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Mantle plumes are oxidised

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ABSTRACT

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

I. INTRODUCTION

Temperature, pressure, volatile content, major element composition and oxygen fugacity (f_{O2}) are the five parameters controlling the occurrence and extent of partial melting in Earth's mantle, ultimately dictating where magmatic activity occurs on our planet. Of those, variables, oxygen fugacity of the mantle remains the least constrained yet its influence on phase relationship, volatile speciation, element partitioning and mantle physical properties is primary (e.g., Arculus, 1985). In terrestrial rocks, oxygen fugacity varies by over nine orders of magnitude (e.g., Parkinson and Arculus, 1999), but it remains to be seen how much oxygen fugacity varies in the upper mantle, especially in regions where melting occurs and if indeed systematic differences exist between tectonic contexts.

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

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

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

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

II. SAMPLES AND METHODS

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

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

2.1 XANES data acquisition

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

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

2.2 Beam damage

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

We used a hydrated experimental glass of basaltic composition (49.36 wt.% SiO_2, 1.47 wt.% TiO_2, 14.36 wt.% Al_2O_3, 8.61 wt.% FeO, 0.16 wt.% MnO, 9.08 wt.% MgO, 11.71 wt.% CaO, 3.26 wt.% Na_2O, 1.3 wt.% K_2O) with a $Fe^{3+}/\sum Fe = 0.22$ (obtained using the Smithsonian basalt glass calibration and Zhang et al., (2018) $Fe^{3+}/\sum Fe$ values from Mössbauer spectroscopy and under the beam damage-free analytical conditions described below). This glass was chosen because it contains 5.2 wt.% H_2O (as determined by SIMS), which is considerably more than any of the natural glasses analysed subsequently, hence it represents a worst-case scenario in terms of beam damage. We positioned the monochromator at a fixed energy of 7114.3 eV, corresponding to the oxidised peak of the pre-edge doublet. We then opened the shutter and counted the fluoresced X-rays every second for 1000 sec (~17 min) (Fig. 1). This beam damage test was popularised by Shorttle et al., (2015) and further used by Cottrell et al., (2018) and has the advantage over the more classic repeated quick-scan approach (e.g., Moussallam et al., 2016, 2014; Wilke et al., 2008) to allow identification of any beam damage occurrence over the first seconds of sample-beam interaction. We found that, under our analytical conditions and using an Al foil of 0.25 mm that attenuates the beam to about 1% of its original flux (calculated based on theoretical absorption, equivalent to ~10^8 photon/s or ~10^7 to 10^8 photon/s/μm^2), no change in fluoresced intensity was recorded under beam exposure. By contrast, using a 0.10 mm Al foil or no attenuation at all produced significant photo-oxidation of the iron. These results indicate that Fe in our natural samples, measured using a 0.25 mm Al foil, was not oxidised during XANES analyses. Note that conditions at each synchrotron beamline are slightly different, so the conditions under which we observe no resolvable beam damage at I18 are entirely reproducible but not directly transposable to another synchrotron/beamline. In the same way that calibration with glass standards is required before

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

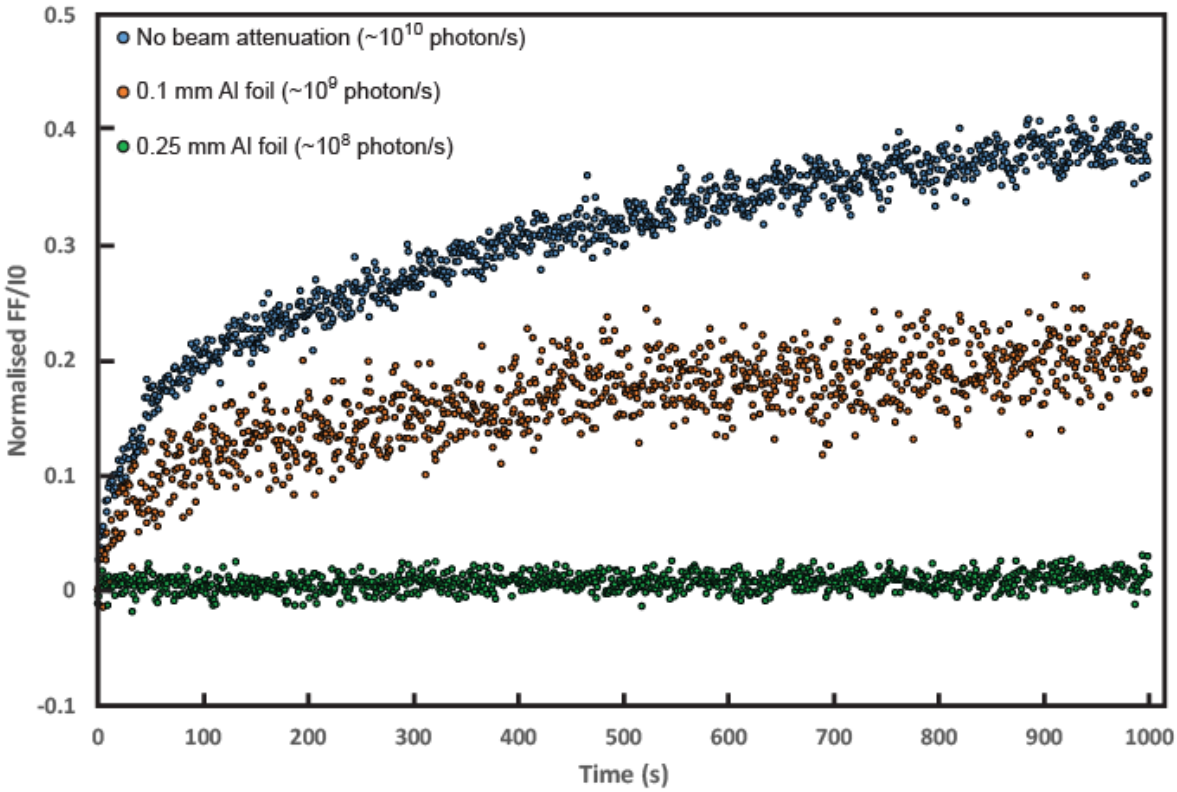

Figure 1*: Time series of normalised fluoresced intensity (FF) over I_0 at 7114.3 eV integrated over 1 s intervals for a hydrated (5.2 wt.% H_2O) basaltic glass under three different beam attenuation conditions. A fresh spot was illuminated with a 2.5 x 1.2 µm^2 beam for each analysis. While photo-oxidation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

2.3 Standards and Mössbauer spectroscopy

Glass standards for the XANES analyses were prepared in a controlled atmosphere furnace at the Department of Earth Sciences, University of Cambridge using a controlled CO_2-CO gas mixture. For each experiment, 50 mg of sample was placed in a platinum crucible. The sample was then introduced into the furnace and heated at 1400°C and left to equilibrate for two hours. At the end of each experiment, rapid quenching preserved chemical equilibrium as the sample dropped into a container of deionised water. The drop was initiated by short-circuiting the thin platinum wire by passing a current through the thick platinum wires. Six basanite standards of 2011-2012 El Hierro magma composition (44.4 wt.% SiO_2, 5.0 wt% TiO_2, 13.7 wt.% Al_2O_3, 12.5 wt.% FeO_t, 0.2 wt.% MnO, 8.1 wt.% MgO, 10.7 wt.% CaO, 3.5 wt.% Na_2O, 1.4 wt.% K_2O and 0.5 wt.% P_2O_5) were equilibrated at various fO_2 conditions (FMQ–1, FMQ, NNO, NNO+0.5, NNO+1 and NNO+1.5). All experiments were performed twice; first, in order to equilibrate the Pt crucible with Fe at each fO_2 (during 24h) and, second, to produce the glass used as standard. All standard glasses were subsequently analysed by electron microprobe. A 20-point electron microprobe transect was made across each standard to ensure all samples were homogeneous and that neither iron nor sodium loss had occurred.

All basanite glass standards were analysed for $Fe^{3+}/\Sigma Fe$ by Mössbauer spectroscopy at the Bayerisches Geoinstitut. Samples were analysed at room temperature using a constant acceleration Mössbauer spectrometer in transmission mode with a nominal 370 MBq ^{57}Co point source in a 12 µm Rh matrix. The active dimensions of the point source were 500 x 500 µm. The velocity scale was calibrated relative to α-Fe and line widths of 0.36 mm/s were obtained for the outer lines of α-Fe at room temperature. Fits to Mössbauer spectra were performed using MossA (Prescher et al., 2012) according to the approach used by Zhang et al. (2018) (xVBF model). A linear baseline was added to account for the shadowing effect and all

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

2.4 XANES spectra processing, $Fe^{3+}/\sum Fe$ calibration and data quality

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

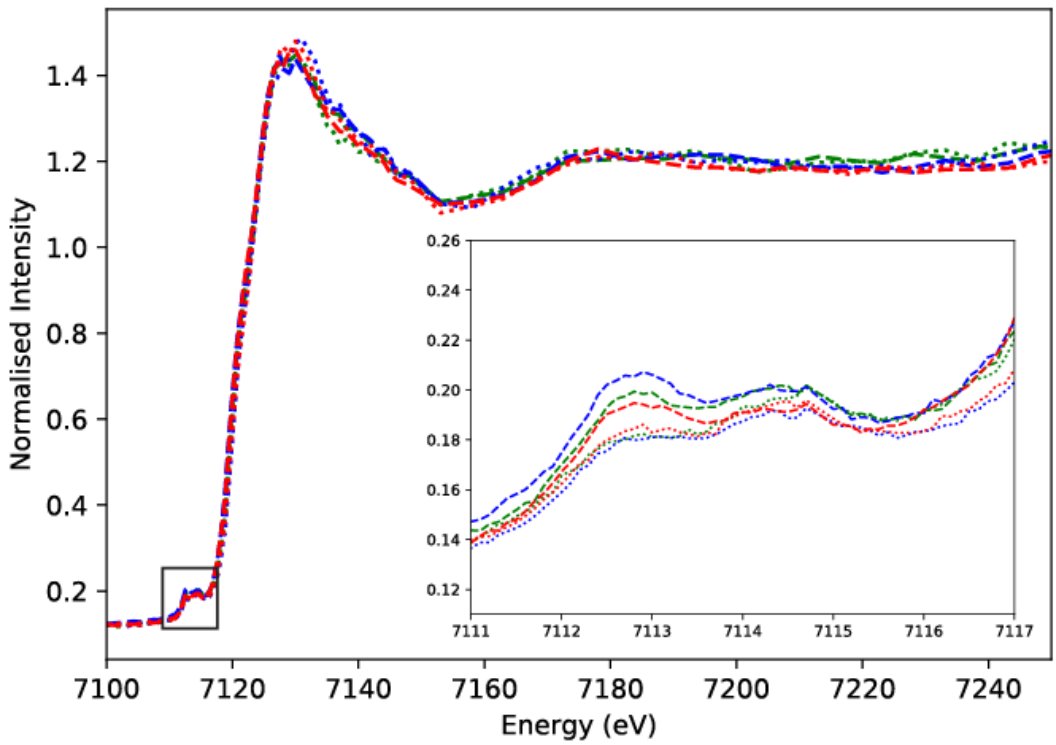

Figure 2*: Example of edge-step normalised XANES spectra (two co-add) obtained using a 0.25 mm Al plate attenuation. Spectra from both more oxidised (dashed lines) and more reduced (dotted lines) melt inclusions are shown for El Hierro (red), Lanzarote (blue) and Fogo (green) volcanoes.*

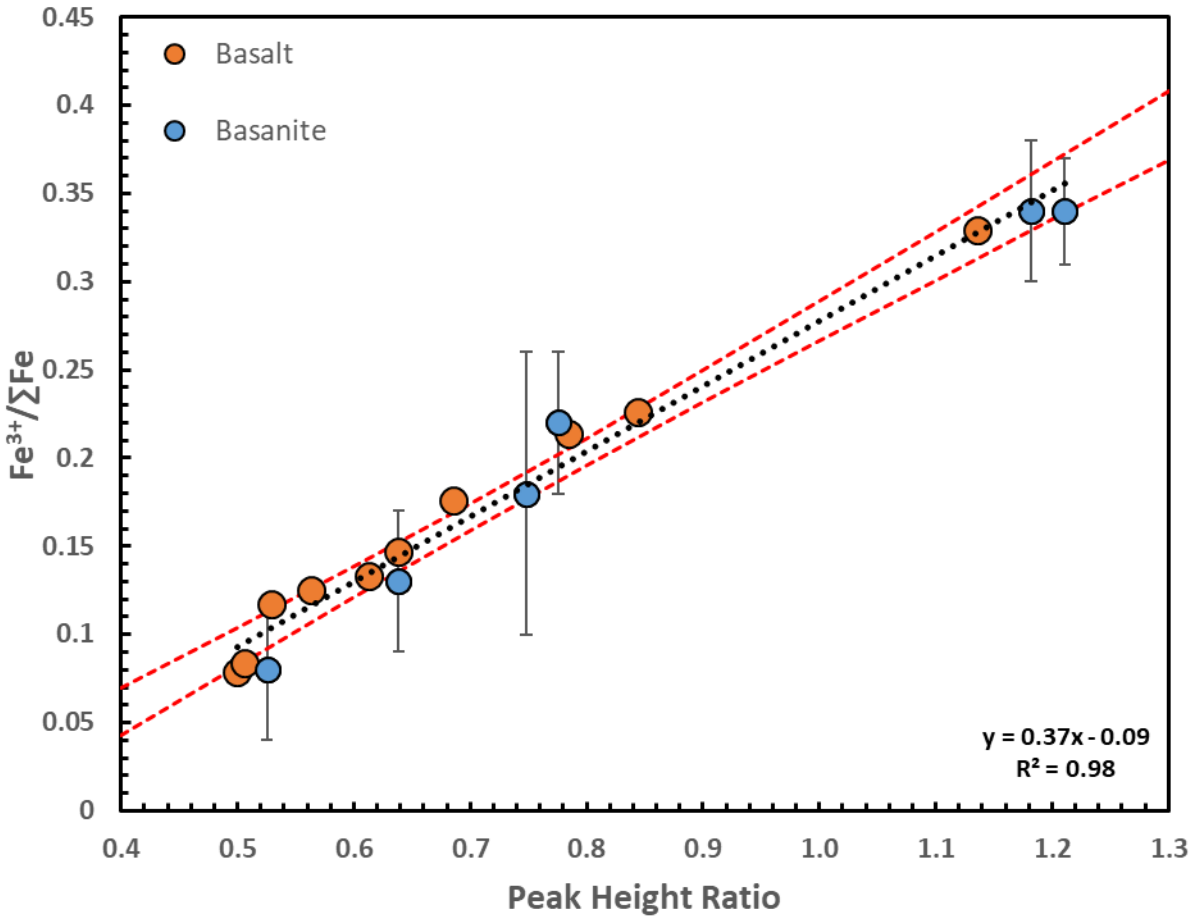

***Figure 3**: : Calibration line of the peak height ratio determined by XANES compared with the $Fe^{3+}/\sum Fe$ ratios determined by Mössbauer spectroscopy in basanite standard glasses (this study) and basaltic standard glasses from the Smithsonian (Mössbauer values from* Zhang et al., (2018)*). A linear regression through the basanite and basalt standards data (dotted black line) yields an equation of $y = 0.37x - 0.09$ with an R^2 of 0.98, a P-value of $1.6x10^{-6}$ and a standard error on the regression of 0.013. Dashed red lines show 95% confidence intervals. Note that the relationship between the peak height ratio and $Fe^{3+}/\sum Fe$ is well captured by a linear regression for $Fe^{3+}/\sum Fe$ between 0.1 and 0.4 (see supplementary Fig. S6), in agreement with previous studies (e.g.,* Cottrell et al., 2009*).*

In order to estimate the effect of lower quality spectra on the estimation of the peak height ratio we compared the ratio obtained from the processing of two co-added low quality spectra

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

2.5 Major elements and volatile analyses

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

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

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

2.6 Assessment of post-entrapment modification of melt inclusions.

2.6.1 Post-entrapment crystallisation

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

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

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

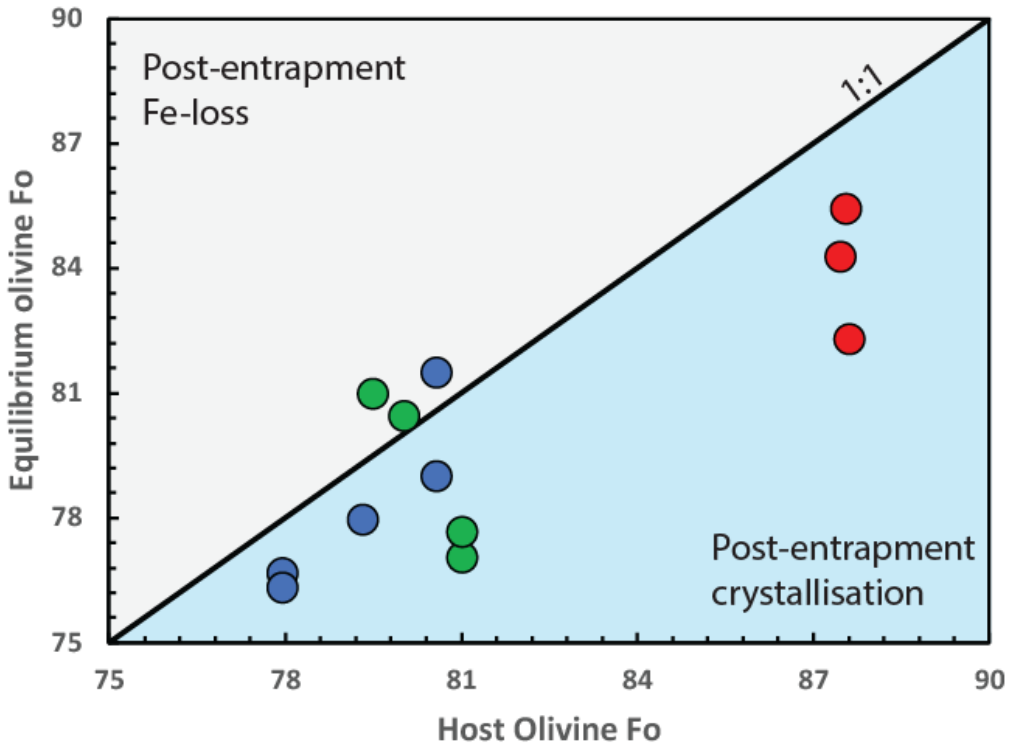

Figure 4: *Comparison between measured and equilibrium Fo content of host olivine for melt inclusions from Fogo (blue), El Hierro (green) and Lanzarote (red). Equilibrium Fo contents are calculated by Petrolog3 software (Danyushevsky and Plechov, 2011) using the model of Toplis, (2005) for the compositional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

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

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

2.6.2 Volatile diffusion

Post-entrapment diffusion of volatiles either through the olivine host (for H) (Hauri, 2002; Massare et al., 2002) or in the vapor bubble (for CO_2) (Anderson and Brown, 1993; Steele-Macinnis et al., 2011) can modify the original volatile content of melt inclusions. As such, our measurements of H_2O and CO_2 can be considered as minimum estimates of the original amounts dissolved in the inclusions even though all of our samples are from rapidly quenched tephra and lava ballons. Higher (than measured) original H_2O and CO_2 contents of the melt inclusions would yield greater calculated entrapment pressures but would make no difference to the conclusions presented here. H diffusion out of a melt inclusion could, however, also have an impact on the oxidation state of the inclusion with a predicted increase of the oxidation state of the melt inclusion with increasing amount of H diffusion (some experiments have shown no effect (Rowe et al., 2007) while others found a complete re-equilibration with the groundmass (Bucholz et al., 2013; Gaetani et al., 2012)). Although this process cannot be ruled out, the opposite correlation between H_2O and oxidation state shown by previous datasets as well as ours (see Results section) strongly argues against this process dominating the observed data variability.

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 $Fe^{3+}/\sum Fe$, 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 Fo_{90} olivine. The results shown in Fig. 5 and Table S8 indicate a modest decrease in $Fe^{3+}/\sum Fe$ with reverse crystallization, demonstrating that melts parental to our melt inclusions were already oxidised.

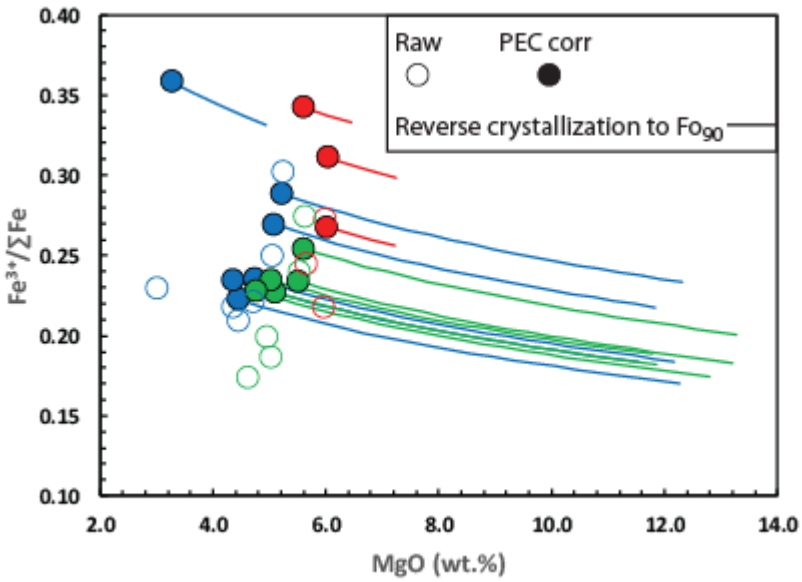

Figure 5: *Sensitivity analysis of the effects of post-entrapment crystallisation and pre-entrapment crystallization of olivine on melt $Fe^{3+}/\sum Fe$. Post-entrapment crystallisation estimated using Petrolog3 software (Danyushevsky and Plechov, 2011) assuming a system closed to oxygen, with Fe^{3+} behaving incompatibly, leads to a decrease in $Fe^{3+}/\sum Fe$ in corrected inclusions. The effect of pre-entrapment crystallization of olivine, modelled with PRIMELT3* (Herzberg and Asimow, 2015) *until melt–Fo_{90} olivine equilibrium is reached, is*

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

III. RESULTS

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

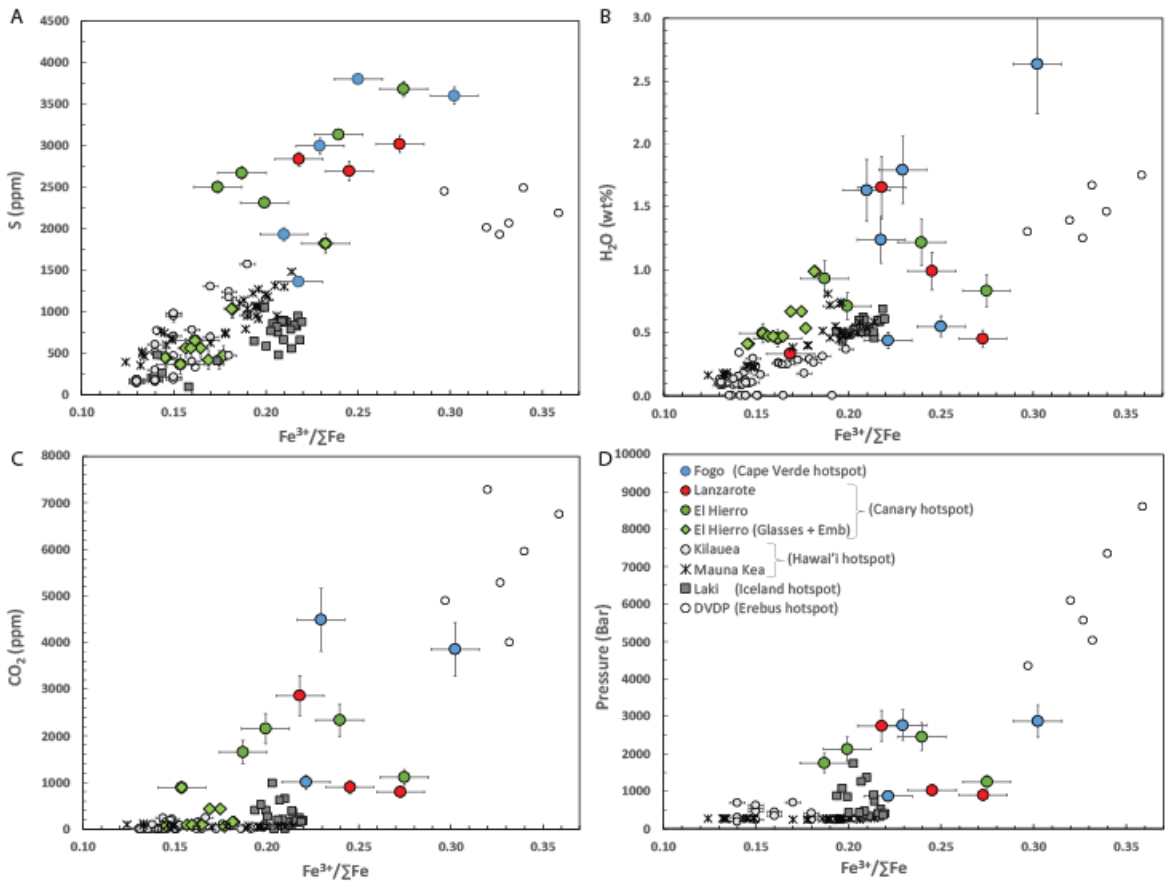

Figure 6: Volatile contents of melt inclusions, embayments and matrix glasses and corresponding volatile saturation pressures, for Fogo, Lanzarote and El Hierro (this study) and for Kīlauea (Moussallam et al., 2016), Mauna Kea (Brounce et al., 2017), Laki (Hartley et al., 2017) and Erebus (Moussallam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

IV. DISCUSSION

4.1 A case for oxidised mantle plumes

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

The most volatile-rich and deeply-entrapped melt inclusions should record conditions closest to the original mantle melt. From our dataset the effect of crystal fractionation on fO_2 appears to be minimal (see methods section). Even the most deeply-entrapped inclusions, however, likely experienced some amount of degassing. The original, pre-degassing, degree of oxidation of the melt can be estimated if we know how volatile-rich, especially how sulfur-rich, that melt was prior to degassing. Previous studies for Lanzarote (Gómez-Ulla, 2018) and El Hierro (Longpré et al., 2017) reported melt inclusions with sulfur contents of up to 3900 and 5000

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

It should be noted that by equating the oxidation state of deep melts to that of their mantle source we are assuming that melts are effectively buffered by their mantle source during partial melting. For MORBs, several lines of evidence support this hypothesis; (i) the lack of correlation between $Fe^{3+}/\Sigma Fe$ of MORB glasses and parameters sensitive to the degree of partial melting (Bézos and Humler, 2005, Cottrell and Kelley, 2011), (ii) the similarity in measured oxidation state of MORB glasses and co-located peridotites (Birner et al., 2018), and (iii) experimental investigations of partial melting showing that the melt $Fe^{3+}/\Sigma Fe$ ratios remain constant over varying degrees of partial melting (Sorbadere et al., 2018). In plume contexts it is currently unknown if this assumption remains valid. The relationship between $Fe^{3+}/\Sigma Fe$ and fO_2 in low-degree, volatile- and alkali-rich, partial melts is not well established, and it is conceivable that partial melting in some contexts would operate as an open system favouring the generation of Fe^{3+}-rich melts (Fe^{3+} being mildly incompatible during partial melting, e.g., Canil et al., 1994; Holloway and Burnham, 1972; Mallmann and O’Neill, 2009; Sorbadere et al., 2018). Given the current lack of evidence of such open-system partial melting processes

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

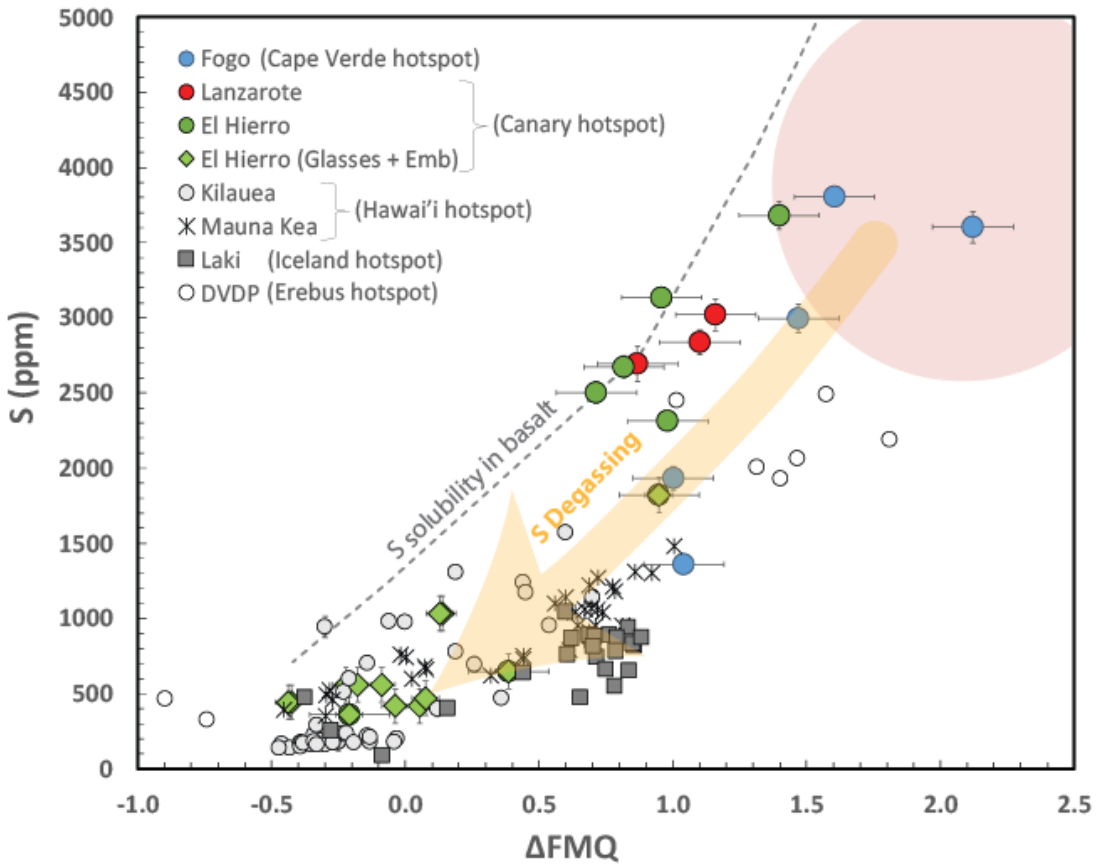

Figure 7: Sulfur contents of melt inclusions, embayments and matrix glasses from this study and for Kīlauea (Moussallam et al., 2016), Mauna Kea (Brounce et al., 2017), Laki (Hartley et al., 2017) and Erebus (Moussallam et al., 2014) compared with the oxygen fugacity of the melt expressed as the deviation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

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

4.2 Recycling of oxidised subducted material

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

(FeO_2 – referred to as P-phase) may form under extreme pressure and temperature in the Earth's interior (Hu et al., 2016). If so, highly oxidised patches containing iron in the 3+ valence state may accumulate in the deep lower mantle (Hu et al., 2017, 2016; Streltsov et al., 2017). Early incorporation of such material into mantle plumes would result in decomposition to Fe_2O_3 and release of O_2 during decompression (reaction 1 in Hu et al., 2016), providing an additional mechanism for generation of oxidised hotspot conditions. The hypothesis we favour, the most simple, is the incorporation of recycled surface-derived material in plumes.

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

Mantle plumes might therefore play a key role in the deep oxygen – and potentially S – cycles, providing a counterflow to subduction zones, and channelling oxidised material out of the deep Earth. The oxidised nature of mantle plumes might also partly explain their seismic velocity structure. It has been shown that the seismic properties of olivine are highly dependent on iron oxidation state, with olivine containing more Fe^{3+} showing enhanced anelastic relaxation (Ii et al., 2018). The low-velocity anomalies found beneath hotspot volcanoes (e.g., French and Romanowicz, 2015; Zhao, 2007) might then not only indicate elevated mantle temperatures but also raised mantle oxygen fugacity.

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

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

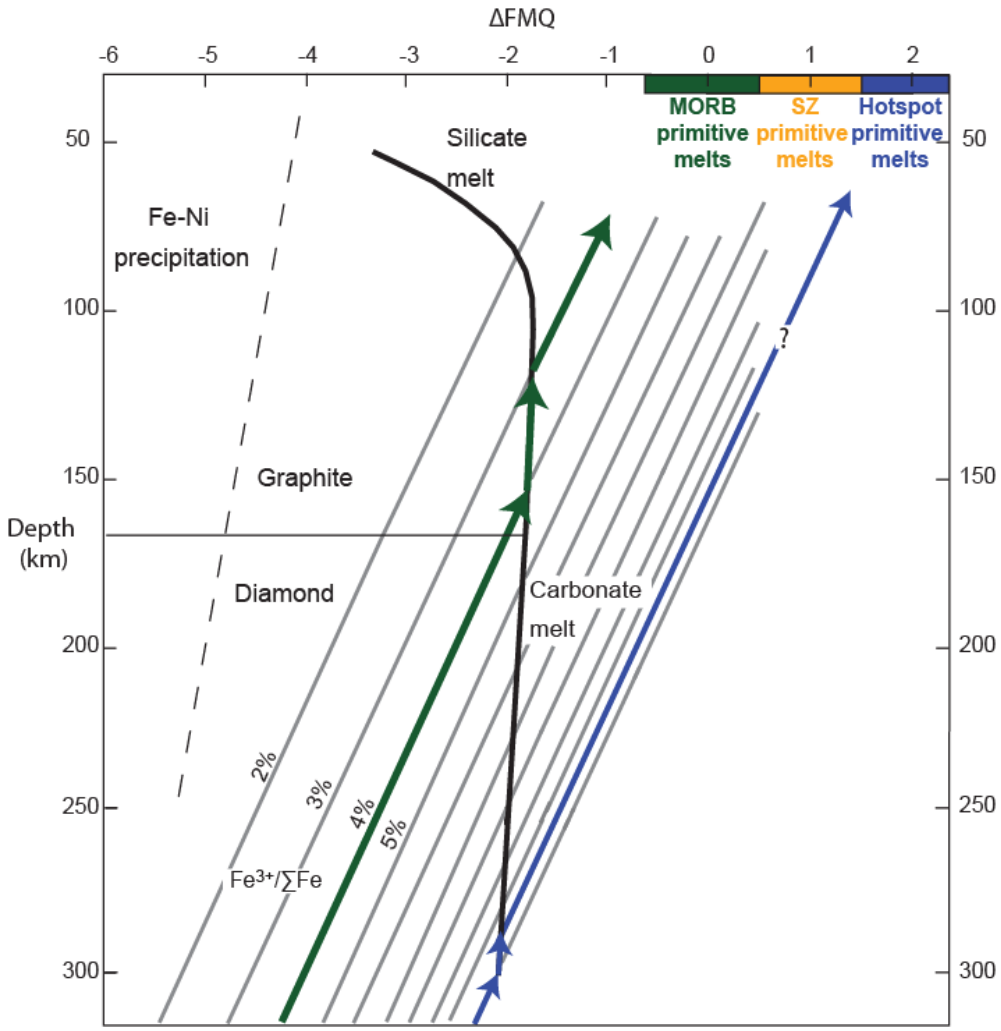

Figure 8: Relationship between depth and oxygen fugacity (expressed as the deviation from the FMQ buffer) for variable $Fe^{3+}/\sum Fe$ from Stagno et al., (2013). The stability fields of diamond and graphite are shown and bounded by the carbonate redox melting reaction line (thick black line). The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

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

V. CONCLUSION

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

We found that the most deeply entrapped samples, i.e., those preserving mantle equilibrium conditions and found at the Canary, Cape Verde and Erebus hotspots, are highly oxidised. This leads us to infer that globally, present day mantle plumes might be up to two orders of magnitude more oxidised than mantle beneath mid-ocean ridges (that is fO_2 two log units above the FMQ buffer) and also more oxidised than the mantle wedge beneath subduction zone volcanoes. What emerges is a novel view of the oxidation state of the mantle, in which large heterogeneities exist both vertically and laterally.

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

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