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# Olivine-hosted melt inclusions as an archive of redox heterogeneity in magmatic systems

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## ABSTRACT

The redox state of volcanic products determines their leverage on the oxidation of Earth's oceans and atmosphere, providing a long-term feedback on oxygen accumulation at the planet's surface. An archive of redox conditions in volcanic plumbing systems from a magma's mantle source, through crustal storage, to eruption, is carried in pockets of melt trapped within crystals. While melt inclusions have long been exploited for their capacity to retain information on a magma's history, their permeability to fast-diffusing elements such as hydrogen is now well documented and their retention of initial oxygen fugacities ($fO_2$) could be similarly diffusion-limited. To test this, we have measured $Fe^{3+}/\Sigma Fe$ by micro-XANES spectroscopy in a suite of 65 olivine-hosted melt inclusions and 9 matrix glasses from the AD 1783 Laki eruption, Iceland. This eruption experienced pre-eruptive mixing of chemically diverse magmas, syn-eruptive degassing at the vent, and post-eruptive degassing during lava flow up to 60 km over land, providing an ideal test of whether changes in the $fO_2$ of a magma may be communicated through to its cargo of crystal-hosted melt inclusions.

Melt inclusions from rapidly quenched tephra samples have $Fe^{3+}/\Sigma Fe$ of $0.206 \pm 0.008$ ($\Delta$QFM of $+0.7 \pm 0.1$), with no correlation between their $fO_2$ and degree of trace element enrichment or differentiation. These inclusions preserve the redox conditions of the mixed pre-eruptive Laki magma. When corrected for fractional crystallisation to 10 wt.% MgO, these inclusions record a parental magma $[Fe^{3+}/\Sigma Fe]_{(10)}$ of 0.18 ($\Delta$QFM of +0.4), significantly more oxidised than the $Fe^{3+}/\Sigma Fe$ of 0.10 that is often assumed for Icelandic basalt magmas. Melt inclusions from quenched lava selvages are more reduced than those from the tephra, having $Fe^{3+}/\Sigma Fe$ between 0.133 and 0.177 ($\Delta$QFM from −0.4 to +0.4). These inclusions have approached equilibrium with their carrier lava, which has been reduced by sulfur degassing. The progressive re-equilibration of $fO_2$ between inclusions and carrier melts occurs on timescales of hours to days, causing a drop in the sulfur content at sulfide saturation (SCSS) and driving the exsolution of immiscible sulfide globules in the inclusions.

Our data demonstrate the roles of magma mixing, progressive re-equilibration, and degassing in redox evolution within magmatic systems, and the open-system nature of melt inclusions to $fO_2$ during these processes. Redox heterogeneity present at the time of inclusion trapping may be overprinted by rapid re-equilibration of melt inclusion $fO_2$ with the external environment, both in the magma chamber and during slow cooling in lava at the surface. This can decouple the melt inclusion archives of $fO_2$, major and trace element chemistry, and mask associations between $fO_2$, magmatic differentiation and mantle source heterogeneity unless the assembly of diverse magmas is rapidly followed by eruption. Our tools for understanding the redox conditions of magmas are thus limited; however, careful reconstruction of pre- and post-eruptive magmatic history has enabled us to confirm the relatively oxidised nature of ocean island-type mantle compared to that of mid-ocean ridge mantle.

## 1. Introduction

Crystal-hosted melt inclusions are a key archive of the geochemical diversity of melts present in magmatic systems, and of

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the pre-eruptive processes they experience. This chemical diversity is both primary, originating from mantle melting (Dungan and Rhodes, 1978; Sobolev and Shimizui, 1993; Slater et al., 2001) and source heterogeneity (Allègre and Turcotte, 1986; Maclennan, 2008b; Shorttle and Maclennan, 2011), and secondary, originating from differentiation processes in the crust (O'Neill and Jenner, 2012; Brounce et al., 2012; Neave et al., 2014) and degassing of volatile species prior to and during eruption (Métrich and Wallace, 2008). These fundamental magmatic processes have been constrained primarily using the major, trace, and volatile element contents of melt inclusions (Lowenstern, 1995; Sobolev, 1996; Kent, 2008). However, none of these elemental abundances directly record the redox state of the magma as it evolves from mantle source through to eruption.

The clearest tracer of the oxygen fugacity ($f\mathrm{O}_2$) of a magma is its iron oxidation state (Kilinc et al., 1983; Kress and Carmichael, 1991). Whilst traditional bulk wet-chemical methods for determining the relative abundances of $\mathrm{Fe}^{3+}$ and $\mathrm{Fe}^{2+}$ in a magma, often expressed as $\mathrm{Fe}^{3+}/\Sigma\mathrm{Fe}$, cannot be applied to melt inclusions, recent advances in synchrotron X-ray absorption near-edge structure (XANES) spectroscopy make it possible to precisely analyse $\mathrm{Fe}^{3+}/\Sigma\mathrm{Fe}$ on the tens-of-microns scale of melt inclusions (Berry et al., 2003, 2008; Cottrell et al., 2009). In principle, this advance makes it possible to track magmatic $f\mathrm{O}_2$ into the earliest stages of magma formation and evolution (Brounce et al., 2014; Moussallam et al., 2014).

The promise of studying melt inclusions is that, following their entrapment, they are a closed system to subsequent changes in the chemistry of their host magma (Sobolev, 1996; Cherniak, 2010). However, there is now abundant evidence, both experimental and in natural samples, that melt inclusions are open to at least hydrogen exchange with their carrier liquid (Gaetani et al., 2012; Hartley et al., 2015). The key question then is the degree to which the $f\mathrm{O}_2$ of melt inclusions is also modified by post-entrapment processes and changes in the chemical environment.

Melt inclusions are strongly influenced by a range of post-entrapment processes, meaning that inclusions may no longer preserve a record of the $f\mathrm{O}_2$ at which they were formed. Firstly, post-entrapment crystallisation is a near-ubiquitous process in crystal-hosted melt inclusions. For olivine-hosted inclusions, this will sequester $\mathrm{Fe}^{2+}$ from the melt into the olivine crystal lattice. Secondly, coupled proton and metal vacancy diffusion through the host olivine allows melt inclusions to approach $\mathrm{H_2O}$ and $f\mathrm{O}_2$ equilibrium with their external environment, with complete re-equilibration achieved on timescales of hours to days at magmatic temperatures when the external $f\mathrm{O}_2$ and $f\mathrm{H_2O}$ are fixed (Gaetani et al., 2012; Bucholz et al., 2013). The external environment surrounding the melt inclusions, i.e. their carrier melt, is in turn modified by magma mixing (Maclennan, 2008a; Shorttle et al., 2016) and volatile outgassing (Gaillard et al., 2011; Moussallam et al., 2014, 2016; Helz et al., 2017) during storage, ascent and eruption. Coupled with the rapid diffusion of metal vacancies through the host olivine crystal, these processes may mean that initial variability in melt inclusion $f\mathrm{O}_2$ present at the time of entrapment is homogenised.

To investigate the effect of post-entrapment processes on the melt inclusion archive of $f\mathrm{O}_2$, we have made new high-precision measurements of $\mathrm{Fe}^{3+}/\Sigma\mathrm{Fe}$ by XANES spectroscopy in a suite of 65 naturally quenched olivine-hosted melt inclusions and 9 matrix glasses from the AD 1783 Laki eruption, Iceland. These well-characterised samples provide an opportunity to identify the post-entrapment processes that modify the $f\mathrm{O}_2$ of olivine-hosted melt inclusions. We show that the $f\mathrm{O}_2$ in olivine-hosted inclusions from Laki is principally controlled by diffusive re-equilibration between the inclusion and its external environment: melt inclusions held at high temperatures during magma storage and lava transport approach $f\mathrm{O}_2$ equilibrium with their carrier melt, which itself has an evolving $f\mathrm{O}_2$ in response to magma mixing and degassing of sulfur. We then use the most pristine and least degassed melt inclusion compositions to determine $\mathrm{Fe}^{3+}/\Sigma\mathrm{Fe}$ and $f\mathrm{O}_2$ in the primary Laki magma. Finally, we assess our dataset for evidence of redox heterogeneity in the diverse melt compositions present at the time of inclusion trapping.

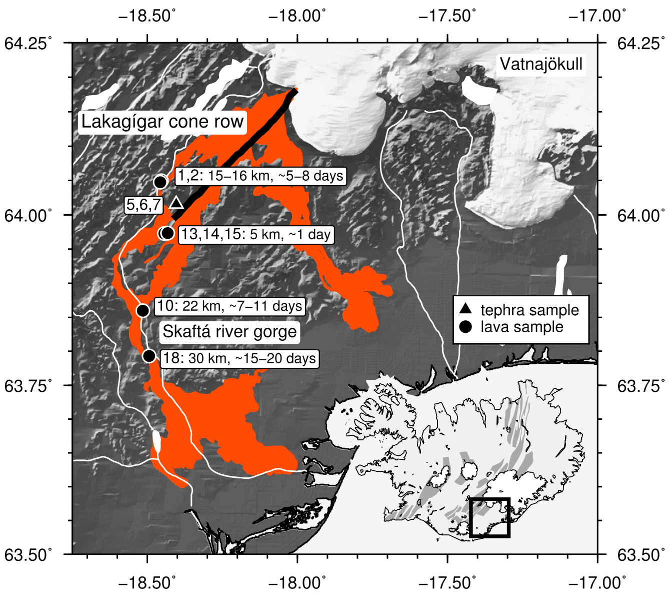

**Fig. 1.** Map of Iceland's Eastern Volcanic Zone (EVZ) showing the AD 1783 Laki lava flow field. The 27 km-long Laki fissure is shown as a thick black line. Numbered locations show where the samples used in this study were collected. For lava samples, the distance to the source vents and the likely transport time (Hartley et al., 2015) are provided in the sample labels. The inset map shows the location of the EVZ with fissure swarms shaded in dark grey.

## 2. Methodology

The AD 1783-84 Laki eruption, southeast Iceland, is one of the best-studied small-scale analogues of a flood basalt eruption, and its eruptive history and products have been documented in detail (Métrich et al., 1991; Thordarson and Self, 1993; Thordarson et al., 1996; Guilbaud et al., 2007; Passmore et al., 2012; Neave et al., 2013; Hartley et al., 2016). Our study focuses on a suite of samples that includes both magmatic tephra from the Laki cone row and quenched glassy lava selvages (Fig. 1). The lava selvages were collected at distances of ∼5, 15, 22 and 30 km from their source vents, and their melt inclusions are likely to have spent <1 d up to ∼15–20 d in insulated lava transport (Hartley et al., 2015). Olivine-hosted melt inclusions and matrix glasses from these samples have previously been analysed for their major, trace and volatile element contents by EPMA, SIMS and Raman spectroscopy (Hartley et al., 2014).

The samples were re-polished to remove pits left by SIMS analysis, then polished on the reverse side to obtain doubly intersected polished wafers in which both sides of the melt inclusions were exposed. Sixty-five previously analysed melt inclusions with obstruction-free areas of at least 10 × 10 μm were selected for XANES analysis.

Fig. 2 shows typical examples of olivine-hosted melt inclusions from tephra and lava samples. Inclusions from tephra samples comprise vitreous, transparent glass with no daughter crystals; some contain a shrinkage bubble, but many are bubble-free (Hartley et al., 2014). Melt inclusions from lava samples are also vitreous, and most contain a vapour bubble. Many lava-hosted in-