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Volatile and light lithophile elements in high-anorthite plagioclase-hosted melt inclusions from Iceland

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Abstract

Melt inclusions formed during the early stages of magmatic evolution trap primitive melt compositions and enable the volatile contents of primary melts and the mantle to be estimated. However, the syn- and post-entrapment behaviour of volatiles in primitive high-anorthite plagioclase-hosted melt inclusions from oceanic basalts remains poorly constrained. To address this deficit, we present volatile and light lithophile element analyses from a well-characterised suite of nine matrix glasses and 102 melt inclusions from the 10 ka Grímsvötn tephra series (i.e., Saksunarvatn ash) of Iceland's Eastern Volcanic Zone (EVZ). High matrix glass H_2O and S contents indicate that eruption-related exsolution was arrested by quenching in a phreatomagmatic setting; Li, B, F and Cl did not exsolve during eruption. The almost uniformly low CO_2 content of plagioclase-hosted melt inclusions cannot be explained by either shallow entrapment or the sequestration of CO_2 into shrinkage bubbles, suggesting that inclusion CO_2 contents were controlled by decrepitation instead. High H_2O/Ce values in primitive plagioclase-hosted inclusions (182–823) generally exceed values expected for EVZ primary melts (~180), and can be accounted for by diffusive H_2O gain following the entrainment of primitive macrocrysts into evolved and H_2O-rich melts a few days before eruption. A strong positive correlation between H_2O and Li in plagioclase-hosted inclusions suggests that diffusive Li gain may also have occurred. Extreme F enrichments in primitive plagioclase-hosted inclusions ($F/Nd = 51$–216 versus ~15 in matrix glasses) possibly reflect the entrapment of inclusions from high-$Al/(Al + Si)$ melt pools formed by dissolution-crystallisation processes (as indicated by HFSE depletions in some inclusions), and into which F was concentrated by uphill diffusion since F is highly soluble in Al-rich melts. The high S/Dy of primitive inclusions (~300) indicates that primary melts were S-rich in comparison with most oceanic basalts. Cl and B are unfractionated from similarly compatible trace elements, and preserve records of primary melt heterogeneity. Although primitive plagioclase-hosted melt inclusions from the 10 ka Grímsvötn tephra series record few primary signals in their volatile contents, they nevertheless record information about crustal magma processing that is not captured in olivine-hosted melt inclusions suites.

Keywords: Plagioclase-hosted melt inclusions; Volatiles; Primitive basalt; Diffusion; Magma mixing; Iceland

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1. INTRODUCTION

Mantle melts are modified by a range of mixing, fractionation and assimilation processes as they rise towards

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the Earth's surface (O'Hara, 1968; Duncan and Green, 1987; Langmuir et al., 1992; Rubin et al., 2009; Shorttle, 2015). Petrological records of mantle melting and magmatic evolution are thus progressively degraded as magmas ascend and differentiate. This degradation is particularly severe in the case of the volatile species (H_2O, CO_2, F, S and Cl) that exsolve and become decoupled from non-volatile species when melts reach vapour saturation (Stolper and Holloway, 1988; Dixon and Stolper, 1995). Melt inclusions – pools of silicate liquid partially insulated from changes in the external magmatic environment by their host crystals – thus represent appealing targets for investigating the behaviour of magmatic volatiles (Anderson and Brown, 1993; Sobolev and Chaussidon, 1996; Métrich and Wallace, 2008). However, before interpreting melt inclusion compositions in terms of primary magmatic processes, it is imperative to assess the degree to which they have been modified by secondary processes. That is, geochemical variability in melt inclusion suites must be interpreted in terms of syn- and post-entrapment processes as well as pre-entrapment processes.

Possible mechanisms for modifying inclusion compositions during entrapment include the accumulation of slowly diffusing elements such as Al, Cl and S against rapidly growing crystals faces resulting in the entrapment of Al-, Cl- and S-enriched boundary layers (Faure and Schiano, 2005; Baker, 2008). However, unambiguous examples of such diffusive pile-up in natural samples are rare, and the importance of this process in melt inclusion formation remains uncertain (Kent, 2008). Geochemically anomalous melt inclusions in plagioclase macrocrysts have nonetheless been accounted for by the incomplete re-equilibration of melt channels and boundary layers generated by dissolution-crystallisation processes during inclusion formation (Nakamura and Shimakita, 1998; Michael et al., 2002).

Prior to final cooling, inclusions commonly experience post-entrapment crystallisation (PEC) (Roedder, 1979; Kress and Ghiorso, 2004). While PEC acts to simply concentrate most volatiles because of their largely incompatible characters – though Newcombe et al. (2014) describe how PEC can induce intra-inclusion heterogeneity – its effect on CO_2 is more complex: alongside contrasts in density and thermal expansivity between host crystals and their inclusions, PEC-driven changes in trapped melt compositions lead to the nucleation of shrinkage bubbles (Roedder, 1984; Lowenstern, 1995; Maclennan, 2017). Although shrinkage bubbles probably do not contain appreciable quantities of H_2O (though see Esposito et al., 2016), they can sometimes sequester significant amounts of CO_2, and must therefore be considered when estimating the total CO_2 content of melt inclusions (Steele-Macinnis et al., 2011; Bucholz et al., 2013; Hartley et al., 2014; Sides et al., 2014; Moore et al., 2015; Wallace et al., 2015). Melt inclusion CO_2 contents can also be affected by decrepitation when pressure differences between inclusions and the external environment exceed the strength of host crystals, causing them to rupture and leak (Tait, 1992; Schiano, 2003; Maclennan, 2017).

Given sufficient time, melt inclusions can also respond to changes in their magmatic environment by diffusive re-equilibration (Qin et al., 1992). Although few melt inclusions show evidence for the re-equilibration of slowly diffusing incompatible trace elements (ITEs; Cottrell et al., 2002), many olivine-hosted inclusions show evidence for the exchange of rapidly diffusing H^+ (Massare et al., 2002; Koleszar et al., 2009; Chen et al., 2013; Lloyd et al., 2013). Indeed, the re-equilibration of H^+ through olivine hosts typically occurs within hours to days in basaltic systems (Portnyagin et al., 2008; Gaetani et al., 2012), providing a useful chronometer for pre-eruptive magma mixing processes (Bucholz et al., 2013; Le Voyer et al., 2014; Hartley et al., 2015). Although OH^- loss from plagioclase macrocrysts has been reported in magmas undergoing progressive H_2O degassing (Hamada et al., 2011), the susceptibility of plagioclase-hosted melt inclusions to H species re-equilibration remains to be clarified.

To date, most studies on melt inclusions from oceanic basalts have focused on olivine for three main reasons: firstly, early-forming olivine macrocrysts are abundant in mafic rocks (e.g., Roeder and Emslie, 1970; Kent, 2008); secondly, olivine-melt equilibria are comparatively simple, making PEC corrections tractable (e.g., Ford et al., 1983; Toplis, 2005; Danyushevsky and Plechov, 2011); and thirdly, olivine is thought to be a more robust than highly cleaved plagioclase and clinopyroxene. However, many erupted magmas contain significantly more plagioclase than olivine (Flower, 1980; Sinton et al., 1993; Nielsen et al., 1995; Lange et al., 2013; Neave et al., 2014b), and plagioclase-hosted melt inclusions may offer the only means of sampling primitive melt compositions; olivine-hosted inclusions may be too small to analyse or simply absent. While high-anorthite plagioclase-hosted melt inclusions may preserve comparable records to high-forsterite olivine-hosted inclusions (Sours-Page et al., 2002; Font et al., 2007), the processes that modify plagioclase-hosted melt inclusion compositions are, with the exceptions of PEC and dissolution-crystallisation (Nielsen et al., 1995, 1998; Nakamura and Shimakita, 1998; Michael et al., 2002; Adams et al., 2011), poorly understood (Kent, 2008). Analyses of multiple volatiles in plagioclase-hosted inclusions from MORB and OIB settings are particularly rare (cf., Helo et al., 2011), and evaluations of the processes controlling their abundances rarer still.

Here we aim to identify the primary and secondary controls on the volatile and light lithophile element contents of primitive plagioclase-hosted melt inclusions from an oceanic setting. We report analyses of Li, B, F, S and Cl in matrix glasses and mainly plagioclase-hosted melt inclusions from the Icelandic 10 ka Grímsvötn tephra series whose H_2O, CO_2, major element and trace element systematics have been investigated by Neave et al. (2015). Although we find that few primary magmatic signals are preserved in the volatile content of primitive-plagioclase-hosted melt inclusions, compositional variability related to syn- and post-entrapment modification processes nevertheless offers insights into magma evolution that are obscured from olivine-hosted records.