17  | 9.48  | 11.2  | 1.86  | 0.90  | 0.42  | 292     | 0.97  |
| GC0901        | 44.4  | 4.83  | 13.0  | 12.0  | 0.18  | 9.14  | 12.2  | 2.80  | 1.00  | 0.44  | 354     | 1.02  |
| EH18          | 43.5  | 5.59  | 11.7  | 13.8  | 0.21  | 9.85  | 10.4  | 3.28  | 1.02  | 0.67  | 368     | 1.11  |
| LP01          | 46.1  | 3.59  | 11.6  | 12.3  | 0.20  | 9.86  | 12.8  | 2.33  | 0.87  | 0.44  | 368     | 1.11  |
| 9CTEN05       | 45.5  | 2.59  | 10.6  | 12.1  | 0.17  | 13.14 | 12.9  | 2.03  | 0.62  | 0.31  | 282     | 1.32  |
| 04PAL05       | 42.8  | 3.40  | 11.6  | 12.9  | 0.18  | 11.69 | 13.5  | 2.47  | 0.84  | 0.63  | 402     | 1.30  |
| Mangaia       | 44.9  | 2.83  | 11.7  | 12.9  | 0.19  | 10.0  | 14.3  | 2.20  | 0.62  | 0.39  | 311     | 1.20  |
| SM0815        | 47.5  | 3.00  | 12.2  | 10.7  | 0.16  | 12.6  | 8.94  | 2.62  | 1.96  | 0.43  | 243     | 1.06  |
| PX0802        | 48.7  | 2.52  | 14.2  | 9.91  | 0.17  | 8.66  | 10.5  | 3.48  | 1.30  | 0.48  | 226     | 0.84  |
| TR0802        | 47.9  | 2.70  | 14.1  | 10.0  | 0.16  | 9.00  | 12.21 | 2.65  | 0.90  | 0.51  | 262     | 0.89  |
| T-25          | 46.8  | 3.06  | 10.5  | 12.9  | 0.19  | 13.2  | 10.3  | 2.00  | 0.79  | 0.35  | 339     | 1.23  |
| OFU04-14      | 46.0  | 3.89  | 8.88  | 13.2  | 0.17  | 13.1  | 12.3  | 1.53  | 0.62  | 0.35  | 339     | 1.36  |
| AVON2-62-2    | 48.2  | 1.99  | 9.02  | 10.3  | 0.17  | 17.3  | 10.5  | 1.58  | 0.70  | 0.22  | 262     | 1.40  |
| AVON3-71-22   | 47.5  | 1.90  | 9.22  | 10.0  | 0.18  | 17.4  | 11.1  | 1.58  | 0.73  | 0.22  | 270     | 1.43  |
Table 3: Average clinopyroxene V concentrations as determined by a LA-ICP-MS procedure identical to the one for olivine. Bulk rock V concentrations used to determine \( f_O^2 \) is also listed, along with a bulk V concentration from which 5%, 10%, 20%, 40% and 50% of the measured clinopyroxene removed. Finally, the calculated \( f_O^2 \) for each sample is listed, along with an \( f_O^2 \) calculated using the bulk rock compositions with varying amounts of clinopyroxene removed. As demonstrated by the modeling shown here, clinopyroxene accumulation has a negligible effect on the calculated \( f_O^2 \) unless extremely large amount of clinopyroxene was accumulated in the bulk rock samples. CPX – clinopyroxene, 2s – two standard deviations, N – number of clinopyroxenes analyzed.

| Sample                 | LP01 | EH18 | LZ0601 |
|------------------------|------|------|--------|
| CPX V (ppm)            | 270  | 294  | 326    |
| 2s                     | 40   | 55   | 101    |
| N                      | 9    | 12   | 10     |
| Bulk V (ppm)           | 328  | 357  | 242    |
| Without 5% CPX         | 331  | 360  | 238    |
| Without 10% CPX        | 335  | 364  | 233    |
| Without 20% CPX        | 343  | 372  | 221    |
| Without 30% CPX        | 353  | 383  | 206    |
| Without 40% CPX        | 367  | 398  | 186    |
| Without 50% CPX        | 386  | 419  | 158    |
| \( f_O^2 (\Delta FMQ) \) | 2.30 | 2.14 | 1.77   |
| Without 5% CPX         | 2.31 | 2.15 | 1.73   |
| Without 10% CPX        | 2.33 | 2.17 | 1.69   |
| Without 20% CPX        | 2.37 | 2.21 | 1.61   |
| Without 30% CPX        | 2.42 | 2.26 | 1.49   |
| Without 40% CPX        | 2.49 | 2.32 | 1.31   |
| Without 50% CPX        | 2.57 | 2.41 | 1.04   |
Table 4: Calculated parental magma $f_O^2$, in log units relative to the FMQ buffer, as well as bulk rock isotope ratios for the studied OIB samples. The preferred values at 1150°C for oxygen fugacity are listed under “FMQ” but also listed are oxygen fugacity values calculated using different olivine crystallization temperatures of 1250°C and 1300° demonstrating the lack of a strong temperature effect on the results. Up – positive uncertainty on the calculated $f_O^2$, down – negative uncertainty on the calculated $f_O^2$. 2s – quoted 2 sigma uncertainties on the isotope ratios. Sources of isotope data: Jackson et al. (2007a); Day et al. (2010); Jackson et al. (2014); Waters et al. (2020); Day et al. (under review) and Day (unpublished data).

| Sample | Location | MgO | FMQ | Up | Down | $^{206}\text{Pb}/^{204}\text{Pb}$ | $^{143}\text{Nd}/^{144}\text{Nd}$ | $^{187}\text{Os}/^{188}\text{Os}$ | $^{2s}$ | FMQ at 1250°C | FMQ at 1300°C |
|--------|----------|-----|-----|-----|-------|------------------|------------------|------------------|-------|--------------|--------------|
| LP03 La Palma | 12.01 | 2.02 | 0.35 | 0.29 | 19.698 | 0.007 | 0.512966 | 0.000017 | 0.14406 | 0.00001 | 1.69 | 1.54 |
| EH10 El Hierro | 10.69 | 2.20 | 0.41 | 0.33 | 19.597 | 0.007 | 0.512942 | 0.000003 | 0.14808 | 0.00005 | 1.87 | 1.72 |
| GOM05 La Gomera | 13.32 | 1.93 | 0.27 | 0.23 | - | - | - | - | - | 1.59 | 1.44 |
| LZ0601 Lanzarote | 9.48 | 1.77 | 0.43 | 0.34 | - | - | - | - | - | 1.44 | 1.29 |
| GC0901 Gran Canaria | 9.14 | 2.86 | 0.28 | 0.24 | - | - | - | - | - | 2.53 | 2.38 |
| EH18 El Hierro | 9.85 | 2.14 | 0.38 | 0.31 | 19.666 | 0.001 | 0.512952 | 0.000005 | 0.15297 | 0.00006 | 1.80 | 1.65 |
| LP01 La Palma | 9.86 | 2.30 | 0.43 | 0.34 | 19.759 | 0.001 | 0.512914 | 0.000004 | 0.14328 | 0.00001 | 1.96 | 1.81 |
| 9CTEN05 Tenerife | 13.14 | 1.79 | 0.27 | 0.23 | - | - | - | - | - | 1.45 | 1.30 |
| 04PAL05 La Palma | 11.69 | 2.71 | 0.27 | 0.23 | - | - | - | - | - | 2.38 | 2.23 |
| MG01 Mangaia | 10.03 | 1.74 | 0.19 | 0.17 | 21.601 | 0.002 | 0.512919 | 0.000005 | 0.14982 | 0.00008 | 1.41 | 1.26 |
| MG02 Mangaia | 10.03 | 1.78 | 0.16 | 0.15 | 21.600 | 0.002 | 0.512914 | 0.000006 | 0.16064 | 0.00009 | 1.45 | 1.30 |
| MG06 Mangaia | 10.03 | 1.67 | 0.19 | 0.16 | 21.640 | 0.002 | 0.512907 | 0.000007 | 0.16600 | 0.00010 | 1.34 | 1.19 |
| MG08 Mangaia | 10.03 | 1.78 | 0.26 | 0.23 | 21.630 | 0.002 | 0.512904 | 0.000008 | 0.15243 | 0.00006 | 1.45 | 1.30 |
| SM0815 Sao Miguel | 12.55 | 1.52 | 0.36 | 0.30 | 19.889 | 0.0002 | 0.512736 | 0.000003 | - | - | 1.19 | 1.04 |
| PX0802 Pico | 8.66 | 1.65 | 0.32 | 0.27 | 19.804 | 0.0003 | 0.512884 | 0.000003 | 0.12460 | 0.00130 | 1.32 | 1.17 |
| TR0802 Terceira | 9.00 | 1.99 | 0.54 | 0.41 | 19.311 | 0.0003 | 0.512938 | 0.000003 | 0.13840 | 0.00272 | 1.66 | 1.51 |
| T-25 Ta'u | 13.17 | 1.95 | 0.32 | 0.27 | 19.2266 | 0.0007 | 0.512790 | 0.000040 | 0.12334 | 0.00009 | 1.62 | 1.47 |
| OFU04-14 Ofu | 13.12 | 1.78 | 0.25 | 0.22 | 19.1260 | 0.00003 | 0.512819 | 0.000025 | 0.12947 | 0.00008 | 1.45 | 1.30 |
| AVON2-62-2 Vailulu'u | 17.44 | 1.56 | 0.49 | 0.38 | - | - | - | - | 0.12826 | 0.00004 | 1.23 | 1.08 |
| AVON3-71-22 Vailulu'u | 17.31 | 2.03 | 0.42 | 0.34 | 19.358 | 0.0002 | 0.512747 | 0.000040 | 0.12762 | 0.00007 | 1.70 | 1.55 |
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Figure 1
Figure 2

(a) 

(b) 

(c) 

ΔFMQ vs. $^{187}\text{Os}/^{188}\text{Os}$

ΔFMQ vs. $^{206}\text{Pb}/^{204}\text{Pb}$

ΔFMQ vs. $^{143}\text{Nd}/^{144}\text{Nd}$
Figure 3.