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Partitioning of light lithophile elements during basalt eruptions on Earth and application to Martian shergottites

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ABSTRACT

An enigmatic record of light lithophile element (LLE) zoning in pyroxenes in basaltic shergottite meteorites, whereby LLE concentrations decrease dramatically from the cores to the rims, has been interpreted as being due to partitioning of LLE into a hydrous vapor during magma ascent to the surface on Mars. These trends are used as evidence that Martian basaltic melts are water-rich (McSween et al., 2001). Lithium and boron are light lithophile elements (LLE) that partition into volcanic minerals and into vapor from silicate melts, making them potential tracers of degassing processes during magma ascent to the surface of Earth and of other planets. While LLE degassing behavior is relatively well understood for silica-rich melts, where water and LLE concentrations are relatively high, very little data exists for LLE abundance, heterogeneity and degassing in basaltic melts. The lack of data hampers interpretation of the trends in the shergottite meteorites. Through a geochemical study of LLE, volatile and trace elements in olivine-hosted melt inclusions from Kilauea Volcano, Hawaii, it can be demonstrated that lithium behaves similarly to the light to middle rare Earth elements during melting, magma mixing and fractionation. Considerable heterogeneity in lithium and boron is inherited from mantle-derived primary melts, which is dominant over the fractionation and degassing signal. Lithium and boron are only very weakly volatile in basaltic melt erupted from Kilauea Volcano, with vapor-melt partition coefficients <0.1. Degassing of LLE is further inhibited at high temperatures. Pyroxene and associated melt inclusion LLE concentrations from a range of volcanoes are used to quantify lithium pyroxene-melt partition coefficients, which correlate negatively with melt H_2O content, ranging from 0.13 at low water contents to <0.08 at H_2O contents >4 wt%. The observed terrestrial LLE partitioning behavior is extrapolated to Martian primitive melts through modeling. The zoning observed in the shergottite pyroxenes is only consistent with degassing of LLE from a Martian melt near its liquidus temperature if the vapor-melt partition coefficient was an order of magnitude larger than observed on Earth. The range in LLE and trace elements observed in shergottite pyroxenes are instead consistent with concurrent mixing and fractionation of heterogeneous melts from the mantle.

1. Introduction

Decreasing light lithophile element (LLE; lithium, boron, beryllium) concentrations in pyroxenes, from core to rim, have been observed in Martian basaltic shergottite meteorites. These trends have been interpreted to be the result of degassing of the LLE into hydrous vapor during magma decompression towards the Martian surface (Herd et al., 2005; Lentz et al., 2004; McSween et al., 2001; Udry and McSween, 2014). These observations have formed a basis for proposing that Martian primary basaltic melts were H_2O-rich (Beck et al., 2004; Lentz et al., 2001; McSween et al., 2001). The role of H_2O during the petrogenesis of Martian magmas has critical implications for understanding hydrogen distribution during planetary accretion, rheological structure of the Martian mantle, for mantle oxidation state, outgassing and climate, as well as for shaping the surface of the planet. It is not yet clear whether degassing is the correct explanation for these trends, as the partitioning of LLE between melt and vapor during magma decompression is not well understood for basaltic melts. There exist a range of alternative explanations: solid state diffusion of LLE through the crystal during late-stage degassing of the carrier liquid; or fractionation of pyroxene accompanying mixing of liquids, each with distinctive trace element and isotopic characteristics. In this paper the behavior of lithium and boron is compared to other trace elements and volatiles in primitive melts on Earth and the degassing mechanism is explored in detail.

Lithium and boron are present in basaltic magmas in low concentrations. Owing to their low atomic masses, they are volatile

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and may exsolve from melts during ascent and eruption. Lithium and boron have an affinity for hydrous fluids in evolved silicic systems during late stage degassing (Webster et al., 1996), in differentiates from Piton de la Fournaise (Vlastélic et al., 2011) and in granitic melts coexisting with fluids (Whitworth and Rankin, 1989). Their abundance in the mantle is influenced strongly by the subduction of lithium-rich sediments into the mantle, inducing heterogeneity both in abundance and in isotopic composition (Kobayashi et al., 2004). Lithium and boron are key tracers for understanding arc geochemical cycling, as they behave like volatile elements during devolatilization, partitioning into fluids at high pressures (Moriguti et al., 2004). Lithium and boron partition weakly into minerals crystallizing from silicate melts, such as pyroxene and plagioclase (Herd et al., 2004), which allows for an observable record of melt lithium and boron contents to be preserved in crystals. If lithium and boron were non-volatile, their abundance in minerals from core to rim in a closed system would increase inversely proportional to the fraction of liquid remaining, for a fixed partition coefficient. Lithium is enriched in the rims of plagioclase and amphiboles from dacitic lava dome rocks from Mount St Helens, inferred to be due to enrichment in the melt shortly before eruption due to the transfer of vapor from depth (Berlo et al., 2004; Kent et al., 2007b). Little is known, in contrast, about the behavior of LLE in water-poor basalts during low-pressure differentiation and degassing. It has been demonstrated that fluid-melt partition coefficients for lithium and boron are >1 for rhyolites (Webster et al., 1996) and <1 for boron in basalts (Hervig et al., 2002), but there is only limited data on the basaltic end member and no data on lithium partitioning into fluids at low pressures and activities of water. Despite this, their dramatic depletion in pyroxenes from core to rim in Martian basaltic shergottite meteorites has been ascribed to their partitioning into hydrous vapor and hence used as evidence for water in Martian melts (Lentz et al., 2001, 2004; McSween and Stolper, 1978; McSween et al., 2001; Udry and McSween, 2014).

Other published data have potential to cast light onto the problem of whether Martian basaltic melts are water-rich. The lithium isotopic composition of the pyroxenes, and trends in lithium isotopes from core to rim are expected to indicate either (a) diffusive loss of lithium from the crystal through solid state diffusion, which has a characteristic large fractionation factor owing to the large mass difference between the two isotopes, with ^{6}Li expected to diffuse faster (Beck et al., 2004) or (b) trends in lithium isotopes consistent with fractionation accompanying degassing of lithium from the melt. In fact the isotopic measurements are inconclusive: δ^7Li increases from core to rim, with a magnitude not consistent with solid state diffusive loss of lithium (Beck et al., 2004). This trend is consistent with the preference for ^{6}Li in the gas phase during kinetic fractionation of isotopes (Beck et al., 2004), albeit of a lesser magnitude than predicted; but is not consistent with experiments at high pressures (GPa) illustrating chemical (rather than kinetic) fractionation effects, which show that ^{7}Li is preferentially fractionated into the fluid phase (Vlastélic et al., 2011; Wunder et al., 2006). This latter mechanism appears to be the mechanism at work for transferring light lithium into the mantle in subduction zones (Zack et al., 2003). An alternative and equally viable explanation for the lithium isotope trends is concurrent melt mixing (between melts with distinctive lithium isotope composition) and fractionation of pyroxene.

The concentrations in the pyroxenes, and the pyroxene-melt partition coefficient for lithium inferred from experiments of $\sim$0.2 (Herd et al., 2004), suggest that the primary melt would have had $>$20 ppm, which is far higher than the lithium content of the whole rocks (Herd et al., 2004). Experiments to reproduce the magnesian cores of the pyroxenes in the shergottites suggest melt water concentrations of $\sim$1.8 wt% H_2O (Dann et al., 2001), although it has been suggested that the melts may have been chlorine-rich instead (Allard et al., 2005). A role for halogens is supported by the fact that most martian hydrous minerals generally have the relevant sites filled with Cl and F instead of H (Patiño Douce and Roden, 2006). Recent studies of nominally anhydrous minerals (Boctor et al., 2003), amphiboles (McCubbin et al., 2010), and apatites (McCubbin et al., 2012, 2014) from Martian meteorites suggest that the martian mantle is as hydrous as that of the Earth. In contrast, olivine melt inclusions in shergottites have undegassed D/H signatures and low total H_2O contents, leading to the conclusion that the Martian mantle is much drier than on Earth (Usui et al., 2012) and would therefore produce relatively dry primary melts. Although both "enriched" and "depleted" shergottites exist, they were both derived from parental magmas with water contents of up to 0.3 wt% and the water contents of their mantle sources were probably somewhat similar (McCubbin et al., 2014).

It is not clear that degassing is the correct explanation for the LLE zoning patterns in shergottite pyroxenes, primarily because we have a poor understanding of the behavior of these elements in basaltic volcanic systems. In order to test the hypothesis, an analogous basaltic system on Earth is used here to quantify the LLE heterogeneity inherited from the mantle and the behavior of lithium and boron during magma decompression, fractionation and degassing. Kilauea Volcano, Hawaii, has oft been cited as a terrestrial analogue to Martian basaltic volcanic system, with its "type I" volcanic gas composition (Gerlach and Graeber, 1985) used to estimate the composition of outgassing volatiles on Mars (Craddock and Greeley, 2009). Kilauea basaltic melts have $\sim$0.7 wt% H_2O prior to degassing (Dixon et al., 1991; Edmonds et al., 2014; Wallace, 1998). Kilauean basaltic melt inclusions, which represent "snapshots" of pre-eruptive melt, contain up to 6.6 ppm Li, up to 3.5 ppm B and up to 330 ppm Cl (Sides et al., 2014b). The behavior of volatile species during magma decompression, fractionation and mixing at Kilauea is well understood (Dixon et al., 1991; Edmonds et al., 2014).

Recently, a dataset comprising $>$450 olivine-hosted melt inclusion analyses was generated, spanning 25 eruptions over 600 yr of eruptive history (for details of the eruptions sampled see Sides et al., 2014b). This dataset provides a rich resource for understanding the controls on lithium and boron partitioning (not published previously) and degassing in relatively H_2O-poor (relative to arcs) basalts on Earth. Kilauea lavas do not contain phenocrystic pyroxenes and therefore a synchronous study of lithium partitioning into pyroxene is not possible within this system. However, a collection of mafic pyroxenes (augite and enstatite) from Merapi (Indonesia), Karymsky (Russia) and South Soufriere Hills (Montserrat, Lesser Antilles), were analyzed for lithium and H_2O in pyroxenes and in their melt inclusions. These data allow assessment of apparent lithium partitioning between pyroxenes and melt at a range of pressures and melt compositions. Empirical models are developed to describe the degassing and partitioning behavior of lithium between melt, pyroxene and vapor, which are used to revisit the data from Martian Shergottite meteorites.

2. Methods

Olivine-hosted melt inclusions were analyzed for major (using electron microprobe), trace (using laser ablation ICP-MS) and volatile (using secondary ion mass spectrometry; SIMS) elements. The major, trace and volatile data were corrected for post-entrapment crystallization (PEC) using Petrolog (which in general resulted in $<$5% addition of olivine) (Danyushevsky and Plechov, 2011) and, excluding the light lithophile element data, have been published previously (Sides et al., 2014b). The PEC corrections assume that the LLE are similarly compatible to hydrogen in olivine (Kent and Rossman, 2002). The Li, H_2O and B concentrations of