This manuscript has been submitted for publication in the journal CHEMICAL GEOLOGY. Please note

that, despite having undergone two rounds of peer-review at the journal EARTH AND PLANETARY

SCIENCE LETTERS, the manuscript has yet to be formally accepted for publication. Subsequent versions

of this manuscript may have slightly different content. Please feel free to contact any of the authors; we

welcome feedback

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

Robert W. Nicklas[1*], Rachel K. M. Hahn[1], Lori N. Willhite[2], Matthew G. Jackson[3],

Vittorio Zanon[4], Ricardo Arevalo Jr.[2] and James M.D. Day[1]

[1]Scripps Institution of Oceanography, University of California San Diego, La Jolla, CA, 92093,

USA

[2]Department of Geology, University of Maryland College Park, College Park, MD, 20742, USA

[3]Department of Earth Science, University of California Santa Barbara, Santa Barbara, CA,

93106, USA

[4]Instituto de Investigação em Vulcanologia e Avaliação de Riscos, Universidade dos Açores,

Rua Mãe de Deus, 9500-321 Ponta Delgada, Portugal

*Corresponding author: R. Willie Nicklas: rnicklas@ucsd.edu

5653 Words (Abstract 231, Supplement 2189), 82 References, 3 Figures, 4 Tables

For submission to *Chemical Geology*

8/31/2021

1   **Abstract:**

2   Oxygen fugacity (fO$_2$) is a fundamental variable in igneous petrology with utility as a

3   potential tracer of recycled surficial materials in the sources of mantle-derived lavas. It has been

4   postulated that ocean island basalts (OIB) have elevated fO$_2$ relative to mid-ocean ridge basalts

5   (MORB) owing to more oxidized source regions. To clarify this issue, trace-element systematics

6   of olivine grains are reported from OIB lavas with HIMU (high-μ; Mangaia, Canary Islands),

7   enriched mantle (EM; Samoa; São Miguel, Azores Islands) and depleted MORB mantle (DMM;

8   Pico, Azores) Sr-Nd-Pb-Os isotopic signatures, to constrain the fO$_2$ of each magmatic system.

9   Despite sampling distinct mantle reservoirs based on radiogenic isotope systematics, these OIB

10   suites show similar fO$_2$, ranging from +1.5 to +2.9 ΔFMQ, with an average of 2.0 ± 0.7 ΔFMQ,

11   significantly higher than MORB at +0.6 ± 0.2 ΔFMQ using the same oxybarometer. OIBs show no

12   correlation between fO$_2$ and bulk rock isotopic ratios or parental magma compositions. The lack

13   of correlations with isotopic signatures likely results from radiogenic isotope signatures being

14   hosted in volumetrically minor trace element enriched mantle lithologies, while fO$_2$ reflects the

15   volumetrically dominant mantle component. Higher fO$_2$ in OIB relative to MORB implies a

16   uniformly oxidizing plume source mantle that may be the result of either a common oxidized

17   oceanic crust-rich reservoir parental to all modern plume lavas, or preservation of un-degassed

18   and oxidized mantle domains formed early in Earth history.

19

20   **Introduction**

21   Oxygen fugacity (fO$_2$) is an intensive variable in igneous petrology that controls the

22   geochemical behavior of redox-sensitive elements such as Fe, V, Cr, S, C and H. It is defined as

23   the chemical potential of molecular oxygen (O_2) in equilibrium with an igneous system and, like

24   all equilibria, oxygen fugacity depends on temperature and pressure. It is therefore normally

25   discussed in igneous petrology relative to mineral redox buffers, with the most common being

26   the fayalite-magnetite-quartz, or FMQ buffer (Lindsley, 1991). Oxygen fugacity varies significantly

27   in natural Earth systems by ~nine orders of magnitude, from the reduced metallic core to an

28   atmosphere that contains ~20% molecular O_2. Igneous systems also show large variations in fO_2,

29   with arc basalts and alkaline continental basalts showing systematically higher fO_2 relative to

30   plume and ridge basalts (Carmichael, 1991; Brounce et al. 2014). Oxygen fugacity in arc basalts is

31   elevated by ~+1 to +5 log units ΔFMQ above ambient mantle, although it is currently debated

32   whether the high value of arc basalts results from subduction-related metasomatism of their

33   mantle source, or from differentiation and degassing processes (Lee et al. 2005; Kelley and

34   Cottrell, 2009; Brounce et al. 2014; Tang et al. 2018).

35   Oxygen fugacity is traditionally constrained in volcanic rocks using the $Fe^{+3}/\Sigma Fe$ ratio of

36   volcanic glasses coupled with the experimental formulation of Kress and Carmichael (1991). The

37   $Fe^{+3}/\Sigma Fe$ ratio of volcanic glasses is determined in several ways, including wet chemistry and

38   Mössbauer spectroscopy. X-ray Absorbance Near-Edge Spectroscopy (XANES) has recently

39   allowed for high spatial resolution coupled with relatively fast sample throughput (Cottrell et al.

40   2011; 2013; Moussallam et al. 2014; 2016; 2019; Brounce et al. 2014). However, XANES

41   qualitative analyses of hydrous glasses and melt inclusions can be compromised by beam damage

42   (Cottrell et al. 2018). Additionally, it has been shown that $Fe^{+3}/\Sigma Fe$ ratio of melts can change on

43   the order of minutes by interaction with atmospheric oxygen (Helz et al. 2017). Due to these

44   challenges and issues, as well as the low preservation potential of pristine volcanic glasses,

45   alternative methods of determining magmatic fO$_2$, such as V/Sc and Zn/Fe ratios in bulk rocks

46   (Lee et al. 2005; 2010), as well as the partitioning of V into olivine (Canil, 1997; Mallmann and

47   O'Neill, 2009; 2013; Nicklas et al. 2018; 2019; 2021), have been developed. The oxidation state

48   of vanadium in magmas varies from V^{+3} to V^{+5}; the former being much more compatible in olivine,

49   regardless of temperature, pressure and melt composition (Canil, 1997; Wang et al. 2019). The

50   most important advantage of Vanadium-in-olivine oxybarometry over XANES Fe oxybarometry,

51   is the possibility to obtain fO$_2$ values of the melt at the first crystallization of primitive olivine, in

52   many cases prior to any magmatic degassing. In contrast, XANES measures the fO$_2$ as glass

53   quenches, after the melt might have been modified by degassing and or assimilation processes.

54   Additionally, V-in-olivine oxybarometry values are relatively hard to reset, as V diffusion in olivine

55   is fairly slow with a diffusion coefficient on the order of 10^{-14} m^2/s (Chakraborty, 2010). This

56   method can give erroneous results however, if the measured olivines are xenocrysts and did not

57   crystallize from the rock in which they are found. Vanadium-in-olivine oxybarometry can be

58   readily applied to primitive olivine-phyric lavas from a variety of settings.

59   In contrast to arc basalts, the fO$_2$ of ocean island basalts (OIB) has only recently received

60   significant attention. It has been postulated, based on XANES measurements in glassy melt

61   inclusions, that Hawaiian basalts are oxidized relative to mid-ocean ridge basalts (MORB),

62   although degassing of sulfur has led to substantial modification of their observed fO$_2$

63   (Moussallam et al. 2016; Brounce et al. 2017). A similar argument for degassing of sulfide and

64   oxidation has also been demonstrated for intraplate alkaline lavas from Mt Erebus in Antarctica

65   (Moussallam et al. 2014). The high values of fO$_2$ (relative to MORB) measured in spinel grains

66   hosted in residual mantle xenoliths from Cape Verde also suggest an oxidized mantle source for

67   Cape Verde magmas (Ryabchikov et al. 1995). Basaltic glasses from the Reykjanes Ridge adjacent

68   to Iceland show a positive correlation between oxygen fugacity and proxies for geochemical

69   enrichment, suggesting that significant amounts of oxidized surficial material are present within

70   the Iceland plume (Shorttle et al. 2015; Novella et al. 2020). The idea that OIB source mantle is

71   uniformly oxidized was extended by Moussallam et al. (2019) using new XANES measurements

72   of melt inclusions of Cape Verde and the Canary Islands, along with a compilation of existing data

73   from Mt. Erebus, Hawaii and Iceland. They showed a strong correlation of $Fe^{+3}/\Sigma Fe$ ratio with

74   volatile concentrations, especially S, suggesting that undegassed OIB lavas have fO_2 of ~+2 log

75   units from the FMQ buffer, substantially higher than MORB, which are close to FMQ (Berry et al.

76   2018). However, this XANES method only gives a minimum fO_2, as even the most oxidized glasses

77   may have experienced some sulfur degassing. Vanadium-in-olivine oxybarometry offers an

78   earlier 'snapshot' of the fO_2 of such lavas, potentially enabling a better approximation of the

79   oxygen fugacity of OIB mantle. In order to examine the fO_2 of OIB, and to determine whether

80   their source is oxidized relative to the MORB source we applied V-in-olivine oxybarometry to a

81   diverse set of OIB lavas from several different hotspots that are considered to contain recycled

82   crustal components.

83

84   **Samples and Methods**

85   Olivines from twenty OIB lava samples were selected for trace element analysis. The lavas

86   sample OIB localities with Sr-Nd-Pb-Os isotope signatures attributed to the recycling of oceanic

87   or continental crustal sources and come from the Canary Islands, the Azores, Samoa, and

88   Mangaia in the Cook Islands. Critically, Mangaia lavas show the highest $^{206}Pb/^{204}Pb$ of any OIB

89   and thus represent the HIMU endmember (high-μ: high long-term $^{238}U/^{204}Pb$) (Woodhead, 1996),

90   while Samoan lavas represent the EM2 (Enriched Mantle) isotopic endmember (Jackson et al.

91   2007a). The Canary Island lavas are 'HIMU-type' (Day et al., 2010), and samples from the same

92   Canary Island volcanos have also been measured by Moussallam et al. (2019) by XANES. The

93   Azores samples span a range of compositions from enriched mantle (EM)-like (eastern São

94   Miguel; Elliot et al. 2007), to akin to MORB-like lavas (Pico; Waters et al., 2020). Background

95   details about the samples are given in the *Supplementary Information.*

96   Vanadium-in-olivine oxybarometry relies upon the experimentally constrained

97   relationship between $D_V^{olivine/melt}$ and fO_2. If the concentration of V in olivine can be measured,

98   and the V concentration of the parental melt of the olivine can be constrained, fO_2 can be

99   calculated. Concentrations of trace elements, including V, in the cores of primitive olivine crystals

100   were measured using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS).

101   The analytical details can be found in the *Supplementary Information*. Calculation of parental

102   magma compositions used previously published bulk rock data and the method of (Nicklas et al.

103   2021) and are detailed in the *Supplementary Information.* In short, literature bulk rock data were

104   used with the major element composition of the analyzed olivine to calculate the MgO content

105   of the parental magma to the olivine. The method assumes FeO in the bulk rock samples are

106   equal to that in the parental magmas, and this assumption has at most a secondary effect on the

107   resulting fO_2 values. The measured composition of the olivine was then subtracted from the bulk

108   rock concentrations until it was in equilibrium with the olivine. This calculation was done for all

109   major elements and for V, to establish the parental magma composition. The partition coefficient

110   was then calculated using the average olivine V concentration and the modeled parental magma

111   V concentration. Oxygen fugacity was then related to $D_V^{olivine/melt}$ using the empirical calibration

112   of Wang et al. (2019).

113

114   **Results**

115   The average concentrations of V, Al, Ca, Ni, Co, Ga and Y in olivine cores from the studied

116   OIB samples are listed in **Table 1**. Vanadium concentrations range from 3.8 ± 0.4 (2SD) ppm (in

117   GC0901) to 6.3 ± 0.7 ppm (in MG1006). Ca concentrations in olivine range from 1017 to 2707

118   ppm, firmly establishing that the olivines crystallized from magmas and are not mantle

119   xenocrysts, which are globally characterized by <700 ppm Ca (Foley et al. 2013). Calculated

120   parental   magma   compositions,   as   well   as   each   parental   magma's   non-bonding

121   oxygen/tetrahedrally bound oxygen (NBO/T) ratios are listed in **Table 2**. Parental magma MgO

122   concentrations varied between 8.7 (in PX0802) and 17.4 wt.% (in AVON3-71-22) and parental

123   magma V concentrations varied between 226 ppm (in PX0802) and 424 ppm (in EH10) while

124   NBO/T ratios varied between 0.84 (in PX0802) and 1.43 (in AVON3-71-22). All parental lavas had

125   >8 wt.% MgO, and therefore in most cases, olivine was the only accumulated phase, whereas for

126   a few samples both olivine and clinopyroxene were accumulated phases. To examine whether

127   clinopyroxene   accumulation   affected   the   oxybarometry   calculations,   we   measured   the

128   concentration of V in pyroxene in LP01, EH18 and LZ0601 samples that host large clinopyroxene

129   crystals. We show that even if the bulk rock contained 50% accumulated pyroxene, the calculated

130   fO_2 would change by 0.27, 0.26, 0.69 log units, respectively. Based on petrographic investigations

131   (see Online Supplementary Materials), the maximum modal clinopyroxene content is less than

132   30%, and therefore pyroxene accumulation had at most a marginal effect on the calculated fO_2

133   values. Information on the modeling of clinopyroxene accumulation can be found in **Table 3**.

134   Calculated fO_2 of the OIB samples are listed in **Table 4**, and are relatively uniform, varying

135   between $+1.52^{+0.36}_{-0.30}$ ΔFMQ (in SM0815) and $+2.86^{+0.28}_{-0.24}$ ΔFMQ (in GC0901). The four Mangaia

136   samples all show fO_2 values that overlap within uncertainties of each other, consistent with the

137   close relationships of lavas in the field and suggesting a statistically identical parental magma.

138   Calculated fO_2 values for all OIB samples show no correlation with either modeled parental

139   magma MgO content (**Figure 1**), olivine Mg# (**Supplemental Figure 1**) or bulk rock isotopic

140   signatures (**Figure 2**), despite wide variation in $^{206}Pb/^{204}Pb$ (from 19.126 to 21.640) and

141    $^{143}Nd/^{144}Nd$ (from 0.512766 to 0.512966). Oxygen fugacity additionally shows no correlation with

142   parental magma Al_2O_3 and Na_2O concentrations (**Tables 2** and **4**), making it unlikely that different

143   partial melting degrees caused the observed variation. A grand average of all the OIB yields a

144   value of +1.96 ± 0.70, significantly more oxidized than the MORB average using the V-in-olivine

145   method at +0.60 ± 0.15 ΔFMQ (Nicklas et al. 2018) and the MORB average using XANES

146   measurements at -0.18 ± 0.16 ΔFMQ (Zhang et al. 2018) or ~+0.1 ΔFMQ (Berry et al. 2018).The

147   OIB average calculated here is also within uncertainties of data for OIB lavas from Kilauea Iki and

148   the Western Rift Zone of Iceland of $+1.64^{+0.19}_{-0.17}$ and $+1.38^{+0.27}_{-0.23}$ ΔFMQ, respectively, calculated

149   using an identical procedure and the olivine and whole rock data of Nicklas et al. (2019). If all the

150   data are recalculated using higher olivine crystallization temperatures of either 1250°C or 1300°C

151   (**Table 4**), the relative positions of the data are unaffected and the average shifts to +1.63 ± 0.70

152   and +1.48 ± 0.70 ΔFMQ, respectively, still significantly higher than MORB.

153

154   **Discussion**

155   Vandium-in-olivine oxybarometry data from this study, combined with those from Hawaii

156   and Iceland (Nicklas et al., 2019) indicate oxidized mantle sources for all OIB measured to date,

157   consistent with the conclusions from XANES measurements (Moussallam et al., 2019). Critically,

158   these observations show that OIB have elevated fO_2 at +2.0 ±0.7 (2SD) ΔFMQ compared to MORB

159   at +0.6 ±0.2 (2SD) ΔFMQ, measured using the same redox proxy, and also lack any correlation

160   between fO_2 and isotopic signatures or with petrological indicators of magmatic differentiation

161   (e.g., parental magma MgO, olivine Mg#). A subset of the samples from the Canary Islands,

162   Mangaia and Samoa have also been analyzed for O and Si stable isotopic systematics (Day et al.

163   2009; Pringle et al. 2016), but these signatures also show no correlation with fO_2, although data

164   are limited. The dichotomy between reduced MORB and oxidized Samoan OIB is also consistent

165   with the relatively high $S^{+6}/\Sigma S$ (0.17 ± 0.11) of Samoan lavas (Labidi et al. 2015). The lack of

166   correlation of fO_2 with isotopic signatures in the OIB dataset contrasts to prior observations made

167   using MORB datasets. For example, the XANES study of Cottrell and Kelley (2013) showed that

168   isotopically enriched MORB have resolvable lower fO_2, which they attributed to reduced carbon

169   amount in their source regions. This correlation could also possibly instead reflect isotopically

170   enriched MORB being generally more volatile rich, and thus having degassed more S. Our new

171   average OIB fO_2 value overlaps with the range of global arc basalts (i.e., Carmichael, 1991; Kelley

172   and Cottrell, 2009) and also coincides with that of high MgO Siberian meimichites (~+2.5 ΔFMQ)

173   estimated using V-in-olivine oxybarometry (Mungall et al. 2005).

174   Although the data of Moussallam et al. (2019) showed that OIB are indeed oxidized, melt

175   inclusions XANES is perhaps not the best way of constraining OIB source region fO_2 for two main

176   reasons. Firstly, degassing has affected the measured fO_2 of the samples, and thus only a

177   minimum fO_2 can be calculated. It has been argued that some modern Canary lavas are the most

178   S-rich contemporary lavas on Earth and are thus especially susceptible to substantial modification

179   by degassing (Taracsak et al. 2019). Secondly, several of the samples from that study showed high

180   volatile concentrations (up to ~3% H_2O) which can cause significant analytical problems during

181   XANES analysis (Cottrell et al. 2018) and those authors also did not seek to correlate fO_2 with

182   isotopic evidence for recycled material in their sample set. The concordance of our average OIB

183   fO_2 with the plume fO_2 inferred by Moussallam et al. (2019) is remarkable, and more V-in-olivine

184   oxybarometry and XANES measurements of the same samples will serve to clarify the utility of

185   these two oxybarometry methods for OIB studies.

186

187   ***Crustal contamination, degassing and fractional crystallization***

188   The uniformly high fO_2 of OIB strongly suggests that their mantle sources are oxidized

189   relative to ambient upper mantle sampled by MORB. Oxygen fugacity can be modified, however,

190   by several post-mantle processes, such as fractional crystallization, crustal contamination, and

191   degassing of volatiles. Fractional crystallization can oxidize an evolving melt if the fractionating

192   mineral assemblage preferentially incorporates Fe^{+2} over Fe^{+3}, as olivine and clinopyroxene do

193   (Cottrell and Kelley, 2011). Modelling has shown that fractional crystallization has a relatively

194   minor effect on melt fO_2 until the lava reaches ~8 wt.% MgO (Kelley and Cottrell, 2012), lower

195   than the parental magma compositions of any of the OIB studied here. Additionally, OIB fO_2

196   shows no correlation with parental magma MgO content (**Figure 1**), indicating negligible effect

197   of mafic mineral fractionation on fO_2. More recent studies of MORB lavas show that fO_2 of lavas

198   can be affected by fractional crystallization (Shorttle et al. 2015) but also found the effect to be

199   minimal, only increasing $Fe^{+3}/\Sigma Fe$ by 0.01 per 2.0 wt.% change in MgO content. Given the spread

200   in parental magma MgO content of the OIB dataset, fractional crystallization will not lead to

201   significant increases in fO_2. Due to the generally lower MgO content of MORB lavas (**Figure 1**) and

202   the fact that crystallization of olivine can only have an oxidizing effect on magma, it is unlikely

203   that the fO_2 difference between OIB and MORB is generated by fractional crystallization. The

204   Mangaia samples have radiogenic Pb isotope ratios, and so are likely to contain the largest AOC

205   contribution yet show among the lowest fO_2 of the OIB samples. The relatively low parental

206   magma MgO content to the Mangaia samples (10 wt.%) shows that the reported fO_2 would be

207   even lower if fractional crystallization had significantly affected these samples. We can therefore

208   rule out significant effects of fractional crystallization on fO_2 for our sample set.

209   Crustal contamination can theoretically oxidize magmas if the assimilated crust is rich in

210   oxidized elements such as Fe^{+3}. Due to the relatively low Fe content of the continental crust (and

211   terrigenous sediments) even ~30% continental crustal assimilation is unlikely to have significantly

212   affected the fO_2 of a mantle-derived melt (Grocke et al 2005). The studied OIB suites are all

213   situated on oceanic crust which is relatively Fe-rich, but not grossly more so than the OIB parental

214   lavas themselves, meaning that significant (>20%) quantities of assimilation would be necessary

215   to modify their fO_2. Large amounts of assimilation of oxidized altered oceanic crust from the

216   underlying plate would affect significantly geochemical signatures of the respective OIB (e.g.,

217   Jackson et al., 2007; Day et al., 2010; Waters et al., 2020), leading to correlations with fO$_2$, which

218   are not observed (**Fig. 3**). In particular, while the available data are limited, no correlation is seen

219   between O isotopes (Day et al., 2009; 2010) and fO$_2$, further demonstrating that assimilation was

220   a minor process. Finally, although crustal assimilation has been documented in selected Azores

221   lavas using B and Li isotopes (Genske et al. 2014), such signatures do not indicate the >20%

222   assimilation necessary to change fO$_2$ beyond uncertainties.

223   It has been shown in the literature that degassing of sulfur in OIB melts can have a strong

224   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}

225   degassed as SO$_2$ (Moussallam et al. 2014; 2016; 2019). Water and CO$_2$ degassing, in contrast,

226   have negligible effects on the fO$_2$ of an evolving melt (Moussallam et al. 2014; Waters et al. 2016).

227   Sulfur degassing is not the cause of the OIB-MORB fO$_2$ dichotomy for three reasons: first and

228   most importantly, as V-in-olivine oxybarometry measures fO$_2$ as olivine is crystallized early in a

229   magma's evolution, it likely avoids much of the degassing that is observed from XANES

230   measurements on glass. Second, S degassing has only been shown to have a reducing effect and

231   could not oxidize OIB relative to MORB, although it is possible that the global MORB signature is

232   underestimated, as most MORB are sulfide-saturated during eruption (Le Voyer et al. 2015).

233   Third, our new OIB average overlaps well with the estimate for global undegassed OIB measured

234   by XANES (Moussallam et al. 2019), which is unlikely if degassing was the root cause of the

235   oxidized OIB signature. For these reasons, we conclude that the oxidized OIB signature is derived

236   from a relatively oxidized OIB source mantle, consistent with the conclusions of Moussallam et

237   al. (2019) and is not the result of later magmatic processes.

238

239   ***Lithologically distinct mantle sources?***

240   It has been postulated that some OIB magmas preferentially sample olivine-free

241   lithologies such as mantle pyroxenites as opposed to normal mantle peridotite (Sobolev et al.

242   2005; 2007) due to the high Ni content (and to a lesser extent low Mn and Ca) at constant Mg#

243   in OIB olivine as opposed to MORB olivine. However, elevated Ni signatures have also been

244   attributed to contamination by core metal (Herzberg et al. 2013), or high-pressure melting of

245   normal mantle peridotite (Matzen et al. 2017; Gleeson and Gibson, 2019). To investigate if

246   different mantle lithologies show different fO_2, oxygen fugacity is plotted against average olivine

247   Ni/MgO in **Figure 3.** No correlation is observed, indicating that any difference in fO_2 between

248   pyroxenite and peridotite in OIB sources is not resolvable in the current dataset. This conclusion

249   only holds, however, if high Ni in olivine reflects a larger pyroxenite component (Sobolev et al.

250   2005), which is disputed (Matzen et al. 2017; Gleeson and Gibson, 2019). It is therefore not

251   simple to determine if OIB lavas originate from melting of peridotite or pyroxenite. For example,

252   it is also disputed whether the isotopically enriched-endmember in the Canary plume derives

253   from pyroxenite or peridotite (Day et al. 2009, 2012; Gurenko et al. 2009). Pyroxenite is

254   conventionally thought to be the result of hybridization of recycled AOC and peridotite (Sobolev

255   et al. 2005), and therefore would likely be more Fe^{+3}-rich (i.e., high fO_2) than ambient peridotite.

256   Either pyroxenite in the sources of the studied OIB is not more oxidized than peridotite, or

257   pyroxenite-derived melt represents a minor portion of the parental melts contributing to the

258   studied lavas so as to be undetectable by the method use here. In either scenario, more data are

259   necessary on pyroxenite and peridotite-derived OIB to clarify the issue. It is worth noting that

260 previous studies have concluded that pyroxenite is lacking in the source of Azores lavas (Sobolev

261 et al. 2007).

262

263 ***Oxidized sources and crustal recycling processes***

264 Oxygen fugacity shows no correlation with bulk-rock isotopic signatures for $^{06}Pb/^{204}Pb$,

265 $^{143}Nd/^{144}Nd$ and $^{187}Os/^{188}Os$ (**Figure 2**). This is unexpected, given that the dataset samples a wide

266 range of geochemical compositions, including some of the most extreme HIMU signatures

267 present in mantle-derived lavas, which are likely to host large amounts of AOC in their source

268 regions. The Mangaia HIMU end-member likely hosts a component of subducted ~2.5 Ga AOC

269 (e.g., Cabral et al., 2013). HIMU is characterized by high $^{206}Pb/^{204}Pb$, which results from high

270 $^{238}U/^{204}Pb$ in a long-lived mantle source (Chauvel et al. 1992; Woodhead et al. 1996). The mantle

271 source of HIMU lavas is thought to host ~5% AOC mixed with ambient mantle (Nebel et al. 2013).

272 Whether the AOC is present as a separate, oxidized pyroxenite lithology or the isotopic signatures

273 of AOC have been imparted onto normal peridotite without a separate lithology being present is

274 unsettled (Herzberg et al. 2014).

275 For the purpose of our modeling, we assume that AOC isotopic signatures in the Mangaia

276 source are accompanied by oxidized AOC Fe. AOC has a relatively high $Fe^{+3}/\Sigma Fe$ of 0.22 ±0.08 but

277 can locally reach values as high as 0.36 (Evans, 2012). Even Archean AOC is likely highly oxidized,

278 as oxidation of AOC is largely the result of serpentinization reactions in the presence of water

279 and has little to do with atmospheric O_2 content (i.e., Kasting, 2014). Assuming that ambient

280 MORB mantle has 8.05 wt.% total FeO (McDonough and Sun, 1995) with a $Fe^{+3}/\Sigma Fe = 0.05$

281   (Cottrell and Kelley, 2011) and recycled AOC has 10.43 wt.% total FeO (Gale et al. 2013) with a

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

283    $Fe^{+3}/\Sigma Fe$ of 0.06 to 0.07. Assuming temperature is constant and mantle spinel does not change

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

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

286   0.58 log units ΔFMQ. These differences are possibly resolvable using our method, which has

287   uncertainties varying from 0.13 to 0.59 log units ΔFMQ.

288   The reason for the uniform OIB fO_2 signature can perhaps be attributed to the differing

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

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

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

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

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

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

295   depleted mantle (Rudnick and Gao, 2003; Salters and Stracke, 2004), and therefore their budget

296   in OIB lavas may be dominated by a volumetrically minor enriched lithology similar to the model

297   of Stracke et al. (2019). For example, extreme EM2 lavas from Samoa show strong isotopic

298   similarities to continental sediments, but the signature can be explained by mixing only ~6%

299   sediment into their mantle source region (Jackson et al. 2007). Indeed, Samoan lavas studied

300   here show average fO_2 that is not resolvable from the global OIB dataset.

301   The radiogenic components responsible for HIMU may not mix as a separate lithology

302   with ambient mantle, but instead melt and mix with melts derived from more depleted mantle

303   lithologies. The chalcophile nature of Pb (Hart and Gaetani, 2006) during mantle melting means

304   that a very small volume of S-rich melt could host radiogenic Pb, dampening such a melt's effect

305   on fO$_2$ and major element abundances. Strong variations in OIB isotopic signatures are generally

306   only present for elements that are highly enriched in crustal lithologies, as demonstrated by the

307   relatively muted variations in major element isotopic signatures in OIB, such as Fe and Si isotopes

308   (Williams et al. 2014; Pringle et al. 2016). Notably, Os is highly compatible during mantle melting,

309   and Os isotope systematics are often decoupled from lithophile isotope systems in OIB as

310   peridotite components will control Os systematics while recycled components control lithophile

311   isotope systematics (Day 2013). Lead isotopic signatures are also decoupled from Nd, Sr, and Hf

312   isotopic systematics, likely because Pb is controlled by mantle sulfide as opposed to silicate

313   phases (Hart and Gaetani, 2006). The high fO$_2$ component in OIB therefore probably samples a

314   common, volumetrically dominant plume component (i.e., depleted plume or ambient mantle

315   component) relative to the volumetrically minor recycled components that are enriched in

316   incompatible elements that control Nd, Sr, Hf and potentially Pb isotope systematics. This simple

317   conceptual model leads to the lack of correlation between oxygen fugacity and long-lived

318   radiogenic or stable isotope systematics.

319

320   ***Oxidation processes in OIB mantle sources***

321   Although isotopic parameters show no systematic variations with oxygen fugacity

322 between OIB samples, it is evident that the OIB probe more isotopically enriched and diverse

323 mantle signatures and are more oxidized than MORB. The presented dataset can be used to

324 constrain the isotopic composition of this mantle component present in OIB but not MORB.

325 Numerous studies have proposed the existence of a common mantle component present in OIB

326 (e.g., Hart et al. 1992; Farley et al. 1992; Stracke et al. 2005), which has been termed either

327 "FOZO" or "PHEM". This component is thought to be located at the intersection of all major OIB

328 isotopic arrays and to carry a high-^{3}He/^{4}He ratio and moderately depleted Sr, Nd, and Hf isotopic

329 signatures and unradiogenic Pb. If this component is indeed present in all the studied OIB

330 samples, it may be volumetrically dominant enough to give all the OIB uniformly elevated fO$_2$.

331 Selected Samoan lavas examined here have been shown to have high ^{3}He/^{4}He (Ofu-04-14 has

332 ^{3}He/^{4}He of 25 Ra; Jackson et al. 2007b), but Canary Islands (Day & Hilton, 2011), and Mangaia

333 lavas have lower ^{3}He/^{4}He, in some cases even lower than MORB lavas (Parai et al., 2009). Azores

334 lavas are largely MORB-like with regard to He isotopes, ranging from 7.2 to 11.1 R$_a$ (Moriera et

335 al. 1999; 2012; Madureira et al. 2014). It is notable that regardless of the wide variation in He

336 isotopic signatures in the studied OIB, there seems to be no variation in their fO$_2$.

337   If the "common" component sampled by OIB is more oxidized relative to the MORB

338 source mantle, then a model explaining its high fO$_2$ is necessary. If the common component is

339 simply a constant amount of relatively young, recycled AOC, as suggested by Stracke et al. (2005),

340 this could be a potential source of the MORB-OIB fO$_2$ dichotomy, but this model does not explain

341 the high-^{3}He/^{4}He signature seen in Samoan OIB, as recycled crust is predicted to have low-

342 ^{3}He/^{4}He. Alternatively, if the high-^{3}He/^{4}He common component is an early, less degassed

343 primordial reservoir (Class and Goldstein, 2005), its high fO_2 may reflect a more oxidized

344 signature for such a reservoir. The DMM likely lost some of its oxidized elements by melting

345 events depleting it in Fe^{+3} over time while the common component could have remained

346 relatively undepleted. More extensive modeling on the effect of melting on the fO_2 of residual

347 mantle lithologies is needed to constrain this model. Alternatively, if the common component is

348 hosted in the lower mantle, and formed early in Earth history, it could be oxidized due to the loss

349 of disproportionated metallic Fe (i.e., metallic Fe formed from the reaction $3Fe^{+2} \rightarrow Fe^0 + 2Fe^{+3}$)

350 from the lowermost mantle during a primordial magma ocean phase (Wood et al. 2006). If the

351 common component was oxidized shortly after core formation and preserved (unmixed with

352 upper mantle) until the present day, it would present an oxidized signature, similar to the model

353 for the source of the 3.55 Ga Schapenburg komatiites (Nicklas et al. 2019). The Schapenburg

354 komatiites show isotopic evidence for early lower mantle processes as well as very high fO_2

355 compared to other Archean komatiites, making it likely that their mantle source region was

356 oxidized by loss of disproportionated Fe early in Earth history. While it may seem implausible that

357 early-formed mantle reservoirs could still be sampled by modern plume lavas, the high-$^3He/^4He$

358 signatures of OIB and the recently discovered $^{182}W/^{184}W$ anomalies in OIB with high-$^3He/^4He$

359 (Mundl et al., 2017) suggest that primordial mantle signatures continue to be sampled in modern

360 lavas. Regardless of whether the high fO_2 of the common OIB component is the result of a

361 uniform recycled source (Stracke et al., 2005) or an early-formed geochemically depleted source

362 (Hart et al., 1992; Mundl-Petermeier et al., 2020), more OIB fO_2 data from more plumes, including

363 those with extreme isotopic signatures, are necessary to clarify the issue. Of particular interest is

364 the measurement of fO_2 in samples with $^{182}W/^{184}W$ anomalies, which are sensitive indicators of

365   the presence of early-formed components in mantle plume sources. The current dataset only

366   includes one such sample, OFU-4-14, that shows a strongly negative $\mu^{182}W$ anomaly of -17.3 ±

367   4.5 (Mundl-Petermeier et al. 2020) and $^3He/^4He$ ratio of 25 Ra (Jackson et al. 2007) but close to

368   average OIB fO_2 of $+1.78^{+0.25}_{-0.22}$ ΔFMQ.

369   Our new fO_2 data support the paradigm that recycled surficial materials such as AOC and

370   sediments are present in the sources of OIB (Hofmann, 1997), possibly leading to their high fO_2

371   value. There is a strong theoretical framework to support this idea, as mass-balance calculations

372   in subduction zones (Evans, 2012; Brounce et al. 2019) show that the majority of contemporary

373   subducted oxidants (Fe^{+3}, S^{+8}, C^{+4}) are not emitted by arc volcanoes, indicating that they are

374   brought into the deep mantle. Indeed, the global study of Evans (2012) suggested that only ~10%

375   of the total subducted oxidants, and almost none of the subducted Fe^{+3}, is emitted by global arc

376   volcanoes. There is substantial isotopic variation found in OIB (Zindler and Hart, 1984; Hofmann,

377   1997) likely because of varying proportions of recycled AOC, as well as terrigenous and pelagic

378   sediments. These different lithologies are likely to show substantially different oxygen fugacity,

379   with AOC and terrigenous sediment being oxidized relative to the mantle, and pelagic organic-

380   rich sediments being reduced. This study shows that the quantity and type of recycled material

381   does not appear to impact the $fO2$ of the lava. Prior to this study, no work has attempted to

382   correlate isotopic signatures of OIB with oxygen fugacity. More data will show whether the OIB

383   source mantle is indeed uniformly more oxidized than MORB and whether any variation is shown

384   with isotopic signatures.

385

386   **Conclusions**

387   In order to investigate the putatively high oxygen fugacity of the mantle source regions

388   of plume lavas relative to the depleted MORB mantle, we measured the trace element

389   systematics of primitive olivine phenocrysts from twenty OIB samples from the Azores, Samoa,

390   the Canary Islands and the Cook Islands. The OIB samples show a wide range of isotopic

391   signatures, likely sampling a wide variety of recycled crustal materials. Olivine trace element

392   systematics was used to constrain magmatic fO_2 in each sample using the V-in-olivine

393   oxybarometry method. All OIB samples are similar in fO_2, ranging from $+1.52^{+0.36}_{-0.30}$ ΔFMQ to

394    $+2.86^{+0.28}_{-0.24}$ ΔFMQ, with an average of 1.96 ± 0.70 ΔFMQ, significantly more oxidized than the

395   V-in-olivine oxybarometry MORB average of +0.60 ± 0.15 ΔFMQ. Additionally, OIB fO_2 shows no

396   correlation with whole rock $^{206}Pb/^{204}Pb$, $^{143}Nd/^{144}Nd$ and $^{187}Os/^{188}Os$ ratios, or with parental

397   magma MgO or inferred pyroxenite content in their source regions. Given the probable presence

398   of oxidized altered oceanic crust in high $^{206}Pb/^{204}Pb$ OIB, such a null result is significant. This is

399   likely due to isotopic signatures being dominated by volumetrically small, trace element-enriched

400   components, while fO_2 reflects the volumetrically dominant component of the OIB source region.

401   The large and consistent gap in fO_2 between MORB and OIB samples indicates that the

402   volumetrically dominant plume component was oxidized relative to the depleted mantle. Two

403   main mechanisms can explain this: either the net OIB source mantle has uniformly high amounts

404   of recycled oceanic crust, or the OIB source reflects a primitive undegassed oxidized reservoir.

405   Early mantle material could have become oxidized shortly after core formation by the

406   segregation of disproportionated Fe metal formed in the lower mantle and be preserved unmixed

407   in the lower mantle till the present day. The presence of $^{182}W/^{184}W$ isotope anomalies in modern

408 OIB lend credence to the idea that plumes may sample early formed mantle reservoirs. The new

409 dataset presented here confirms that the modern mantle is heterogeneous with respect to fO_2

410 and that different mantle reservoirs can be accurately characterized using the V-in-olivine

411 oxybarometry method in the future.

412

418

419 **Author Contributions:**

420 RWN and JMDD designed the project. RKMH and RWN prepared and performed the

421 analyses, data reduction and calculations. The manuscript was written by RWN and RKMH with

422 editing from JMDD, MGJ, VZ, RA and LNW. Samples were collected by JMDD, VZ and MGJ. JMDD

423 provided funding and technical support for the project.

Figure Captions

Figure 1. Calculated fO_2 of the OIB samples plotted against MgO content of parental magmas. MORB fO_2 field based on olivine-glass pairs from Nicklas et al. (2019).

Figure 2a. Calculated fO_2 of the OIB samples plotted against bulk rock $^{187}Os/^{188}Os$ ratios. **b.** Calculated fO_2 of the OIB samples plotted against bulk rock $^{206}Pb/^{204}Pb$ ratios. **c.** Calculated fO_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 fO_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 fO_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, SiO_2 – 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
04PAL05	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

2s			26.7	469	0.55	33.3	125	0.03	0.04
AVON2-62-2	20	40.34	314.2	2187	4.95	159.1	2340	0.19	0.12
2s			133.1	943	1.16	30.5	653	0.05	0.04
AVON3-71-2	20	40.38	208.0	2273	5.00	156.8	1923	0.14	0.11
2s			75.5	460	0.99	15.0	493	0.05	0.03

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	SiO_2	TiO_2	Al_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	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 fO_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 fO_2 for each sample is listed, along with an fO_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 fO_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*O2 (ΔFMQ)**	*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 fO_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 fO_2, down – negative uncertainty on the calculated fO_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	$^{206}Pb/^{204}Pb$	2s	$^{143}Nd/^{144}Nd$	2s	$^{187}Os/^{188}Os$	2s	FMQ at 1250C	FMQ at 1300C
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

Works Cited:

Ballhaus, C., Berry, R. F., Green, D. H. (1991). High pressure experimental calibration of the olivine-orthopyroxene-spinel oxygen geobarometer: implications for the oxidation state of the upper mantle. *Contrib. Mineral. Petrol.* **107**: 27-40.

Berry A. J., Stewart G. A., O'Neill H. St. C., Mallmann G., Mosselmans J. F. W. (2018) A re-assessment of the oxidation state of iron in MORB glasses. *Earth and Planetary Science Letters* **483**: 114-123.

Brounce, M. N., Cottrell, E., Kelley, K. A. (2019). The Redox Budget of the Marianas Subduction Zone. *Earth and Planetary Science Letters* **528:** 115859.

Brounce M. N., Stolper E., Eiler, J. (2017) Redox variations in Mauna Kea lavas, the oxygen fugacity of the Hawaiian plume, and the role of volcanic gases in Earth's oxygenation. *Proc. Natl. Acad. Sci*. **114**, 8997–9002.

Brounce M. N., Kelley K. A., Cottrell E. (2014) Variations in $Fe^{+3}/\Sigma Fe$ of Mariana Arc Basalts and Mantle Wedge fO_2. *J. Petrol.* **55**, 2513–2536.

Cabral, R. A., Jackson, M. G., Rose-Koga, E. F., Koga, K. T., Whitehouse, M. J., Antonelli, M. A., Farquhar, J., Day, J. M. D., Hauri, E. H. (2013) Anomalous sulphur isotopes in plume lavas reveal deep mantle storage of Archaean crust. *Nature* **496**: 490-493.

Canil D. (1997) Vanadium partitioning and the oxidation state of Archaean komatiite magmas. *Nature* **389**, 842–845.

Carmichael I. S. (1991) The redox states of basic and silicic magmas: A reflection of their source regions? *Contrib. Mineral. Petrol.* **106**, 129–141.

Chakraborty, S. (2010) Diffusion coefficients in Olivine, Wadleysite and Ringwoodite. *Reviews in Mineralogy and Geochemistry* **72**: 603-639.

Chauvel C., Hofmann A. W., Vidal P. (1992) HIMU-EM: The French Polynesian connection. *Earth and Planetary Science Letters* **110**: 99-119.

Class C., Goldstein S. L. (2005) Evolution of helium isotopes in the Earth's mantle. *Nature* **436**: 1107-1112.

Cottrell E., Lanzirotti A., Mysen B., Birner S., Kelley K. A., Botcharnikov R., Davis F. A., Newville M. (2018) A Mössbauer-based XANES calibration for hydrous basalt glasses reveals radiation-induced oxidation of Fe. *American Mineralogist* **103**: 489-501.

Cottrell E., Kelley K. A. (2013) Redox Heterogeneity in Mid-Ocean Ridge Basalts as a Function of Mantle Source. *Science* **340**(6138): 1314-1317.

Cottrell E. Kelley K. A. (2011) The oxidation state of Fe in MORB glasses and the oxygen fugacity of the upper mantle. *Earth Planet. Sci. Lett.* **305**, 270–282.

Day J. M. D., Walker R. J., Watanbe S., Hanski E., Jackson M. G., Widom E. (2020) Osmium-186 anomalies in ocean island basalts from early Earth differentiation. *Science Advances* (*under review*)

Day J. M. D. (2013) Hotspot volcanism and highly siderophile elements. *Chemical Geology* **341**: 50-74.

Day J. M. D., Hilton D. R. (2011) Origin of ^{3}He/^{4}He ratios in HIMU-type basalts constrained from Canary Island lavas. *Earth and Planetary Science Letters* **305**: 226-234.

Day J. M. D., Pearson D. G., Macpherson C. G., Lowry D., Carracedo J.-C. (2010) Evidence for distinct proportions of subducted oceanic crust and lithosphere in HIMU-type mantle beneath El Hierro and La Palma, Canary Islands. *Geochimica et Cosmochimica Acta* **74**: 6565-6589.

Day J. M. D., Pearson D. G., Macpherson C. G., Lowry D., Carracedo J.-C. (2009) Pyroxenite-rich mantle formed by recycled oceanic lithosphere: Oxygen-osmium isotope evidence from Canary Island lavas. *Geology* **37**(6): 555-558.

Evans K. A. (2012) The redox budget of subduction zones. *Earth-Sci. Rev.* **113**, 11–32.

Farley K. A., Natland J. H., Craig H. (1992) Binary mixing of enriched and undegassed (primitive?) mantle components (He, Sr, Nd, Pb) in Samoan lavas. *Earth and Planetary Science Letters* **111**: 183-199.

Foley S. F., Prelevic D., Rehfeldt T., Jacob D. E. (2013) Minor and trace elements in olivine as probes into early igneous and mantle melting processes. *Earth and Planetary Letters* **363**: 181-191.

Gale A., Dalton C. A., Langmuir C. H., Su Y., Schilling J.-G. (2013) The mean composition of ocean ridge basalts. *Geochemistry, Geophysics, Geosystems* **14**(3): 489-518.

Genske F. S., Turner S. P., Beier C., Chu M.-F., Tonarini S., Pearson N. J., Haase K. M. (2014) Lithium and boron isotope systematics in lavas from the Azores islands reveal crustal assimilation. *Chemical Geology* **373**: 27-36.

Gleeson M. L. M., Gibson S. A. (2019) Crustal controls on apparent mantle pyroxenite signals in ocean-island basalts. *Geology* **47**(4): 321-324.

Grocke S. B., Cottrell E., Silva S. D. and Kelley K. A. (2016) The role of crustal and eruptive processes versus source variations in controlling the oxidation state of iron in Central Andean magmas. *Earth Planet. Sci. Lett.* **440,** 92–104.

Gurenko A. A., Sobolev A. V., Hoernle K. A., Hauff F., Schmincke H.-U. (2009) Enriched, HIMU-type peridotite and depleted recycled pyroxenite in the Canary plume: A mixed-up mantle. *Earth and Planetary Science Letters* **277**: 514-524.

Hart, S. R., Gaetani, G. A. (2006). Mantle Pb paradoxes: the sulfide solution. *Contrib. Mineral. Petrol.* **152**: 295-308.

Hart, S. R., Hauri, E. H., Oschmann, L. A., Whitehead, J. A. (1992). Mantle Plumes and Entrainment: Isotopic Evidence. *Science* **256**: 517-520.

Helz R. T., Cottrell E., Brounce M. N., Kelley K. A. (2017). Olivine-melt relationships and syneruptive redox variations in the 1959 eruption of Kīlauea Volcano as revealed by XANES. *Journal of Volcanology and Geothermal Research* **333-334**: 1-14.

Herzberg C., Cabral C. A., Jackson M. G., Vidito C., Day J. M. D., Hauri E. H. (2014). Phantom Archean crust in Mangaia Hotspot Lavas and the meaning of heterogeneous mantle. *Earth and Planetary Science Letters* **396**: 97-106.

Herzberg C., Asimow P. D., Ionov D. A., Vidito C., Jackson M. G., Geist D. (2013). Nickel and helium evidence for melt above the core-mantle boundary. *Nature* **493**: 393-397.

Hofmann A. W. (1997). Mantle geochemistry: the message from oceanic volcanism. *Nature* **385**: 219-229.

Jackson, M.G. Hart S. R., Konter, J. G., Kurz, M. D., Blusztajn, J., Farley, K. A. (2014). Helium and lead isotopes reveal the geochemical geometry of the Samoan plume. *Nature* **514**: 355-358.

Jackson M. G., Hart S. R., Koppers A. A. P., Staudigel H., Konter J., Blusztajn J., Kurz M., Russell J. A. (2007) The return of subducted continental crust in Samoan lavas. *Nature* **448**: 684-687.

Kasting J. (2014) Mantle Cooling, Seafloor Serpentinization, and the Rise of Atmospheric O_2. American Geophysical Union Fall Meeting, Abstract #P11C-3782.

Kelley K. A. and Cottrell E. (2012) The influence of magmatic differentiation on the oxidation state of Fe in a basaltic arc magma. *Earth Planet. Sci. Lett.* **329-330**, 109–121.

Kelley K. A. and Cottrell E. (2009) Water and the Oxidation State of Subduction Zone Magmas. *Science* **325**: 605-607.

Kress V. C. and Carmichael I. S. E. (1991) The compressibility of silicate liquidus containing Fe_2O_3 and the effect of composition, temperature, oxygen fugacity and pressure on their redox states. *Contrib. Mineral. Petrol.* **103**, 82–92.

Labidi J., Cartigny, P. Jackson M. G. (2015). Multiple sulfur isotope composition of oxidized Samoan melts and the implications of a sulfur isotope 'mantle array' in chemical geodynamics. *Earth and Planetary Science Letters* **417**: 28-39.

Lee C.-T. A., Luffi P., Le Roux V., Dasgupta R., Albarede F., Leeman W. P. (2010) The redox state of arc mantle using Zn/Fe systematics. *Nature* **468**: 681-685.

Lee C.-T. A., Leeman W. P., Canil D., and Li Z.-X. A. (2005) Similar V/Sc Systematics in MORB and Arc Basalts: Implications for the Oxygen Fugacities of their Mantle Source Regions. Journal of Petrology **46**(11): 2313-2336.

Le Voyer M., Cottrell E., Kelley K. A., Brounce M. and Hauri E. H. (2015) The effect of primary versus secondary processes on the volatile content of MORB glasses: An example from the equatorial Mid-Atlantic Ridge (5°N-3°S). *J. Geophys. Res.* **120**, 125–144.

Lindsley D. H. (Ed.). 1991. Oxygen Barometry of Spinel Peridotites. In B.R. Frost (Author), Reviews in Mineralogy and Geochemistry (Vol. 25, 417-432). Mineralogical Society of America.

Madureira, P., Moreira, M., Mata, J., Nunes, J.C., Gautheron, C., Lourenço, N., Carvalho, R., de Abreu, M.P. (2014). Helium isotope systematics in the vicinity of the Azores triple junction: Constraints on the Azores geodynamics. *Chemical Geology* **372**: 62-71.

Matzen A. K., Wood B. J., Baker M. B., Stolper E. M. (2017). The roles of pyroxenite and peridotite in the mantle sources of oceanic basalts. *Nature Geoscience* **10**: 530-535.

McDonough W. F., Sun S.-S. (1995) The composition of the Earth. *Chemical Geology* **120**: 223-253.

Moreira M., Kanzari A., Madureira P. (2012). Helium and neon isotopes in São Miguel island basalts, Azores Archipelago: new constraints on the "low 3He" hotspot origin. *Chemical Geology* **322**: 91-98.

Moreira, M., Doucelance, R., Dupré, B., Kurz, M., Allègre, C.J. (1999). Helium and lead isotope geochemistry in the Azores archipelago. *Earth and Planetary Science Letters* **169**, 189–205.

Moussallam Y. *et al.* (2019) Mantle Plumes are oxidized. *Earth and Planetary Science Letters* **527**, 115798.

Moussallam Y., Edmonds M., Scaillet B., Peters N., Gennaro E., Sides I. and Oppenheimer C. (2016) The impact of degassing on the oxidation state of basaltic magmas: A case study of Kīlauea volcano. *Earth Planet. Sci. Lett.* **450**, 317–325.

Moussallam Y., Oppenheimer C., Scaillet B., Gaillard F., Kyle P., Peters N., Hartley M., Berlo K. and Donovan A. (2014) Tracking the changing oxidation state of Erebus magmas, from

mantle to surface, driven by magma ascent and degassing. *Earth Planet. Sci. Lett.* **393,** 200–209.

Mundl A., Touboul M., Jackson M. G., Day J. M. D., Kurz M. D., Lekic V., Helz R. T., Walker R. J. (2017). Tungsten-182 heterogeneity in modern ocean island basalts. *Science* **356**: 66-69.

Mundl-Petermeier A., Walker, R. J., Fischer, R. A., Lekic, V., Jackson, M. G., Kurz, M. D. (2020). Anomalous 182W in high 3 He/4 He ocean island basalts: Fingerprints of Earth's core? *Geochimica et Cosmochimica Acta* **271**: 194-211.

Mungall J. E., Hanley J. J., Arndt N. T., Debecdelievre A. (2006). Evidence from meimechites and other low-degree mantle melts for redox controls on mantle-crust fractionation of platinum-group elements. *PNAS* **103**(34): 12695-12700.

Nicklas R. W., Day J. M. D., Vaci Z., Udry A., Liu Y., Tait K. T. (2021). Uniform Ambient Mantle Oxygen Fugacity and a Highly Oxidized Lithospheric Mantle on Mars. *Earth and Planetary Science Letters* **564**: 116876.

Nicklas R. W., Puchtel I. S., Ash R. D., Piccoli P. M., Hanski E., Nisbet E. G., Waterton P, M., Pearson D. G., Anbar A. D. (2019) Secular Mantle Oxidation across the Archean-Proterozoic Boundary: Evidence from V Partitioning in Komatiites and Picrites. *Geochimica et Cosmochimica Acta* **250**: 49-75.

Nicklas R. W., Puchtel I. S., Ash R. D. (2018). Redox state of the Archean mantle: Evidence from V partitioning in 3.5–2.4 Ga komatiites. *Geochim. Cosmochim. Acta* **222**, 447–466.

Novella D., Maclennan J., Shorttle O., Prytulak J., Murton B. J. (2020). A multi-proxy investigation of mantle oxygen fugacity along the Reykjanes Ridge. *Earth and Planetary Science Letters* **531**: 115973.

Padron-Navarta J. A., Sanchez-Vizcaino V. L., Garrido C. J., Gomez-Pugnaire M. T. (2011) Metamorphic record of high-pressure dehydration of antigorite serpentinite to chlorite harzburgite in a subduction setting (Cerro del Almirez, Nevado-Filabride Complex, Southern Spain). *J. Petrol.* **52**, 2047–2078.

Parai R., Mukhopadhyay S., Lassiter J. C. (2009). New constraints on the HIMU mantle from neon and helium compositions of basalts from the Cook-Austral Islands. *Earth and Planetary Science Letters* **277:** 253-261.

Pringle E. A., Moynier F., Savage P. S., Jackson M. G., Moreira M., Day J. M. D. (2016). Silicon isotopes reveal recycled altered oceanic crust in the mantle sources of Ocean Island Basalts. *Geochimica et Cosmochimica Acta* **189**: 282-295.

Rudnick R. L., Gao S. (2003). The composition of the continental crust, in *The Crust*, vol. 3, edited by R. L. Rudnick, p. 1-64, Elsevier Sci., New York.

Ryabchikov I. D., Ntaflos T., Kurat G., Kogarko L. N. (1995). Glass-bearing xenoliths from Cape Verde: evidence for a hot rising mantle jet. *Mineralogy and Petrology* **55**: 217-237.

Salters V. J. M., Stracke A. (2004). Composition of the depleted mantle. *Geochemistry, Geophysics, Geosystems* **5**(5).

Shorttle O., Moussallam Y., Hartley M. E., Maclennan J., Edmonds M., Murton B. J. (2015). Fe-XANES analyses of Reykjanes Ridge basalts: Implications for oceanic crust's role in the solid Earth oxygen cycle. *Earth and Planetary Science Letters* **427**: 272-285.

Sobolev A. V., Hofmann A. W., Kuzmin D. V., Yaxley G. M., Arndt N. T., Chung S.-L., Danyushevsky L. V., Elliott T., Frey F. A., Garcia M. O., Gurenko A. A., Kamenetsky V. S., Kerr A. C., Krivolutskaya N. A., Matvienkov V. V., Nikogosian I. K., Rocholl A., Sigurdsson I. A., Sushchevskaya N. M., Teklay M. (2007). The Amount of Recycled Crust in Sources of Mantle-Derived Melts. *Science* **316**: 412-417.

Sobolev A. V., Hofmann A. W., Sobolev S. V., Nikogosian I. K. (2005) An olivine-free mantle source of Hawaiian shield basalts. *Nature* **434**: 590-597.

Stracke A., Genske F., Berndt J., Koorneef J. (2019) Ubiquitous ultra-depleted domains in Earth's mantle. *Nature Geoscience* **12**: 851-855.

Stracke A., Hofmann, A. W., Hart, S. R. (2005) FOZO, HIMU, and the rest of the mantle zoo. *Geochemistry, Geophysics, Geosystems* **6**(5).

Tang M., Erdman M., Eldridge G., Lee C.-T. A. (2018) The redox "filter" beneath magmatic orogens and the formation of continental crust. *Scientific Advances* **4**(5): 1-7.

Taracsak Z., Hartley M. E., Burgess R., Edmonds M., Iddon F., Longpre M.-A. (2019). High fluxes of deep volatiles from ocean island volcanoes: Insights from El Hierro, Canary Islands. *Geochimica et Cosmochimica Acta* **258**: 19-36.

Wang J., Xiong X., Takahashi E., Zhang L., Li L., Liu X. (2019). Oxidation State of Arc Mantle Revealed by Partitioning of V, Sc and Ti Between Mantle Minerals and Basaltic Melts. *Journal of Geophysical Research: Solid Earth* **124**: 4617-4638.

Waters C. L., Day, J. M. D., Watanabe, S., Sayit, K., Zanon, V., Olson, K. M., Hanan, B. B., Widom, E. (2020). Sulfide mantle source heterogeneity recorded in basaltic lavas from the Azores. *Geochimica et Cosmochimica Acta* **268**: 422-445.

Waters L. E. and Lange R. A. (2016) No effect of H_2O degassing on the oxidation state of magmatic liquids. *Earth Planet. Sci. Lett.* **447,** 48–59.

Wood B. J., Walter M. J., Wade J. (2006). Accretion of the Earth and segregation of its core. Nature, **441**(7095): 825-833.

Workman R. K., Hart S. R. (2005). Major and trace element composition of the depleted MORB mantle (DMM). *Earth and Planetary Science Letters* **231**: 53-72.

Workman R. K., Hart S. R., Jackson M., Regelous M., Farley K. A., Blusztajn J., Kurz M., Staudigel H. (2004). Recycled metasomatized lithosphere as the origin of the Enriched Mantle II (EM2) endmember: evidence from the Samoan volcanic chain. *Geochem. Geophys. Geosys.* **5**(4): 1-44.

Williams H. M., Bizimis M. (2014). Iron isotope tracing of mantle heterogeneity within the source regions of oceanic basalts. *Earth and Planetary Science Letters* **404**: 396-407.

Woodhead J. D. (1996) Extreme HIMU in an oceanic setting: the geochemistry of Mangaia Island (Polynesia), and temporal evolution of the Cook-Austral hotspot. *Journal of Volcanology and Geothermal Research* **72**: 1-19.

Zhang H. L., Cottrell E., Solheid P. A., Kelley K. A., Hirschmann M. M. (2018) Determination of Fe3+/ΣFe of XANES basaltic glass standards by Mössbauer spectroscopy and its application to the oxidation state of iron in MORB. *Chemical Geology* **479**: 166-175.

Zindler A., Hart S. (1986) Chemical Geodynamics. *Ann. Rev. Earth Planet. Sci.* **14**: 493-571.

424

Figure 1

Figure 2

Figure 3.