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1 Mantle plumes are oxidised

2 **Yves Moussallam^{1,2}, Marc-Antoine Longpré³, Catherine McCammon⁴, Alejandra**
3 **Gomez-Ulla¹, Estelle F. Rose-Koga¹, Bruno Scaillet⁵, Nial Peters⁶, Emanuela Gennaro⁷,**
4 **Raphael Paris¹, Clive Oppenheimer⁶**

5

6 *¹ Université Clermont Auvergne, CNRS, IRD, OPGC, Laboratoire Magmas et Volcans, F-63000*
7 *Clermont-Ferrand, France*

8 *² Lamont-Doherty Earth Observatory, Columbia University, New York, USA*

9 *³ School of Earth and Environmental Sciences, Queens College, City University of New York, Queens,*
10 *NY 11367, USA*

11 *⁴ Bayerisches Geoinstitut, University of Bayreuth, D-95440 Bayreuth, Germany*

12 *⁵ ISTO, UMR 7327, Université d'Orléans-CNRS-BRGM, 1A rue de la Férollerie, 45071 Orléans cedex*
13 *2, France*

14 *⁶ Department of Geography, University of Cambridge, Downing Place, Cambridge, CB2 3EN, UK*

15 *⁷ Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo, Via Ugo La Malfa, 153, 90146*
16 *Palermo, Italy*

17

18 Corresponding author: Yves Moussallam; yves.moussallam@gmail.com

19

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21

22 **ABSTRACT**

23 From oxic atmosphere to metallic core, the Earth's components are broadly stratified with
24 respect to oxygen fugacity. A simple picture of reducing oxygen fugacity with depth may be
25 disrupted by the accumulation of oxidised crustal material in the deep lower mantle, entrained
26 there as a result of subduction. While hotspot volcanoes are fed by regions of the mantle likely
27 to have incorporated such recycled material, the oxygen fugacity of erupted hotspot basalts had
28 long been considered comparable to slightly more oxidised than that of mid-ocean ridge basalt
29 (MORB) and more reduced than subduction zone basalts. Here we report measurements of the
30 redox state of glassy crystal-hosted melt inclusions from tephra and quenched lava samples
31 from the Canary and Cape Verde Islands, that we can independently show were entrapped prior
32 to extensive sulfur degassing. We find high ferric iron to total iron ratios ($\text{Fe}^{3+}/\sum\text{Fe}$) of up to
33 0.27–0.30, indicating that mantle plume primary melts are significantly more oxidised than
34 those at mid-ocean ridges and even subduction zone contexts. These results, together with
35 previous investigations from the Erebus, Hawaiian and Icelandic hotspots, confirm that mantle
36 upwelling provides a return flow from the deep Earth for components of oxidised subducted
37 lithosphere and suggest that highly oxidised material accumulates or is generated in the lower
38 mantle. The oxidation state of the Earth's interior must therefore be highly heterogeneous and
39 potentially locally inversely stratified.

40 I. INTRODUCTION

41

42 Temperature, pressure, volatile content, major element composition and oxygen fugacity (f_{O_2})
43 are the five parameters controlling the occurrence and extent of partial melting in Earth's
44 mantle, ultimately dictating where magmatic activity occurs on our planet. Of those, variables,
45 oxygen fugacity of the mantle remains the least constrained yet its influence on phase
46 relationship, volatile speciation, element partitioning and mantle physical properties is primary
47 (e.g., Arculus, 1985). In terrestrial rocks, oxygen fugacity varies by over nine orders of
48 magnitude (e.g., Parkinson and Arculus, 1999), but it remains to be seen how much oxygen
49 fugacity varies in the upper mantle, especially in regions where melting occurs and if indeed
50 systematic differences exist between tectonic contexts.

51

52 Our understanding of the oxygen fugacity of the upper mantle feeding volcanoes and their
53 magmatic systems has been largely derived from measurements of the oxidation state
54 (expressed as the $Fe^{3+}/\Sigma Fe$ ratio) of erupted basalts (e.g., Christie et al., 1986; Carmichael,
55 1991; Bezos and Humler, 2005; Rhodes and Vollinger, 2005; Cottrell and Kelley, 2011).
56 Basaltic lavas sampled at hotspot volcanoes (e.g., Mallmann and O'Neill, 2009; Rhodes and
57 Vollinger, 2005; Roeder et al., 2003) have an oxidation state typically more reduced than
58 basaltic lavas from subduction zone volcanoes and comparable to that of global mid-ocean
59 ridge basalt (MORB), implying that the oxygen fugacity of mantle plumes is similar to that of
60 the mantle feeding MORB, i.e., near the fayalite–magnetite–quartz (FMQ) oxygen buffer (e.g.,
61 Bezos and Humler, 2005; Birner et al., 2018; Cottrell and Kelley, 2011; O'Neill et al., 2018;
62 Zhang et al., 2018). However, it has become increasingly clear, from both theoretical
63 considerations (e.g., Anderson and Wright, 1972; Burgisser and Scaillet, 2007; Métrich et al.,
64 2009; Gaillard et al., 2011, 2015) and observations (e.g., Anderson and Wright, 1972;

65 Carmichael and Ghiorso, 1986; Kelley and Cottrell, 2012; Moussallam et al., 2014, 2016; Helz
66 et al., 2017; Brounce et al., 2017; Longpré et al., 2017), that the oxygen fugacity of mantle
67 melts can be strongly affected by the degassing of volatiles (especially sulfur) during magma
68 ascent to the surface. While this effect can be minor for MORB magmas erupted under high
69 hydrostatic pressure (e.g., Shorttle et al., 2015), it may be significant for shallow submarine
70 and subaerial eruptions of hotspot volcanoes. Investigation of the oxygen fugacity of the upper
71 mantle feeding hotspot volcanoes therefore demands identification and study of un-degassed
72 melts that preserve the oxidation state acquired in equilibrium with the mantle.

73

74 In this work, we examine a series of olivine-hosted melt inclusions, embayments and matrix
75 glasses from tephra and lava ballon samples erupted at the hotspots of the Canary (El Hierro
76 and Lanzarote volcanoes) and Cape Verde (Fogo volcano) Islands whose mantle plume origin
77 from the lower mantle is demonstrated from geophysical observations (French and
78 Romanowicz, 2015). Melt inclusions represent samples of the melt taken at various stages
79 during the degassing process, and previous investigations at these volcanoes have highlighted
80 the presence of volatile-rich melt inclusions entrapped at depths exceeding 10 km (Gómez-
81 Ulla, 2018; Longpré et al., 2017) and little affected by sulfur degassing. We report here on
82 measurements of the oxidation state of these melt inclusions obtained by X-ray absorption near-
83 edge structure (XANES) spectroscopy at the iron K-edge.

84

85 Throughout the text, melt fO_2 is calculated from $Fe^{3+}/\sum Fe$ using Equation 7 from Kress and
86 Carmichael (1991) and ΔFMQ refers to the difference in fO_2 between the melt and the Fayalite-
87 Magnetite-Quartz (FMQ) mineral redox buffer as reported in Frost (1991).

88

89 II. SAMPLES AND METHODS

90

91 Olivine-hosted melt inclusions, matrix glasses and embayments from rapidly-quenched tephra
92 and lava balloon samples collected from the 1824 Lanzarote, 2011-2012 El Hierro, as well as
93 tephra samples from Fogo volcano were polished on both sides to obtain doubly-exposed
94 wafers with at least a 10 x 10 μm obstruction-free area through the inclusion. The analysed
95 melt inclusions vary in minimum size from 36 to 181 μm in diameter (Table S1) and consist
96 of brown-coloured transparent glass of ovoid shape (Fig. S1).

97

98 Two samples from Fogo volcano eruption were used in this study. The first (Fogo05) was
99 collected on the western part of the Bordeira caldera wall at lat 14.936°; long -24.391°; 2190
100 m asl and consists of amalgamated tephra (poorly sorted, coarse-ash to fine-lapilli size) with
101 abundant orthopyroxene (up to 15%) and rare olivine phenocrysts. The second (Fogo11) was
102 collected on the western part of the Bordeira caldera wall at lat 14.937°; long -24.392°; 2340
103 m asl and consists of nearly aphyric (small pyroxenes and very rare olivine) phreatomagmatic
104 tephra (moderately sorted, medium-to-coarse ash size) deposits. Tephra from “Volcan de Tao”
105 (TAO) 1824 eruption at Lanzarote were used in this study (lat 29.03C; long -13.63V). Tephra
106 are highly vesiculated (50–60 vol%), fine to coarse lapilli in size, with olivine phenocrysts
107 ranging from 5 to 10% and trace amounts of clinopyroxene and plagioclase (see details in
108 Gómez-Ulla, 2018). Samples from El Hierro (EH) used in this study came from seawater-
109 quenched lava balloons, with shell ≤ 5 cm thick collected at lat 27.697°; long -17.993°. The
110 lavas contains olivine, clinopyroxenes and Fe-Ti oxides (see details in Longpré et al., 2017).

111

112 2.1 XANES data acquisition

113 All samples were analysed on Beamline I18 at the Diamond Light Source (DLS) using Fe K-
114 edge XANES (X-ray absorption near-edge structure spectroscopy). The X-rays were focused

115 with Kirkpatrick-Baez mirrors down to $2\ \mu\text{m}$ (horizontal) \times $1.2\ \mu\text{m}$ (vertical) beam size. The
116 beamline utilises a liquid nitrogen-cooled double-crystal monochromator with silicon crystals
117 and the Si (333) reflection was used to increase the energy resolution. Measurements were
118 performed in fluorescence mode, where we used two energy-dispersive Vortex ME-4 silicon
119 drift detectors positioned at 45 degrees to the incident beam (one located directly above the
120 other and pointing towards the sample). The sample was positioned so that the normal to the
121 sample surface was at 45 degrees to the incident X-ray beam. Default analytical conditions for
122 XANES at I18 yield a photon flux of 10^{10} ph/s by attenuating (using a combination of
123 aluminium foils and slit) a 10^{12} ph/s primary beam upstream of the ion chamber. The beam can
124 then be further attenuated (using Al foil). For melt inclusions, the incident X-ray beam was
125 additionally filtered with an Al foil of 0.25 mm thickness to remove the effect of beam damage
126 on the sample (see section below). Matrix glasses, which are water-poor, were analysed using
127 an additional 0.1 mm Al foil attenuation. The energy step sizes and dwell times used are given
128 in **Table S2**. For melt inclusions, two spectra were acquired and co-added for each analysis.
129 All XANES spectra of melt inclusions were examined for contamination from the olivine host.
130 Spectra showing any structure in the edge and post-edge region were rejected (see Fig. S6 in
131 Moussallam et al., 2014 for an example of contaminated spectra).

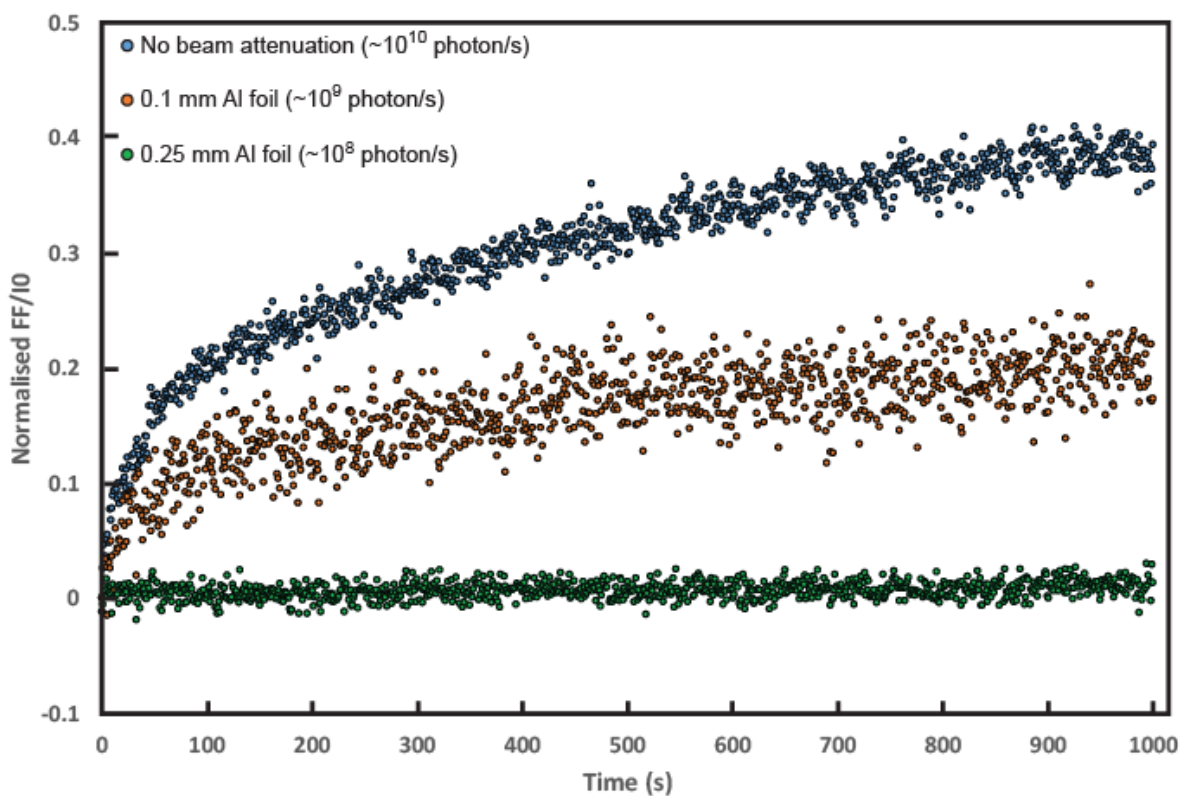
132

133 **2.2 Beam damage**

134 The effect of sample exposure to focused beams of X-rays on iron speciation has been
135 investigated in several studies under a range of beam and sample conditions (e.g., Cottrell et
136 al., 2018, 2009; Moussallam et al., 2016, 2014; Shorttle et al., 2015). These works showed that
137 the stronger the photon flux and the more water-rich the sample, the higher the amount of
138 photo-oxidation. Accordingly, we performed a series of tests in order to determine the
139 analytical conditions required to avoid beam damage for our samples.

140
141 We used a hydrated experimental glass of basaltic composition (49.36 wt.% SiO₂, 1.47 wt.%
142 TiO₂, 14.36 wt.% Al₂O₃, 8.61 wt.% FeO, 0.16 wt.% MnO, 9.08 wt.% MgO, 11.71 wt.% CaO,
143 3.26 wt.% Na₂O, 1.3 wt.% K₂O) with a $\text{Fe}^{3+}/\sum\text{Fe} = 0.22$ (obtained using the Smithsonian basalt
144 glass calibration and Zhang et al., (2018) $\text{Fe}^{3+}/\sum\text{Fe}$ values from Mössbauer spectroscopy and
145 under the beam damage-free analytical conditions described below). This glass was chosen
146 because it contains 5.2 wt.% H₂O (as determined by SIMS), which is considerably more than
147 any of the natural glasses analysed subsequently, hence it represents a worst-case scenario in
148 terms of beam damage. We positioned the monochromator at a fixed energy of 7114.3 eV,
149 corresponding to the oxidised peak of the pre-edge doublet. We then opened the shutter and
150 counted the fluoresced X-rays every second for 1000 sec (~17 min) (Fig. 1). This beam damage
151 test was popularised by Shorttle et al., (2015) and further used by Cottrell et al., (2018) and has
152 the advantage over the more classic repeated quick-scan approach (e.g., Moussallam et al.,
153 2016, 2014; Wilke et al., 2008) to allow identification of any beam damage occurrence over
154 the first seconds of sample-beam interaction. We found that, under our analytical conditions
155 and using an Al foil of 0.25 mm that attenuates the beam to about 1% of its original flux
156 (calculated based on theoretical absorption, equivalent to $\sim 10^8$ photon/s or $\sim 10^7$ to 10^8
157 photon/s/ μm^2), no change in fluoresced intensity was recorded under beam exposure. By
158 contrast, using a 0.10 mm Al foil or no attenuation at all produced significant photo-oxidation
159 of the iron. These results indicate that Fe in our natural samples, measured using a 0.25 mm Al
160 foil, was not oxidised during XANES analyses. Note that conditions at each synchrotron
161 beamline are slightly different, so the conditions under which we observe no resolvable beam
162 damage at I18 are entirely reproducible but not directly transposable to another
163 synchrotron/beamline. In the same way that calibration with glass standards is required before

164 each XANES analytical session, we recommend that a beam damage test and identification of
 165 beam damage-free analytical conditions be performed before each XANES analytical session.
 166



167
 168 **Figure 1:** Time series of normalised fluoresced intensity (FF) over I_0 at 7114.3 eV integrated
 169 over 1 s intervals for a hydrated (5.2 wt.% H_2O) basaltic glass under three different beam
 170 attenuation conditions. A fresh spot was illuminated with a $2.5 \times 1.2 \mu m^2$ beam for each
 171 analysis. While photo-oxidation can clearly be seen with no beam attenuation and with an
 172 attenuation down to about 16% of the original beam flux (using a 0.1 mm Al foil), no photo-
 173 oxidation can be detected once the beam has been attenuated down to 1% of its original flux
 174 (using a 0.25 mm Al foil). Note that in order to improve the signal/noise level during the test
 175 with a 0.25 mm Al foil, the detectors were moved closer to the (another time series acquired
 176 on another spot without the detector adjustment is shown in [Fig. S5](#)).
 177

178 **2.3 Standards and Mössbauer spectroscopy**

179 Glass standards for the XANES analyses were prepared in a controlled atmosphere furnace at
180 the Department of Earth Sciences, University of Cambridge using a controlled CO₂-CO gas
181 mixture. For each experiment, 50 mg of sample was placed in a platinum crucible. The sample
182 was then introduced into the furnace and heated at 1400°C and left to equilibrate for two hours.
183 At the end of each experiment, rapid quenching preserved chemical equilibrium as the sample
184 dropped into a container of deionised water. The drop was initiated by short-circuiting the thin
185 platinum wire by passing a current through the thick platinum wires. Six basanite standards of
186 2011-2012 El Hierro magma composition (44.4 wt.% SiO₂, 5.0 wt.% TiO₂, 13.7 wt.% Al₂O₃,
187 12.5 wt.% FeO_t, 0.2 wt.% MnO, 8.1 wt.% MgO, 10.7 wt.% CaO, 3.5 wt.% Na₂O, 1.4 wt.%
188 K₂O and 0.5 wt.% P₂O₅) were equilibrated at various fO_2 conditions (FMQ-1, FMQ, NNO,
189 NNO+0.5, NNO+1 and NNO+1.5). All experiments were performed twice; first, in order to
190 equilibrate the Pt crucible with Fe at each fO_2 (during 24h) and, second, to produce the glass
191 used as standard. All standard glasses were subsequently analysed by electron microprobe. A
192 20-point electron microprobe transect was made across each standard to ensure all samples
193 were homogeneous and that neither iron nor sodium loss had occurred.

194

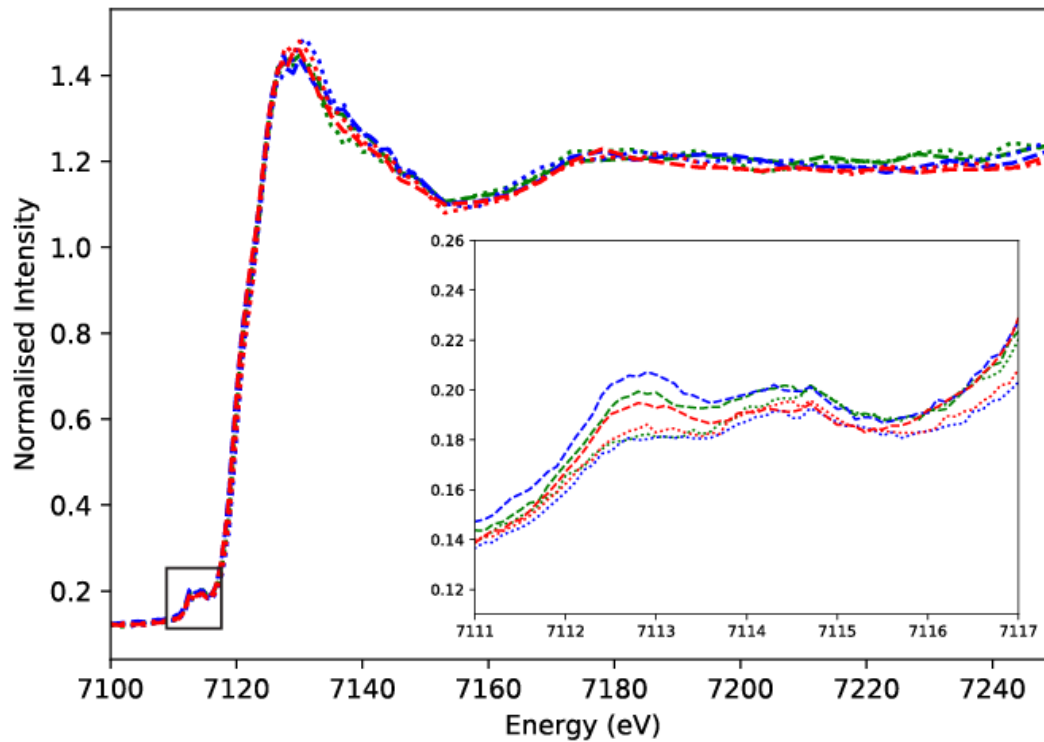
195 All basanite glass standards were analysed for Fe³⁺/ΣFe by Mössbauer spectroscopy at the
196 Bayerisches Geoinstitut. Samples were analysed at room temperature using a constant
197 acceleration Mössbauer spectrometer in transmission mode with a nominal 370 MBq ⁵⁷Co
198 point source in a 12 μm Rh matrix. The active dimensions of the point source were 500 x 500
199 μm. The velocity scale was calibrated relative to α-Fe and line widths of 0.36 mm/s were
200 obtained for the outer lines of α-Fe at room temperature. Fits to Mössbauer spectra were
201 performed using MossA (Prescher et al., 2012) according to the approach used by Zhang et al.
202 (2018) (xVBF model). A linear baseline was added to account for the shadowing effect and all

203 fits used the full transmission integral to account for thickness effects of source and absorber
204 (Rancourt, 1989). Conventional constraints (doublet components with equal widths and areas)
205 were used and $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios were determined from the relative areas corrected for recoil-free
206 fraction effects according to Zhang et al. (2018). All Mössbauer spectra are shown in Fig. S2
207 and values are reported in Table S3.

208

209 **2.4 XANES spectra processing, $\text{Fe}^{3+}/\Sigma\text{Fe}$ calibration and data quality**

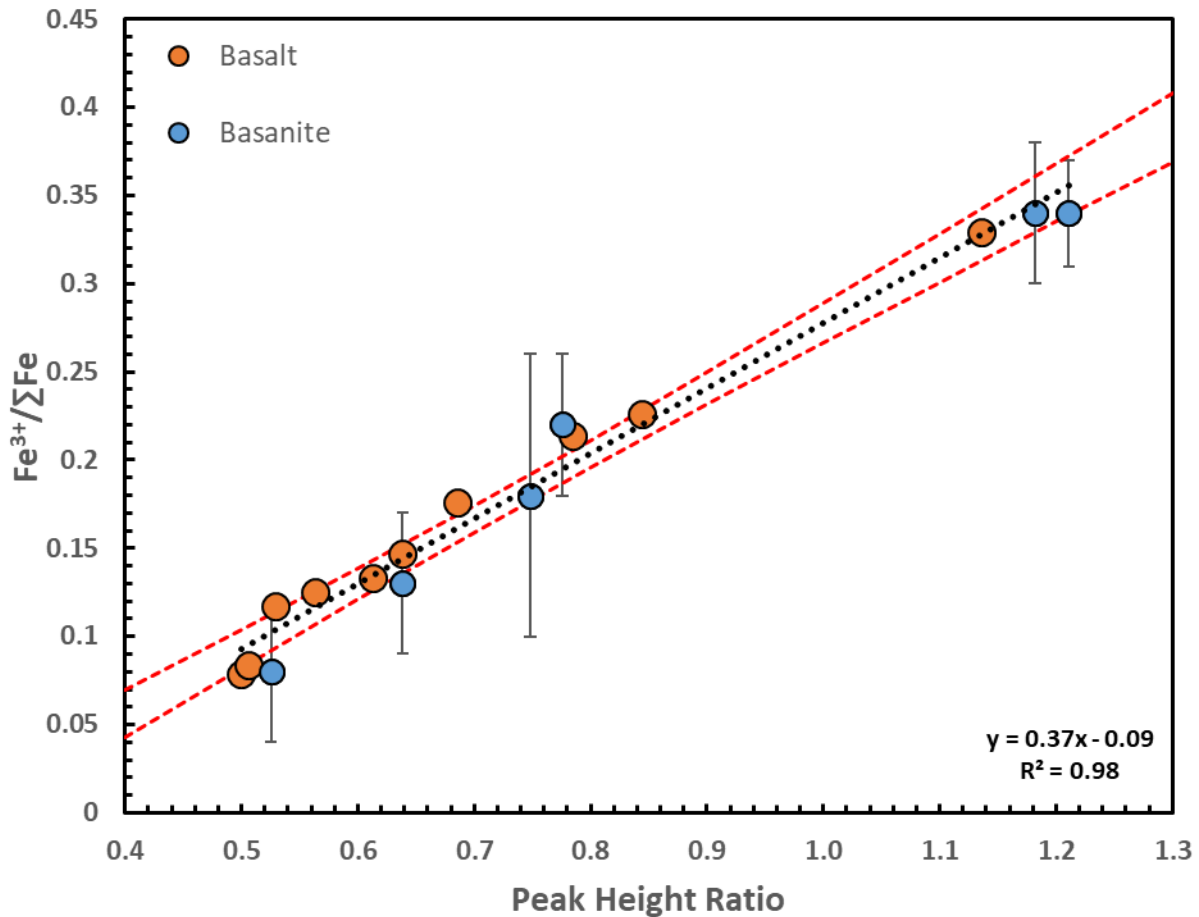
210 As stated above, in order to avoid any beam damage and photo-oxidation of iron under the X-
211 ray beam, all analyses of melt inclusions were performed using a highly attenuated beam (1%
212 of initial photon flux). These analytical conditions resulted in acquired spectra of lower quality
213 than typical for XANES analyses at the Fe K-edge (examples of such spectra are shown in Fig.
214 2). Noise in the acquired spectra made typical fitting of the pre-edge region with a combination
215 of a linear function and a damped harmonic oscillator function (DHO), and subsequent centroid
216 determination (e.g., Wilke et al., 2001; Farges, 2001; Berry et al., 2003; Wilke et al., 2004;
217 Cottrell et al., 2009; Moussallam et al., 2014) imprecise. To circumvent this problem, we used
218 the ratio of the pre-edge peak heights, on which we found spectra quality had a lesser effect, to
219 derive $\text{Fe}^{3+}/\Sigma\text{Fe}$ from natural spectra. In detail, the pre-edge region was still fitted with a
220 combination of a linear function and a damped harmonic oscillator function (DHO) but instead
221 of determining the centroid we measured the relative height of the $1s \rightarrow 3d$ pre-edge feature
222 absorption multiplet peaks. The peak height ratio was then parameterised against the Fe valence
223 state using our basanite glasses standards (Fig. 3).



224

225 **Figure 2:** Example of edge-step normalised XANES spectra (two co-add) obtained using a 0.25
 226 mm Al plate attenuation. Spectra from both more oxidised (dashed lines) and more reduced
 227 (dotted lines) melt inclusions are shown for El Hierro (red), Lanzarote (blue) and Fogo (green)
 228 volcanoes.

229



230

231 **Figure 3:** : Calibration line of the peak height ratio determined by XANES compared with the232 $Fe^{3+}/\Sigma Fe$ ratios determined by Mössbauer spectroscopy in basanite standard glasses (this

233 study) and basaltic standard glasses from the Smithsonian (Mössbauer values from Zhang et

234 al., (2018)). A linear regression through the basanite and basalt standards data (dotted black

235 line) yields an equation of $y = 0.37x - 0.09$ with an R^2 of 0.98, a P -value of 1.6×10^{-6} and a

236 standard error on the regression of 0.013. Dashed red lines show 95% confidence intervals.

237 Note that the relationship between the peak height ratio and $Fe^{3+}/\Sigma Fe$ is well captured by a238 linear regression for $Fe^{3+}/\Sigma Fe$ between 0.1 and 0.4 (see [supplementary Fig. S6](#)), in agreement

239 with previous studies (e.g., Cottrell et al., 2009).

240

241 In order to estimate the effect of lower quality spectra on the estimation of the peak height ratio

242 we compared the ratio obtained from the processing of two co-added low quality spectra

243 produced with a 0.25 mm Al plate attenuation to the ratio retrieved from normal high quality
244 spectra obtained with 0.1 mm Al plate attenuation for twelve basaltic Smithsonian standards
245 (Fig. S3). The standard deviation between these analyses was used to determine the error on
246 the peak height ratio ($1\sigma = 0.03$) which translates to a standard deviation of 0.012 on the
247 measured $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio. Note that this is the relative error from XANES analyses, the absolute
248 error in term of $\text{Fe}^{3+}/\Sigma\text{Fe}$ is given by the standard error on the calibration curve ($1\sigma = 0.013$).
249 Matrix glasses were acquired with lower attenuation (0.1 mm Al plate) and hence processed
250 using the more commonly used centroid method (e.g., Cottrell et al., 2009; Moussallam et al.,
251 2016, 2014).

252

253 **2.5 Major elements and volatile analyses**

254 Major and volatile (S, Cl, and F) element concentrations were measured on a Cameca SX-100
255 electron microprobe at the Laboratoire Magmas et Volcans, in Clermont-Ferrand using an
256 accelerating voltage of 15 keV, a beam current of 6 nA for major elements and 40 nA for
257 volatiles with a 10 μm spot diameter. Sodium was analysed first to prevent Na loss. The
258 counting time was 10 s for Na, Ca, Ti, P and Si, 20 s for Mg and Al, 30 s for Mn and finally 40
259 s for Fe and K. The instrument was calibrated on natural and synthetic mineral standards and
260 glasses. The Kilauea basaltic glass VG-A99 (Jarosewich et al., 1979) and a pantellerite glass
261 from Eburru Kenya KE12 (Mosbah et al., 1991), which are all international glass standards,
262 were used as an inter-laboratory check for major element, S and Cl and F concentrations,
263 respectively.

264

265 H_2O and CO_2 concentrations were determined by FTIR spectroscopy using a Vertex 70 Bruker
266 spectrometer equipped with an infrared microscope (Hyperion) and an MCT detector at the
267 Laboratoire Magmas et Volcans, in Clermont-Ferrand. Absorption spectra were acquired with

268 128 scans in the near-infrared region at a resolution of 4 cm^{-1} . The total amount of water was
269 calculated from the absorbance of the fundamental OH-stretching vibration at about 3535 cm^{-1}
270 while the amount of CO_2 was calculated using the “carbonate doublet” (Blank and Brooker,
271 1994) at 1515 and 1430 cm^{-1} . The sample thickness was measured on a Raman microscope
272 and background correction (using a cubic function for CO_2 and a linear function for H_2O) was
273 performed using PeakFit software (Jandel Scientific) to measure absorption peak heights. We
274 used molar absorptivity values for basanite from Shishkina et al., (2014). Melt inclusions major
275 and volatile compositions are given in **Tables S4 and S5**.

276

277 **2.6 Assessment of post-entrapment modification of melt inclusions.**

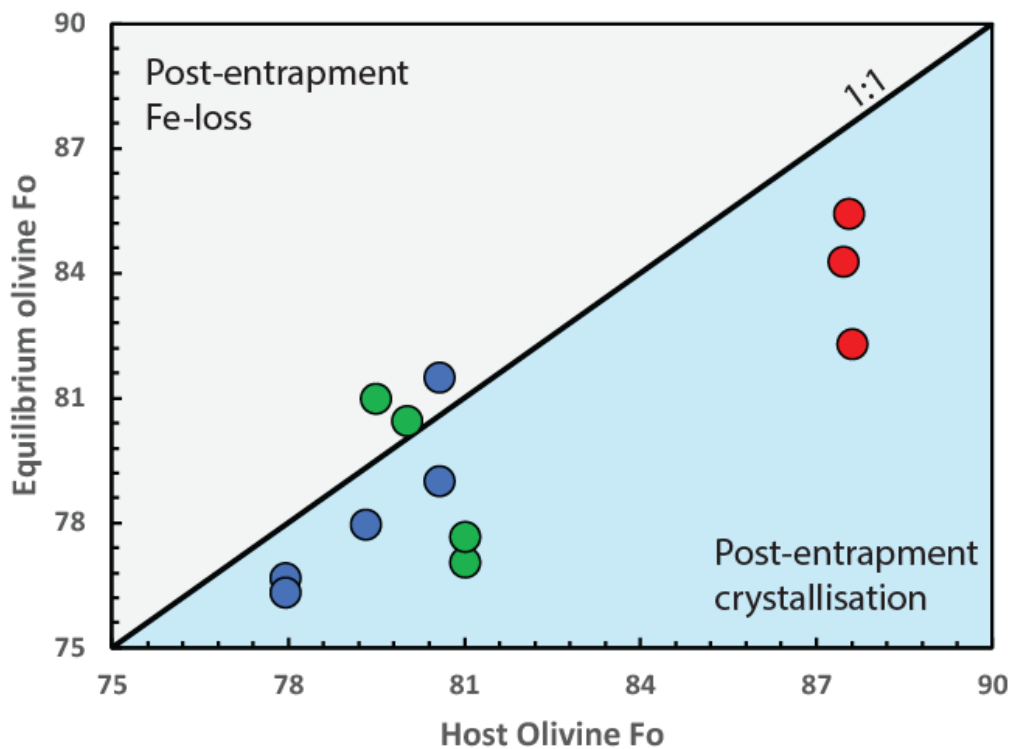
278 2.6.1 Post-entrapment crystallisation

279 The amount of post-entrapment crystallisation was estimated using the Petrolog3 software
280 (Danyushevsky and Plechov, 2011). Calculations were performed using the olivine-melt model
281 of Danyushevsky, (2001), the density model of Lange and Carmichael, (1990), the model for
282 melt oxidation of Kress and Carmichael, (1988) and the model of Toplis, (2005) for the
283 compositional dependence of the olivine-liquid Fe-Mg exchange coefficient (K_d). Note that
284 calculations in Petrolog3 are performed under anhydrous conditions at 1 atm. Calculations were
285 performed assuming a system closed to oxygen, in which case Fe^{3+} is treated as an incompatible
286 element. The $\text{Fe}^{3+}/\sum\text{Fe}$ ratios measured by XANES were used to calculate Fe_2O_3 and FeO
287 contents for each melt inclusion as input for the calculations.

288

289 **Fig. 4** compares the measured Fo content of the host olivine to its expected value at equilibrium
290 based on uncorrected melt inclusion composition. Most calculated olivine compositions agree
291 with measured compositions within a few Fo% suggesting a limited amount of post-entrapment
292 crystallisation or Fe-loss by re-equilibration. Another method to estimate if iron has been loss

293 from melt inclusions is to compare measured melt inclusion compositions to liquid lines of
 294 descent defined by published bulk rocks and glasses at each hotspot locality (Fig. S7). Using
 295 this method, we find that melt inclusions from Lanzarote and to a lesser extent, El Hierro, might
 296 have suffered some amount of iron loss. We consider this second method to be less accurate,
 297 however, as it assumes a co-genetic link between rock sequences that might be unrelated.
 298



299
 300 **Figure 4:** Comparison between measured and equilibrium Fo content of host olivine for melt
 301 inclusions from Fogo (blue), El Hierro (green) and Lanzarote (red). Equilibrium Fo contents
 302 are calculated by Petrolog3 software (Danyushevsky and Plechov, 2011) using the model
 303 of Toplis, (2005) for the compositional dependence of the olivine-liquid Fe-Mg exchange
 304 coefficient (K_d).
 305

306 Since post-entrapment crystallisation and re-equilibration calculations are highly model
 307 dependent and current models of Fe-Mg exchange coefficient are not well calibrated for

308 basanite composition, we choose not to use PEC results from Petrolog3 to “correct” the
309 measured oxidation state of iron in the melt inclusions. We note that the calculated amount of
310 PEC from Petrolog3 is small (from 0 to 3.7%, average of 1.3%, median of 1%) and hence that
311 the measured oxidation states of the melt inclusions are representative of the melt oxidation
312 states at the time of entrapment. Post-entrapment crystallisation corrected compositions are
313 reported in [Table S7](#).

314

315 2.6.2 Volatile diffusion

316 Post-entrapment diffusion of volatiles either through the olivine host (for H) (Hauri, 2002;
317 Massare et al., 2002) or in the vapor bubble (for CO₂) (Anderson and Brown, 1993; Steele-
318 Macinnis et al., 2011) can modify the original volatile content of melt inclusions. As such, our
319 measurements of H₂O and CO₂ can be considered as minimum estimates of the original
320 amounts dissolved in the inclusions even though all of our samples are from rapidly quenched
321 tephra and lava balloons. Higher (than measured) original H₂O and CO₂ contents of the melt
322 inclusions would yield greater calculated entrapment pressures but would make no difference
323 to the conclusions presented here. H diffusion out of a melt inclusion could, however, also have
324 an impact on the oxidation state of the inclusion with a predicted increase of the oxidation state
325 of the melt inclusion with increasing amount of H diffusion (some experiments have shown no
326 effect (Rowe et al., 2007) while others found a complete re-equilibration with the groundmass
327 (Bucholz et al., 2013; Gaetani et al., 2012)). Although this process cannot be ruled out, the
328 opposite correlation between H₂O and oxidation state shown by previous datasets as well as
329 ours (see Results section) strongly argues against this process dominating the observed data
330 variability.

331

332

2.7 Effect of differentiation

Fig. S8 shows an absence of correlation between three proxies of melt differentiation and the oxidation state of the melt, indicating that differentiation is not the dominant factor affecting melt oxidation state in our data set. To assess the potential effect of pre-entrapment crystallization of olivine on $\text{Fe}^{3+}/\Sigma\text{Fe}$, we modelled reverse crystallization paths for our melt inclusions along olivine-control lines using PRIMELT3 (Herzberg and Asimow, 2015) until the melts reached equilibrium with Fo₉₀ olivine. The results shown in Fig. 5 and Table S8 indicate a modest decrease in $\text{Fe}^{3+}/\Sigma\text{Fe}$ with reverse crystallization, demonstrating that melts parental to our melt inclusions were already oxidised.

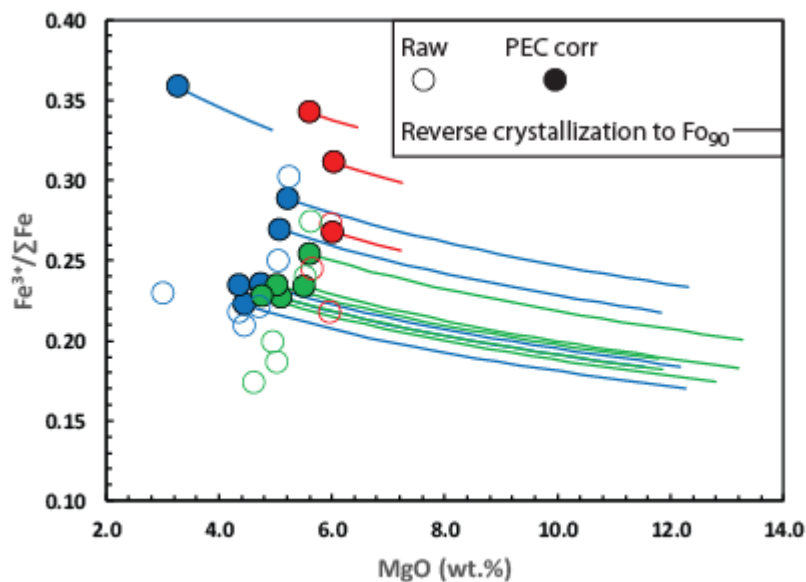
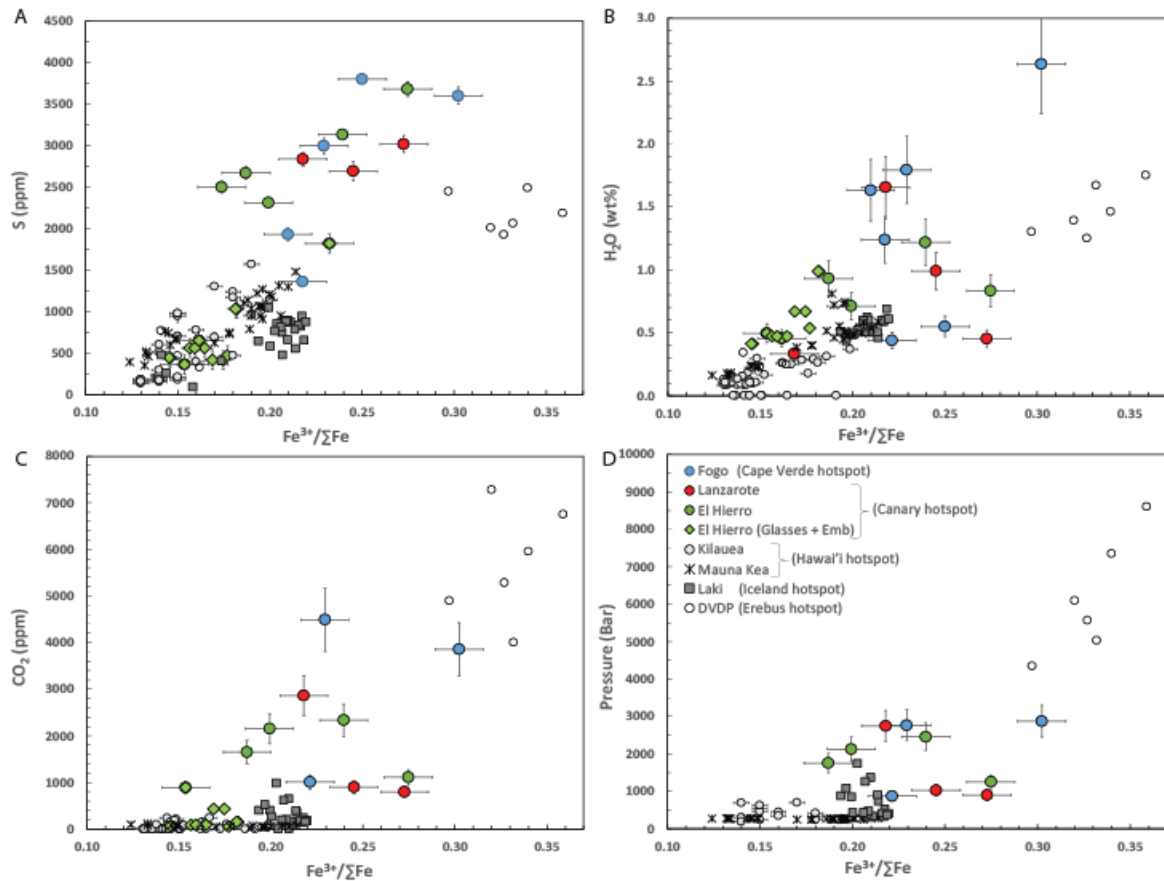


Figure 5: Sensitivity analysis of the effects of post-entrapment crystallisation and pre-entrapment crystallization of olivine on melt $\text{Fe}^{3+}/\Sigma\text{Fe}$. Post-entrapment crystallisation estimated using Petrolog3 software (Danyushevsky and Plechov, 2011) assuming a system closed to oxygen, with Fe^{3+} behaving incompatibly, leads to a decrease in $\text{Fe}^{3+}/\Sigma\text{Fe}$ in corrected inclusions. The effect of pre-entrapment crystallization of olivine, modelled with PRIMELT3 (Herzberg and Asimow, 2015) until melt–Fo₉₀ olivine equilibrium is reached, is

350 *shown to have modest effects on $Fe^{3+}/\sum Fe$ over large MgO ranges, suggesting that primary*
351 *magmas were oxidised. Note that samples from Lanzarote (red) might have experienced Fe-*
352 *loss (Fig. S9).*

353 **III. RESULTS**

354 Melt inclusions from all three localities have $Fe^{3+}/\sum Fe$ ratios of 0.17 to 0.30 (with one sigma
355 error of 0.012). These values are representative of the oxidation state of the melt at the time of
356 entrapment and of their parental primitive magmas (see calculation of the effect of pre-
357 entrapment processes in the methods section). The $Fe^{3+}/\sum Fe$ ratios of the melt inclusions do
358 not correlate with major element composition (see methods section) but they are strongly
359 correlated with volatile contents (Fig. 6 A to C). More volatile-rich melt inclusions, i.e., those
360 entrapped at greater depths, are systematically more oxidised than their volatile-poor
361 counterparts. This trend is even clearer when comparing our results with reported analyses for
362 the Erebus (Moussallam et al., 2014), Icelandic (Hartley et al., 2017) and Hawaiian
363 (Moussallam et al., 2016; Brounce et al., 2017) hotspots.



364

365 **Figure 6:** Volatile contents of melt inclusions, embayments and matrix glasses and
 366 corresponding volatile saturation pressures, for Fogo, Lanzarote and El Hierro (this study) and
 367 for Kīlauea (Moussallam et al., 2016), Mauna Kea (Brounce et al., 2017), Laki (Hartley et al.,
 368 2017) and Erebus (Moussallam et al., 2014) versus $Fe^{3+}/\Sigma Fe$, determined by XANES. **A.** S
 369 concentration (in ppm; determined by electron microprobe). **B.** H_2O concentration (in wt%;
 370 determined by Fourier transform infrared spectroscopy). **C.** CO_2 concentration (in ppm;
 371 determined by Fourier transform infrared spectroscopy). **D.** Calculated entrapment pressure
 372 (using the model of Iacono-Marziano et al., 2012 and accounting for S in the data of this study),
 373 with CO_2 - H_2O saturation curves shown in the **supplementary** information. Note that
 374 entrapment pressure estimates are always a minimum and that samples from Lanzarote might
 375 have experienced Fe-loss.

376 IV. DISCUSSION

377

378 4.1 A case for oxidised mantle plumes

379 The most volatile-rich inclusions from El Hierro, Lanzarote and Fogo record $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios
380 ranging from 0.27 to 0.30, corresponding to oxygen fugacities around 1.5 to 2 log units above
381 the FMQ buffer. The only available comparable data, from very-deeply entrapped melt
382 inclusions recording conditions prior to extensive degassing, are from Ross Island, Antarctica
383 where similarly high oxygen fugacities have been found (Moussallam et al., 2014). The finding
384 that all investigated hotspot volcanoes (El Hierro, Lanzarote, Fogo and Erebus), for which
385 deeply-entrapped (> 8 km) melt inclusions are available, are associated with strongly oxidised
386 primitive melts suggests a global relationship. This is corroborated by three other lines of
387 evidence: (i) the observation of increasingly-oxidised MORB approaching hotspots such as
388 Iceland (Shorttle et al., 2015); (ii) the abundance of S^{6+} in hotspot basalts (Brounce et al., 2017;
389 Jugo et al., 2010); and (iii) the determination of slightly more oxidizing (up to FMQ+1)
390 conditions in the least-degassed melt inclusions and glasses available from other hotspot
391 volcanoes (Hawai'i (Brounce et al., 2017; Moussallam et al., 2016) and Iceland (Hartley et al.,
392 2017)).

393

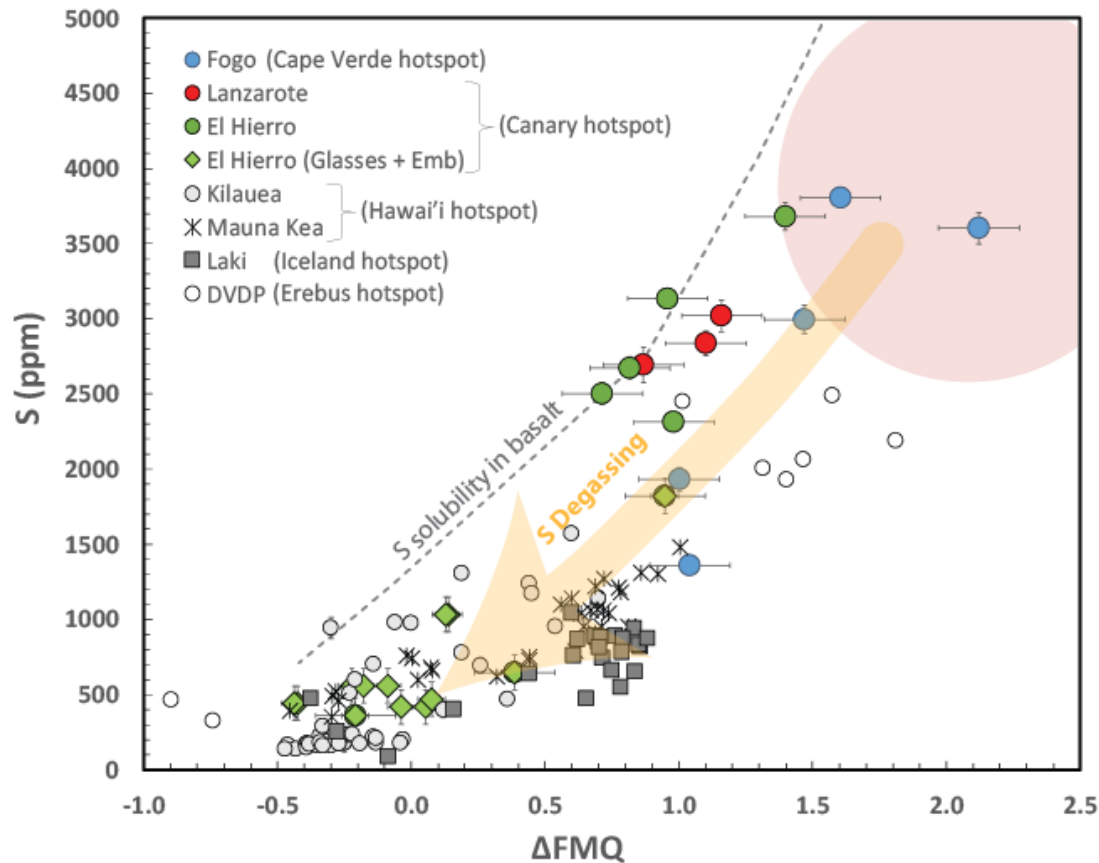
394 The most volatile-rich and deeply-entrapped melt inclusions should record conditions closest
395 to the original mantle melt. From our dataset the effect of crystal fractionation on $f\text{O}_2$ appears
396 to be minimal (see methods section). Even the most deeply-entrapped inclusions, however,
397 likely experienced some amount of degassing. The original, pre-degassing, degree of oxidation
398 of the melt can be estimated if we know how volatile-rich, especially how sulfur-rich, that melt
399 was prior to degassing. Previous studies for Lanzarote (Gómez-Ulla, 2018) and El Hierro
400 (Longpré et al., 2017) reported melt inclusions with sulfur contents of up to 3900 and 5000

401 ppm, respectively, while for Hawaii (at Lō‘ihi) sulfur contents of up to 3300 ppm have been
402 reported (Hauri, 2002). Extrapolating from our dataset, and in coherence with previous
403 degassing models (Moussallam et al., 2014), such sulfur contents would imply a mantle melt
404 oxygen fugacity about 2.0 log units above the FMQ buffer (Fig. 7), hence a mantle source about
405 two log units more oxidised than that feeding mid-ocean ridges (around FMQ; e.g., Berry et
406 al., 2018; Bezos and Humler, 2005; Birner et al., 2018, 2017; Bryndzia and Wood, 1990;
407 Cottrell and Kelley, 2011; Zhang et al., 2018). These estimates are also significantly more
408 oxidised than those inferred for primitive melts in the mantle wedge feeding arc magmas
409 (around FMQ+1; e.g., Bénard et al., 2018; Brandon and Draper, 1996; Parkinson and Arculus,
410 1999).

411

412 It should be noted that by equating the oxidation state of deep melts to that of their mantle
413 source we are assuming that melts are effectively buffered by their mantle source during partial
414 melting. For MORBs, several lines of evidence support this hypothesis; (i) the lack of
415 correlation between $\text{Fe}^{3+}/\Sigma\text{Fe}$ of MORB glasses and parameters sensitive to the degree of partial
416 melting (Bézos and Humler, 2005, Cottrell and Kelley, 2011), (ii) the similarity in measured
417 oxidation state of MORB glasses and co-located peridotites (Birner et al., 2018), and (iii)
418 experimental investigations of partial melting showing that the melt $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios remain
419 constant over varying degrees of partial melting (Sorbadere et al., 2018). In plume contexts it
420 is currently unknown if this assumption remains valid. The relationship between $\text{Fe}^{3+}/\Sigma\text{Fe}$ and
421 $f\text{O}_2$ in low-degree, volatile- and alkali-rich, partial melts is not well established, and it is
422 conceivable that partial melting in some contexts would operate as an open system favouring
423 the generation of Fe^{3+} -rich melts (Fe^{3+} being mildly incompatible during partial melting, e.g.,
424 Canil et al., 1994; Holloway and Burnham, 1972; Mallmann and O’Neill, 2009; Sorbadere et
425 al., 2018). Given the current lack of evidence of such open-system partial melting processes

426 taking place, we assume here that partial melting in plume contexts operates similarly to partial
 427 melting in mid-ocean ridge contexts in terms of oxidation state, and hence that the oxidation
 428 state of partial melts pre-degassing is similar to that of their source.



429
 430 **Figure 7:** Sulfur contents of melt inclusions, embayments and matrix glasses from this study
 431 and for Kīlauea (Moussallam et al., 2016), Mauna Kea (Brounce et al., 2017), Laki (Hartley et
 432 al., 2017) and Erebus (Moussallam et al., 2014) compared with the oxygen fugacity of the melt
 433 expressed as the deviation from the fayalite–magnetite–quartz buffer. The pink shaded area
 434 represents inferred conditions of the primitive mantle melt feeding hotspots, extrapolated from
 435 the data trend to the maximum reported sulfur contents (of around 3000 to 5000 ppm) in melt
 436 inclusions from hotspot volcanoes. The light orange arrow shows the expected relationship
 437 between sulfur content and melt oxidation state due to sulfur degassing (e.g., Moussallam et
 438 al., 2014, 2016). The dashed grey line shows the maximum amount of sulfur that can be

439 dissolved at a given oxidation state in common basaltic melts at 200 MPa (Botcharnikov et al.,
440 2011). Note that samples from Lanzarote might have experienced Fe-loss.

441

442 **4.2 Recycling of oxidised subducted material**

443 Mantle plumes, as the source of hotspot volcanism, might therefore be considerably more
444 oxidised than their surrounding mantle. The simplest explanation for this phenomenon is that
445 these plumes entrain recycled surface-derived material such as subducted oceanic crust. Indeed,
446 isotopic and trace element evidence indicating the presence of recycled oceanic (and sometimes
447 continental) crust in mantle plumes is abundant (Chauvel et al., 1992; Day et al., 2010; Gómez-
448 Ulla et al., 2017; Hauri, 1996; Hofmann and White, 1982). In particular, helium, argon, lead
449 and strontium isotopic ratios suggest that in both the Canary (e.g., Day and Hilton, 2011;
450 Hiltona et al., 2000)) and Cape Verde (e.g., Christensen et al., 2001; Doucelance et al., 2003;
451 Millet et al., 2008) hotspots a lower mantle and a HIMU component (interpreted as recycled
452 subducted oceanic crust) must have mixed to explain the isotopic composition of extruded
453 lavas. The observation that oxidised mantle melts in hotspot settings are also S-rich (Fig. 7)
454 might additionally suggest the presence of recycled oceanic crust in their parental mantle since
455 hydrothermally-altered crust is enriched in S (Alt et al., 1993), although multiple lines of
456 evidence suggest that most of the S in the subducting slab might migrate to the mantle wedge,
457 with potentially limited amounts being brought deep into the mantle (Bénard et al., 2018; Jégo
458 and Dasgupta, 2014, 2013; Prouteau and Scaillet, 2013; Tomkins and Evans, 2015). An
459 alternative mechanism to explain the oxidised nature of mantle plumes is the decomposition of
460 subducted Fe_2O_3 from banded iron formations to Fe_3O_4 and $\text{Fe}_{25}\text{O}_{32}$ at pressures above ~ 60
461 and ~ 70 GPa, respectively (Bykova et al., 2016). This would generate an oxygen-rich fluid in
462 the lower mantle that could be sampled by ascending plumes. Yet another possibility relies on
463 pressure effects on iron coordination. It has been proposed that pyrite-structured iron oxide

464 (FeO₂ – referred to as P-phase) may form under extreme pressure and temperature in the Earth's
465 interior (Hu et al., 2016). If so, highly oxidised patches containing iron in the 3+ valence state
466 may accumulate in the deep lower mantle (Hu et al., 2017, 2016; Streltsov et al., 2017). Early
467 incorporation of such material into mantle plumes would result in decomposition to Fe₂O₃ and
468 release of O₂ during decompression (reaction 1 in Hu et al., 2016), providing an additional
469 mechanism for generation of oxidised hotspot conditions. The hypothesis we favour, the most
470 simple, is the incorporation of recycled surface-derived material in plumes.

471

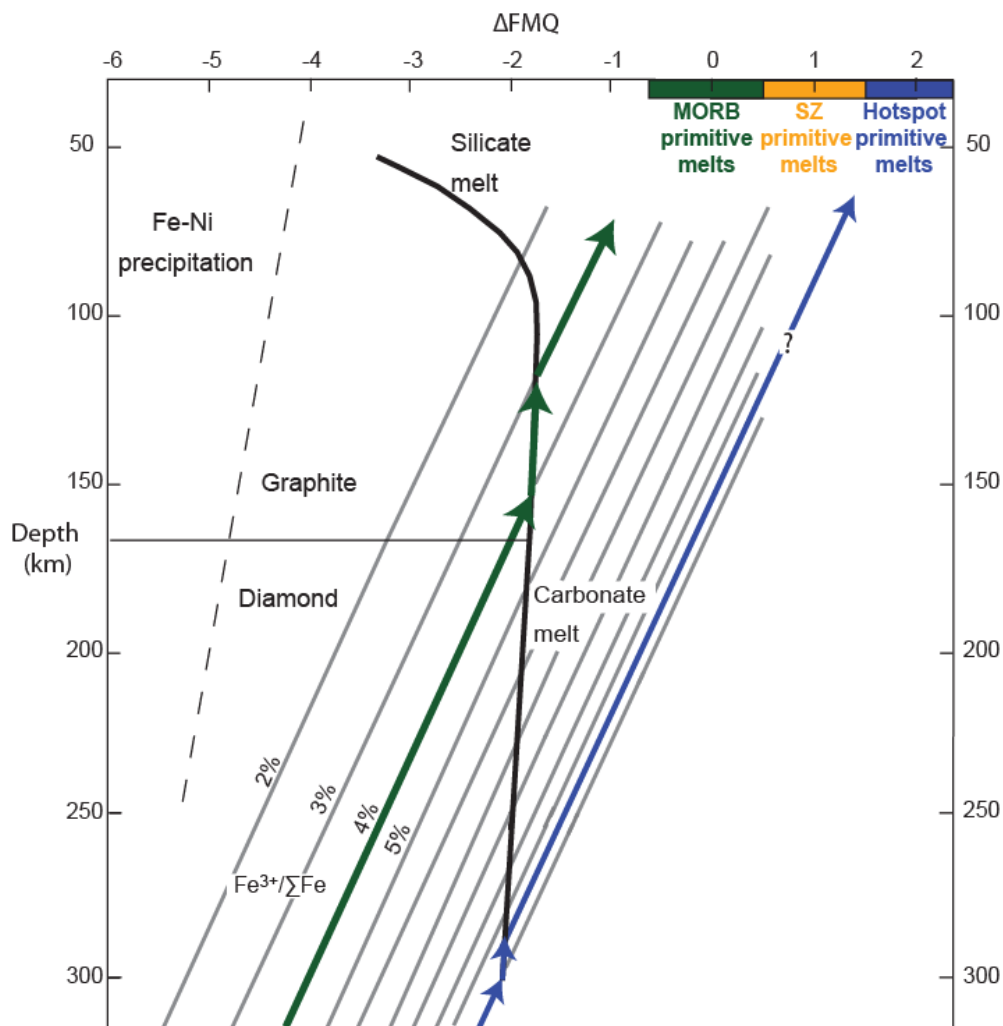
472 **4.3 Implication for fO_2 stratification and partial melting in Earth's mantle**

473 Mantle plumes might therefore play a key role in the deep oxygen – and potentially S – cycles,
474 providing a counterflow to subduction zones, and channelling oxidised material out of the deep
475 Earth. The oxidised nature of mantle plumes might also partly explain their seismic velocity
476 structure. It has been shown that the seismic properties of olivine are highly dependent on iron
477 oxidation state, with olivine containing more Fe³⁺ showing enhanced anelastic relaxation (Ii et
478 al., 2018). The low-velocity anomalies found beneath hotspot volcanoes (e.g., French and
479 Romanowicz, 2015; Zhao, 2007) might then not only indicate elevated mantle temperatures
480 but also raised mantle oxygen fugacity.

481

482 While the geochemically-layered view of the Earth's mantle that prevailed in the twentieth
483 century has been progressively dismantled over the past four decades (e.g., White, 2015), our
484 picture of mantle oxidation state has remained mostly one-dimensional, i.e., fO_2 decreasing
485 steadily with depth (Frost and McCammon, 2008; Rohrbach and Schmidt, 2011; Woodland
486 and Koch, 2003). Our findings suggest that geochemical, geophysical and redox
487 heterogeneities should be linked in the Earth's mantle. A heterogeneous mantle in terms of
488 oxidation state implies that processes such as carbon redox melting (the production of

489 carbonated melts from the oxidation of CH_4 or native carbon (Taylor and Green, 1988; Foley,
 490 2010; Rohrbach and Schmidt, 2011)) should occur over a wide range of depths in distinct
 491 regions of the mantle. Following Stagno et al., (2013), for instance, and considering that the
 492 mantle domains feeding hotspots are two log units more oxidised than those beneath mid-ocean
 493 ridges, redox melting associated with hotspots should prevail at much greater depths (Fig. 8),
 494 especially if these domains are also more carbon-rich.



495

496 **Figure 8:** Relationship between depth and oxygen fugacity (expressed as the deviation from
 497 the FMQ buffer) for variable $\text{Fe}^{3+}/\Sigma\text{Fe}$ from Stagno et al., (2013). The stability fields of
 498 diamond and graphite are shown and bounded by the carbonate redox melting reaction line
 499 (thick black line). The green arrows (from Stagno et al., (2013)) show the expected evolution
 500 of an upwelling mantle with $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio of 0.04, initiating carbonate melting at ~150 km.
 501 The blue arrows show the expected evolution of an upwelling mantle with a $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio of

502 0.12, initiating carbonate melting at ~300 km depth. Both scenarios arbitrarily consider mantle
503 sources with 30 ppm carbon (causing a reduction of the bulk rock $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio by 1% during
504 redox melting). For greater carbon contents in the mantle sources (likely for hotspot mantle
505 sources), a greater initial $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio is required for the oxygen fugacity to remain in the
506 range estimated for MORB and hotspot sources. The relationship between $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio and
507 oxygen fugacity for the mantle is calculated from equation 6 of Stagno et al., (2013) and differs
508 from that for the melts (calculated using Kress and Carmichael, (1991)). The boxes for hotspot
509 (this study and Moussallam et al., 2014), subduction zone (SZ) (e.g., Bénard et al., 2018;
510 Brandon and Draper, 1996; Parkinson and Arculus, 1999) and MORB (e.g., Berry et al., 2018;
511 Bezos and Humler, 2005; Christie et al., 1986; Zhang et al., 2018) primitive melts indicate
512 oxidation state only (not depth).

513

514 **V. CONCLUSION**

515 We have investigated the redox state of glassy crystal-hosted melt inclusions in lavas of the
516 Canary and Cape Verde Islands by XANES and compared them with similar measurements
517 from Ross Island, Hawaii and Iceland. We showed that, at all five investigated hotspots to date,
518 the apparently reduced state of erupted lavas is primarily acquired from degassing during
519 magma ascent.

520

521 We found that the most deeply entrapped samples, i.e., those preserving mantle equilibrium
522 conditions and found at the Canary, Cape Verde and Erebus hotspots, are highly oxidised. This
523 leads us to infer that globally, present day mantle plumes might be up to two orders of
524 magnitude more oxidised than mantle beneath mid-ocean ridges (that is $f\text{O}_2$ two log units above
525 the FMQ buffer) and also more oxidised than the mantle wedge beneath subduction zone
526 volcanoes. What emerges is a novel view of the oxidation state of the mantle, in which large
527 heterogeneities exist both vertically and laterally.

528

529 We further argue that mantle plumes play a key role in the deep oxygen cycle, providing a
530 counterflow to subduction zones by channelling oxidised material out of the deep Earth. This
531 can help to explain why the mean oxidation state of the upper mantle has changed little since
532 the Archean, despite several billion years of subduction of oxidised material. Our findings also
533 have implications for the interpretation of low seismic velocity anomalies beneath hotspot
534 volcanoes, as these might reflect the presence of more oxidised mantle as well as higher mantle
535 temperatures. The more oxidised conditions imply in turn that carbonate redox melting
536 underneath hotspots should take place at much greater depths than underneath mid-ocean
537 ridges.

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545

546 **REFERENCES**

- 547 Alt, J.C., Shanks, W.C., Jackson, M.C., 1993. Cycling of sulfur in subduction zones: The
 548 geochemistry of sulfur in the Mariana Island Arc and back-arc trough. *Earth and*
 549 *Planetary Science Letters* 119, 477–494. [https://doi.org/10.1016/0012-821X\(93\)90057-](https://doi.org/10.1016/0012-821X(93)90057-G)
 550 [G](https://doi.org/10.1016/0012-821X(93)90057-G)
- 551 Anderson, A.T., Brown, G.G., 1993. CO₂ contents and formation pressures of some Kilauean
 552 melt inclusions. *American Mineralogist* 78, 794–803.
- 553 Anderson, A.T., Wright, R., 1972. Phenocrysts and glass inclusions and their bearing on
 554 oxidation and mixing of basaltic magmas, Kilauea Volcano, Hawaii 57, 188–216.
- 555 Arculus, R.J., 1985. Oxidation status of the mantle: past and present. *Annu. Rev. Earth Planet.*
 556 *Sci.* 13, 75–95. <https://doi.org/10.1146/annurev.earth.13.050185.000451>
- 557 Bénard, A., Klimm, K., Woodland, A.B., Arculus, R.J., Wilke, M., Botcharnikov, R.E.,
 558 Shimizu, N., Nebel, O., Rivard, C., Ionov, D.A., 2018. Oxidising agents in sub-arc
 559 mantle melts link slab devolatilisation and arc magmas. *Nature Communications* 9,
 560 3500. <https://doi.org/10.1038/s41467-018-05804-2>
- 561 Berry, A.J., O'Neill, H.S.C., Jayasuriya, K.D., Campbell, S.J., Foran, G.J., 2003. XANES
 562 calibrations for the oxidation state of iron in a silicate glass. *American Mineralogist* 88,
 563 967–977. <https://doi.org/10.2138/am-2003-0704>
- 564 Berry, A.J., Stewart, G.A., O'Neill, H.St.C., Mallmann, G., Mosselmans, J.F.W., 2018. A re-
 565 assessment of the oxidation state of iron in MORB glasses. *Earth and Planetary Science*
 566 *Letters* 483, 114–123. <https://doi.org/10.1016/j.epsl.2017.11.032>
- 567 Bezos, A., Humler, E., 2005. The Fe³ /Sigma Fe ratios of MORB glasses and their implications
 568 for mantle melting. *Geochimica Et Cosmochimica Acta* 69, 711–725.
- 569 Birner, S.K., Cottrell, E., Warren, J.M., Kelley, K.A., Davis, F.A., 2018. Peridotites and basalts
 570 reveal broad congruence between two independent records of mantle fO₂ despite local
 571 redox heterogeneity. *Earth and Planetary Science Letters* 494, 172–189.
 572 <https://doi.org/10.1016/j.epsl.2018.04.035>
- 573 Birner, S.K., Warren, J.M., Cottrell, E., Davis, F.A., Kelley, K.A., Falloon, T.J., 2017. Forearc
 574 Peridotites from Tonga Record Heterogeneous Oxidation of the Mantle following
 575 Subduction Initiation. *J Petrology* 58, 1755–1780.
 576 <https://doi.org/10.1093/petrology/egx072>

- 577 Blank, J.G., Brooker, R.A., 1994. Experimental studies of carbon dioxide in silicate melts;
578 solubility, speciation, and stable carbon isotope behavior. *Reviews in Mineralogy and*
579 *Geochemistry* 30, 157–186.
- 580 Botcharnikov, R.E., Linnen, R.L., Wilke, M., Holtz, F., Jugo, P.J., Berndt, J., 2011. High gold
581 concentrations in sulphide-bearing magma under oxidizing conditions. *Nature*
582 *Geoscience* 4, 112–115. <https://doi.org/10.1038/ngeo1042>
- 583 Brandon, A.D., Draper, D.S., 1996. Constraints on the origin of the oxidation state of mantle
584 overlying subduction zones: An example from Simcoe, Washington, USA. *Geochimica*
585 *et Cosmochimica Acta* 60, 1739–1749. [https://doi.org/10.1016/0016-7037\(96\)00056-7](https://doi.org/10.1016/0016-7037(96)00056-7)
- 586 Brounce, M., Stolper, E., Eiler, J., 2017. Redox variations in Mauna Kea lavas, the oxygen
587 fugacity of the Hawaiian plume, and the role of volcanic gases in Earth's oxygenation.
588 *PNAS* 114, 8997–9002. <https://doi.org/10.1073/pnas.1619527114>
- 589 Bryndzia, L.T., Wood, B.J., 1990. Oxygen thermobarometry of abyssal spinel peridotites; the
590 redox state and C-O-H volatile composition of the Earth's sub-oceanic upper mantle.
591 *Am J Sci* 290, 1093–1116. <https://doi.org/10.2475/ajs.290.10.1093>
- 592 Bucholz, C.E., Gaetani, G.A., Behn, M.D., Shimizu, N., 2013. Post-entrapment modification
593 of volatiles and oxygen fugacity in olivine-hosted melt inclusions. *Earth and Planetary*
594 *Science Letters* 374, 145–155. <https://doi.org/10.1016/j.epsl.2013.05.033>
- 595 Burgisser, A., Scaillet, B., 2007. Redox evolution of a degassing magma rising to the surface.
596 *Nature* 445, 194–197.
- 597 Bykova, E., Dubrovinsky, L., Dubrovinskaia, N., Bykov, M., McCammon, C., Ovsyannikov,
598 S.V., Liermann, H.-P., Kuppenko, I., Chumakov, A.I., Ruffer, R., Hanfland, M.,
599 Prakashenka, V., 2016. Structural complexity of simple Fe₂O₃ at high pressures and
600 temperatures. *Nature Communications* 7, 10661.
601 <https://doi.org/10.1038/ncomms10661>
- 602 Canil, D., O'Neill, H.St.C., Pearson, D.G., Rudnick, R.L., McDonough, W.F., Carswell, D.A.,
603 1994. Ferric iron in peridotites and mantle oxidation states. *Earth and Planetary Science*
604 *Letters* 123, 205–220. [https://doi.org/10.1016/0012-821X\(94\)90268-2](https://doi.org/10.1016/0012-821X(94)90268-2)
- 605 Carmichael, I.S.E., 1991. The redox states of basic and silicic magmas: a reflection of their
606 source regions? *Contr. Mineral. and Petrol.* 106, 129–141.
607 <https://doi.org/10.1007/BF00306429>
- 608 Carmichael, I.S.E., Ghiorso, M.S., 1986. Oxidation-reduction relations in basic magma: a case
609 for homogeneous equilibria. *Earth and Planetary Science Letters* 78, 200–210.
610 [https://doi.org/10.1016/0012-821X\(86\)90061-0](https://doi.org/10.1016/0012-821X(86)90061-0)
- 611 Chauvel, C., Hofmann, A.W., Vidal, P., 1992. himu-em: The French Polynesian connection.
612 *Earth and Planetary Science Letters* 110, 99–119. [https://doi.org/10.1016/0012-821X\(92\)90042-T](https://doi.org/10.1016/0012-821X(92)90042-T)
- 613
- 614 Christensen, B.P., Holm, P.M., Jambon, A., Wilson, J.R., 2001. Helium, argon and lead
615 isotopic composition of volcanics from Santo Antão and Fogo, Cape Verde Islands.
616 *Chemical Geology* 178, 127–142. [https://doi.org/10.1016/S0009-2541\(01\)00261-3](https://doi.org/10.1016/S0009-2541(01)00261-3)
- 617 Christie, D.M., Carmichael, I.S.E., Langmuir, C.H., 1986. Oxidation states of mid-ocean ridge
618 basalt glasses. *Earth and Planetary Science Letters* 79, 397–411.
619 [https://doi.org/10.1016/0012-821X\(86\)90195-0](https://doi.org/10.1016/0012-821X(86)90195-0)
- 620 Cottrell, E., Kelley, K.A., 2011. The oxidation state of Fe in MORB glasses and the oxygen
621 fugacity of the upper mantle. *Earth and Planetary Science Letters* 305, 270–282.
622 <https://doi.org/10.1016/j.epsl.2011.03.014>
- 623 Cottrell, E., Kelley, K.A., Lanzirrotti, A., Fischer, R.A., 2009. High-precision determination of
624 iron oxidation state in silicate glasses using XANES. *Chemical Geology* 268, 167–179.
625 <https://doi.org/10.1016/j.chemgeo.2009.08.008>

- 626 Cottrell, E., Lanzirrotti, A., Mysen, B., Birner, S., Kelley, K.A., Botcharnikov, R., Davis, F.A.,
627 Newville, M., 2018. A Mössbauer-based XANES calibration for hydrous basalt glasses
628 reveals radiation-induced oxidation of Fe. *American Mineralogist* 103, 489–501.
629 <https://doi.org/10.2138/am-2018-6268>
- 630 Danyushevsky, L.V., 2001. The effect of small amounts of H₂O on crystallisation of mid-ocean
631 ridge and backarc basin magmas. *Journal of Volcanology and Geothermal Research*
632 110, 265–280. [https://doi.org/10.1016/S0377-0273\(01\)00213-X](https://doi.org/10.1016/S0377-0273(01)00213-X)
- 633 Danyushevsky, L.V., Plechov, P., 2011. Petrolog3: Integrated software for modeling
634 crystallization processes. *Geochemistry, Geophysics, Geosystems* 12, n/a–n/a.
635 <https://doi.org/10.1029/2011GC003516>
- 636 Day, J.M.D., Hilton, D.R., 2011. Origin of ³He/⁴He ratios in HIMU-type basalts constrained
637 from Canary Island lavas. *Earth and Planetary Science Letters* 305, 226–234.
638 <https://doi.org/10.1016/j.epsl.2011.03.006>
- 639 Day, J.M.D., Pearson, D.G., Macpherson, C.G., Lowry, D., Carracedo, J.C., 2010. Evidence
640 for distinct proportions of subducted oceanic crust and lithosphere in HIMU-type
641 mantle beneath El Hierro and La Palma, Canary Islands. *Geochimica et Cosmochimica*
642 *Acta* 74, 6565–6589. <https://doi.org/10.1016/j.gca.2010.08.021>
- 643 Doucelance, R., Escrig, S., Moreira, M., Gariépy, C., Kurz, M.D., 2003. Pb-Sr-He isotope and
644 trace element geochemistry of the Cape Verde Archipelago. *Geochimica et*
645 *Cosmochimica Acta* 67, 3717–3733. [https://doi.org/10.1016/S0016-7037\(03\)00161-3](https://doi.org/10.1016/S0016-7037(03)00161-3)
- 646 Farges, F., 2001. Crystal chemistry of iron in natural grandierites: an X-ray absorption fine-
647 structure spectroscopy study. *Phys Chem Min* 28, 619–629.
648 <https://doi.org/10.1007/s002690100170>
- 649 French, S.W., Romanowicz, B., 2015. Broad plumes rooted at the base of the Earth's mantle
650 beneath major hotspots. *Nature* 525, 95–99. <https://doi.org/10.1038/nature14876>
- 651 Frost, B.R., 1991. Introduction to oxygen fugacity and its petrologic importance. *Reviews in*
652 *Mineralogy and Geochemistry* 25, 1–9.
- 653 Frost, D.J., McCammon, C.A., 2008. The Redox State of Earth's Mantle. *Annual Review of*
654 *Earth and Planetary Sciences* 36, 389–420.
655 <https://doi.org/10.1146/annurev.earth.36.031207.124322>
- 656 Gaetani, G.A., O'Leary, J.A., Shimizu, N., Bucholz, C.E., Newville, M., 2012. Rapid
657 reequilibration of H₂O and oxygen fugacity in olivine-hosted melt inclusions. *Geology*
658 40, 915–918. <https://doi.org/10.1130/G32992.1>
- 659 Gaillard, F., Scaillet, B., Arndt, N.T., 2011. Atmospheric oxygenation caused by a change in
660 volcanic degassing pressure. *Nature* 478, 229–232.
661 <https://doi.org/10.1038/nature10460>
- 662 Gaillard, F., Scaillet, B., Pichavant, M., Iacono-Marziano, G., 2015. The redox geodynamics
663 linking basalts and their mantle sources through space and time. *Chemical Geology*
664 418, 217–233. <https://doi.org/10.1016/j.chemgeo.2015.07.030>
- 665 Gómez-Ulla, A., 2018. Historical eruptions of Lanzarote, Canary Islands: Inference of magma
666 source and melt generation from olivine and its melt inclusions. University of Clermont
667 - Auvergne, Clermont-Ferrand.
- 668 Gómez-Ulla, A., Sigmarsson, O., Gudfinnsson, G.H., 2017. Trace element systematics of
669 olivine from historical eruptions of Lanzarote, Canary Islands: Constraints on mantle
670 source and melting mode. *Chemical Geology* 449, 99–111.
671 <https://doi.org/10.1016/j.chemgeo.2016.11.021>
- 672 Hartley, M.E., Shorttle, O., Maclennan, J., Moussallam, Y., Edmonds, M., 2017. Olivine-
673 hosted melt inclusions as an archive of redox heterogeneity in magmatic systems. *Earth*
674 *and Planetary Science Letters* 479, 192–205. <https://doi.org/10.1016/j.epsl.2017.09.029>

- 675 Hauri, E., 2002. SIMS analysis of volatiles in silicate glasses, 2: isotopes and abundances in
676 Hawaiian melt inclusions. *Chemical Geology* 183, 115–141.
677 [https://doi.org/10.1016/S0009-2541\(01\)00374-6](https://doi.org/10.1016/S0009-2541(01)00374-6)
- 678 Hauri, E.H., 1996. Major-element variability in the Hawaiian mantle plume. *Nature* 382, 415–
679 419. <https://doi.org/10.1038/382415a0>
- 680 Helz, R.T., Cottrell, E., Brounce, M.N., Kelley, K.A., 2017. Olivine-melt relationships and
681 syneruptive redox variations in the 1959 eruption of Kīlauea Volcano as revealed by
682 XANES. *Journal of Volcanology and Geothermal Research* 333–334, 1–14.
683 <https://doi.org/10.1016/j.jvolgeores.2016.12.006>
- 684 Herzberg, C., Asimow, P.D., 2015. PRIMELT3 MEGA.XLSM software for primary magma
685 calculation: Peridotite primary magma MgO contents from the liquidus to the solidus.
686 *Geochemistry, Geophysics, Geosystems* 16, 563–578.
687 <https://doi.org/10.1002/2014GC005631>
- 688 Hiltona, D.R., Macphersona, C.G., Elliottb, T.R., 2000. Helium isotope ratios in mafic
689 phenocrysts and geothermal fluids from La Palma, the Canary Islands (Spain):
690 implications for HIMU mantle sources. *Geochimica et Cosmochimica Acta* 64, 2119–
691 2132. [https://doi.org/10.1016/S0016-7037\(00\)00358-6](https://doi.org/10.1016/S0016-7037(00)00358-6)
- 692 Hofmann, A.W., White, W.M., 1982. Mantle plumes from ancient oceanic crust. *Earth and*
693 *Planetary Science Letters* 57, 421–436. [https://doi.org/10.1016/0012-821X\(82\)90161-](https://doi.org/10.1016/0012-821X(82)90161-3)
694 3
- 695 Holloway, J.R., Burnham, C.W., 1972. Melting Relations of Basalt with Equilibrium Water
696 Pressure Less Than Total Pressure. *J Petrology* 13, 1–29.
697 <https://doi.org/10.1093/petrology/13.1.1>
- 698 Hu, Q., Kim, D.Y., Liu, J., Meng, Y., Yang, L., Zhang, D., Mao, W.L., Mao, H., 2017.
699 Dehydrogenation of goethite in Earth's deep lower mantle. *PNAS* 114, 1498–1501.
700 <https://doi.org/10.1073/pnas.1620644114>
- 701 Hu, Q., Kim, D.Y., Yang, W., Yang, L., Meng, Y., Zhang, L., Mao, H.-K., 2016. FeO₂ and
702 FeOOH under deep lower-mantle conditions and Earth's oxygen–hydrogen cycles.
703 *Nature* 534, 241–244. <https://doi.org/10.1038/nature18018>
- 704 Iacono-Marziano, G., Morizet, Y., Le Trong, E., Gaillard, F., 2012. New experimental data and
705 semi-empirical parameterization of H₂O–CO₂ solubility in mafic melts. *Geochimica et*
706 *Cosmochimica Acta* 97, 1–23. <https://doi.org/10.1016/j.gca.2012.08.035>
- 707 Ii, C.J.C., Faul, U.H., David, E.C., Berry, A.J., Jackson, I., 2018. Redox-influenced seismic
708 properties of upper-mantle olivine. *Nature* 555, 355–358.
709 <https://doi.org/10.1038/nature25764>
- 710 Jarosewich, E., Parkes, A.S., Wiggins, L.B., 1979. Microprobe Analyses of Four Natural
711 Glasses and One Mineral: An Interlaboratory Study of Precision and Accuracy.
712 *Smithsonian Contributions to the Earth Sciences* 22, 53–67.
- 713 Jégo, S., Dasgupta, R., 2014. The Fate of Sulfur During Fluid-Present Melting of Subducting
714 Basaltic Crust at Variable Oxygen Fugacity. *J Petrology* 55, 1019–1050.
715 <https://doi.org/10.1093/petrology/egu016>
- 716 Jégo, S., Dasgupta, R., 2013. Fluid-present melting of sulfide-bearing ocean-crust:
717 Experimental constraints on the transport of sulfur from subducting slab to mantle
718 wedge. *Geochimica et Cosmochimica Acta* 110, 106–134.
719 <https://doi.org/10.1016/j.gca.2013.02.011>
- 720 Jugo, P.J., Wilke, M., Botcharnikov, R.E., 2010. Sulfur K-edge XANES analysis of natural and
721 synthetic basaltic glasses: Implications for S speciation and S content as function of
722 oxygen fugacity. *Geochimica et Cosmochimica Acta* 74, 5926–5938.
723 <https://doi.org/10.1016/j.gca.2010.07.022>

- 724 Kelley, K.A., Cottrell, E., 2012. The influence of magmatic differentiation on the oxidation
725 state of Fe in a basaltic arc magma. *Earth and Planetary Science Letters* 329–330, 109–
726 121. <https://doi.org/10.1016/j.epsl.2012.02.010>
- 727 Kress, V.C., Carmichael, I.S.E., 1991. The compressibility of silicate liquids containing Fe₂O₃
728 and the effect of composition, temperature, oxygen fugacity and pressure on their redox
729 states. *Contr. Mineral. and Petrol.* 108, 82–92. <https://doi.org/10.1007/BF00307328>
- 730 Kress, V.C., Carmichael, I.S.E., 1988. Stoichiometry of the iron oxidation reaction in silicate
731 melts. *American Mineralogist* 73, 1267–1274.
- 732 Lange, R.L., Carmichael, I.S.E., 1990. Thermodynamic properties of silicate liquids with
733 emphasis on density, thermal expansion and compressibility. *Reviews in Mineralogy*
734 and *Geochemistry* 24, 25–64.
- 735 Longpré, M.-A., Stix, J., Klügel, A., Shimizu, N., 2017. Mantle to surface degassing of carbon-
736 and sulphur-rich alkaline magma at El Hierro, Canary Islands. *Earth and Planetary*
737 *Science Letters* 460, 268–280. <https://doi.org/10.1016/j.epsl.2016.11.043>
- 738 Mallmann, G., O'Neill, H.S.C., 2009. The Crystal/Melt Partitioning of V during Mantle
739 Melting as a Function of Oxygen Fugacity Compared with some other Elements (Al, P,
740 Ca, Sc, Ti, Cr, Fe, Ga, Y, Zr and Nb). *J. Petrology* 50, 1765–1794.
741 <https://doi.org/10.1093/petrology/egp053>
- 742 Massare, D., Métrich, N., Clocchiatti, R., 2002. High-temperature experiments on silicate melt
743 inclusions in olivine at 1 atm: inference on temperatures of homogenization and H₂O
744 concentrations. *Chemical Geology, Melt Inclusions at the Millennium: Toward a*
745 *Deeper Understanding of Magmatic Processes* 183, 87–98.
746 [https://doi.org/10.1016/S0009-2541\(01\)00373-4](https://doi.org/10.1016/S0009-2541(01)00373-4)
- 747 Métrich, N., Berry, A.J., O'Neill, H.St.C., Susini, J., 2009. The oxidation state of sulfur in
748 synthetic and natural glasses determined by X-ray absorption spectroscopy.
749 *Geochimica et Cosmochimica Acta* 73, 2382–2399.
750 <https://doi.org/10.1016/j.gca.2009.01.025>
- 751 Millet, M.-A., Doucelance, R., Schiano, P., David, K., Bosq, C., 2008. Mantle plume
752 heterogeneity versus shallow-level interactions: A case study, the São Nicolau Island,
753 Cape Verde archipelago. *Journal of Volcanology and Geothermal Research* 176, 265–
754 276. <https://doi.org/10.1016/j.jvolgeores.2008.04.003>
- 755 Mosbah, M., Métrich, N., Massiot, P., 1991. PIGME fluorine determination using a nuclear
756 microprobe with application to glass inclusions. *Nuclear Instruments and Methods in*
757 *Physics Research Section B: Beam Interactions with Materials and Atoms* 58, 227–231.
758 [https://doi.org/10.1016/0168-583X\(91\)95592-2](https://doi.org/10.1016/0168-583X(91)95592-2)
- 759 Moussallam, Y., Edmonds, M., Scaillet, B., Peters, N., Gennaro, E., Sides, I., Oppenheimer,
760 C., 2016. The impact of degassing on the oxidation state of basaltic magmas: A case
761 study of Kīlauea volcano. *Earth and Planetary Science Letters* 450, 317–325.
762 <https://doi.org/10.1016/j.epsl.2016.06.031>
- 763 Moussallam, Y., Oppenheimer, C., Scaillet, B., Gaillard, F., Kyle, P., Peters, N., Hartley, M.,
764 Berlo, K., Donovan, A., 2014. Tracking the changing oxidation state of Erebus
765 magmas, from mantle to surface, driven by magma ascent and degassing. *Earth and*
766 *Planetary Science Letters* 393, 200–209. <https://doi.org/10.1016/j.epsl.2014.02.055>
- 767 O'Neill, H.St.C., Berry, A.J., Mallmann, G., 2018. The oxidation state of iron in Mid-Ocean
768 Ridge Basaltic (MORB) glasses: Implications for their petrogenesis and oxygen
769 fugacities. *Earth and Planetary Science Letters* 504, 152–162.
770 <https://doi.org/10.1016/j.epsl.2018.10.002>
- 771 Parkinson, I.J., Arculus, R.J., 1999. The redox state of subduction zones: insights from arc-
772 peridotites. *Chemical Geology* 160, 409–423. [https://doi.org/10.1016/S0009-
773 2541\(99\)00110-2](https://doi.org/10.1016/S0009-2541(99)00110-2)

- 774 Prescher, C., McCammon, C., Dubrovinsky, L., 2012. MossA: a program for analyzing energy-
775 domain Mössbauer spectra from conventional and synchrotron sources. *J Appl Cryst*, *J*
776 *Appl Crystallogr* 45, 329–331. <https://doi.org/10.1107/S0021889812004979>
- 777 Prouteau, G., Scaillet, B., 2013. Experimental Constraints on Sulphur Behaviour in Subduction
778 Zones: Implications for TTG and Adakite Production and the Global Sulphur Cycle
779 since the Archean. *J Petrology* 54, 183–213. <https://doi.org/10.1093/petrology/egs067>
- 780 Rancourt, D.G., 1989. Accurate site populations from Mössbauer spectroscopy. *Nuclear*
781 *Instruments and Methods in Physics Research Section B: Beam Interactions with*
782 *Materials and Atoms* 44, 199–210. [https://doi.org/10.1016/0168-583X\(89\)90428-X](https://doi.org/10.1016/0168-583X(89)90428-X)
- 783 Rhodes, J.M., Vollinger, M.J., 2005. Ferric/ferrous ratios in 1984 Mauna Loa lavas: a
784 contribution to understanding the oxidation state of Hawaiian magmas. *Contrib Mineral*
785 *Petrol* 149, 666–674. <https://doi.org/10.1007/s00410-005-0662-y>
- 786 Roeder, P.L., Thornber, C., Poustovetov, A., Grant, A., 2003. Morphology and composition of
787 spinel in Pu'u 'O'o lava (1996–1998), Kilauea volcano, Hawaii. *Journal of*
788 *Volcanology and Geothermal Research* 123, 245–265. [https://doi.org/10.1016/S0377-0273\(02\)00508-5](https://doi.org/10.1016/S0377-0273(02)00508-5)
- 790 Rohrbach, A., Schmidt, M.W., 2011. Redox freezing and melting in the Earth's deep mantle
791 resulting from carbon-iron redox coupling. *Nature* 472, 209–212.
792 <https://doi.org/10.1038/nature09899>
- 793 Rowe, M.C., Kent, A.J.R., Nielsen, R.L., 2007. Determination of sulfur speciation and
794 oxidation state of olivine hosted melt inclusions. *Chemical Geology* 236, 303–322.
795 <https://doi.org/10.1016/j.chemgeo.2006.10.007>
- 796 Foley, S. F. 2010. A Reappraisal of Redox Melting in the Earth's Mantle as a Function of
797 Tectonic Setting and Time. *Journal of Petrology* 52, 1363–1391.
798 <https://doi.org/10.1093/petrology/egq061>
- 799 Shishkina, T.A., Botcharnikov, R.E., Holtz, F., Almeev, R.R., Jazwa, A.M., Jakubiak, A.A.,
800 2014. Compositional and pressure effects on the solubility of H₂O and CO₂ in mafic
801 melts. *Chemical Geology* 388, 112–129.
802 <https://doi.org/10.1016/j.chemgeo.2014.09.001>
- 803 Shorttle, O., Moussallam, Y., Hartley, M.E., MacLennan, J., Edmonds, M., Murton, B.J., 2015.
804 Fe-XANES analyses of Reykjanes Ridge basalts: Implications for oceanic crust's role
805 in the solid Earth oxygen cycle. *Earth and Planetary Science Letters* 427, 272–285.
806 <https://doi.org/10.1016/j.epsl.2015.07.017>
- 807 Sorbadere, F., Laurenz, V., Frost, D.J., Wenz, M., Rosenthal, A., McCammon, C., Rivard, C.,
808 2018. The behaviour of ferric iron during partial melting of peridotite. *Geochimica et*
809 *Cosmochimica Acta* 239, 235–254. <https://doi.org/10.1016/j.gca.2018.07.019>
- 810 Stagno, V., Ojwang, D.O., McCammon, C.A., Frost, D.J., 2013. The oxidation state of the
811 mantle and the extraction of carbon from Earth's interior. *Nature* 493, 84–88.
812 <https://doi.org/10.1038/nature11679>
- 813 Steele-Macinnis, M., Esposito, R., Bodnar, R.J., 2011. Thermodynamic Model for the Effect
814 of Post-entrapment Crystallization on the H₂O–CO₂ Systematics of Vapor-saturated,
815 Silicate Melt Inclusions. *J Petrology* 52, 2461–2482.
816 <https://doi.org/10.1093/petrology/egr052>
- 817 Streltsov, S.S., Shorikov, A.O., Skorniyakov, S.L., Poteryaev, A.I., Khomskii, D.I., 2017.
818 Unexpected 3+ valence of iron in FeO₂, a geologically important material lying “in
819 between” oxides and peroxides. *Scientific Reports* 7, 13005.
820 <https://doi.org/10.1038/s41598-017-13312-4>
- 821 Taylor, W.R., Green, D.H., 1988. Measurement of reduced peridotite-C-O-H solidus and
822 implications for redox melting of the mantle. *Nature* 332, 349.
823 <https://doi.org/10.1038/332349a0>

- 824 Tomkins, A.G., Evans, K.A., 2015. Separate zones of sulfate and sulfide release from
825 subducted mafic oceanic crust. *Earth and Planetary Science Letters* 428, 73–83.
826 <https://doi.org/10.1016/j.epsl.2015.07.028>
- 827 Toplis, M.J., 2005. The thermodynamics of iron and magnesium partitioning between olivine
828 and liquid: criteria for assessing and predicting equilibrium in natural and experimental
829 systems. *Contrib Mineral Petrol* 149, 22–39. [https://doi.org/10.1007/s00410-004-0629-](https://doi.org/10.1007/s00410-004-0629-4)
830 4
- 831 White, W.M., 2015. Probing the Earth's Deep Interior through Geochemistry. *Geochemical*
832 *Perspectives* 4, 95–96.
- 833 Wilke, M., Farges, F., Petit, P.-E., Brown, G.E., Martin, F., 2001. Oxidation state and
834 coordination of Fe in minerals: An Fe K-XANES spectroscopic study. *American*
835 *Mineralogist* 86, 714–730. <https://doi.org/10.2138/am-2001-5-612>
- 836 Wilke, M., Jugo, P.J., Klimm, K., Susini, J., Botcharnikov, R., Kohn, S.C., Janousch, M., 2008.
837 The origin of S⁴⁺ detected in silicate glasses by XANES. *American Mineralogist* 93,
838 235–240. <https://doi.org/10.2138/am.2008.2765>
- 839 Wilke, M., Partzsch, G.M., Bernhardt, R., Lattard, D., 2004. Determination of the iron
840 oxidation state in basaltic glasses using XANES at the K-edge. *Chemical Geology, 7th*
841 *Silicate Melt Workshop* 213, 71–87. <https://doi.org/10.1016/j.chemgeo.2004.08.034>
- 842 Woodland, A.B., Koch, M., 2003. Variation in oxygen fugacity with depth in the upper mantle
843 beneath the Kaapvaal craton, Southern Africa. *Earth and Planetary Science Letters* 214,
844 295–310. [https://doi.org/10.1016/S0012-821X\(03\)00379-0](https://doi.org/10.1016/S0012-821X(03)00379-0)
- 845 Zhang, H.L., Cottrell, E., Solheid, P.A., Kelley, K.A., Hirschmann, M.M., 2018. Determination
846 of Fe³⁺/ΣFe of XANES basaltic glass standards by Mössbauer spectroscopy and its
847 application to the oxidation state of iron in MORB. *Chemical Geology* 479, 166–175.
848 <https://doi.org/10.1016/j.chemgeo.2018.01.006>
- 849 Zhao, D., 2007. Seismic images under 60 hotspots: Search for mantle plumes. *Gondwana*
850 *Research* 12, 335–355. <https://doi.org/10.1016/j.gr.2007.03.001>
- 851