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Melt mixing causes negative correlation of trace element enrichment and CO_2 content prior to an Icelandic eruption

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ABSTRACT

Major elements, trace elements and volatiles were measured in 110 olivine-hosted melt inclusions from the subglacial Skuggafjöll eruption in the Eastern Volcanic Zone of Iceland. Variations in melt inclusion trace element concentrations can be accounted for by incomplete mixing of diverse mantle parental melts accompanied by variable extents of fractional crystallisation. Binary mixing between an incompatible trace element-enriched and depleted melts provides a good fit to observed variations in trace element ratios such as Ce/Y. Surprisingly, the CO_2 contents of melt inclusions correlate negatively with their degree of trace element enrichment. Depleted, low-Ce/Y inclusions with $\sim$1200 ppm CO_2 have high CO_2/Nb contents ($\sim$400), suggesting that melts experienced little or no CO_2 exsolution before inclusion entrapment. Enriched, high-Ce/Y inclusions contain $\sim$300 ppm CO_2, have low CO_2/Nb (contents 50–100) and melts are likely to have exsolved much of their original CO_2 contents prior to inclusion entrapment. The negative correlation between CO_2 content and trace element enrichment may arise either from the more efficient exsolution of CO_2 from enriched melts, or from the intrusion of CO_2-supersaturated depleted melts into enriched melts that had already exsolved much of their original CO_2 contents. Some inclusions have lower CO_2 contents than predicted from binary mixing models, which suggests that at least some CO_2 exsolution occurred concurrently with mixing. Enriched inclusions record entrapment pressures of $\sim$0.5 kbar. These pressures probably correspond to the depth of mixing. Higher pressures recorded in depleted inclusions may have resulted from the development of CO_2 supersaturation during ascent from storage at $\geq$1.5 kbar. The presence of CO_2 supersaturation in melt inclusions has the potential to constrain timescales of melt inclusion entrapment.

1. Introduction

Dissolved volatile species play a crucial role in controlling the physical properties of silicate melts (e.g. Ochs and Lange, 1997; Giordano et al., 2008), determining the stability of crystal phases (e.g. Danyushevsky, 2001; Putirka, 2005) and driving eruptions (e.g. Blake, 1984; Woods, 1995; Roggensack et al., 1997). Furthermore, volatiles play an important role in mantle melting (e.g. Green, 1973; Eggler, 1976; Wyllie and Huang, 1976). Direct determination of the concentration and distribution of volatiles in primary melts and hence the mantle is difficult because volatiles often exsolve from melts prior to eruption. The solubility of CO_2 in basaltic melts is significantly less than that of H_2O, S, F or Cl, and depending on their initial CO_2 concentration, melts may become saturated with a CO_2-dominated vapour at depths of 25 km or more (Dixon, 1997; Shishkina et al., 2010; Ni and Keppler, 2013). Melt inclusions trapped in primitive crystals during early phases of magmatic evolution can provide estimates of initial volatile contents, but are prone to post-entrapment modification (e.g. Danyushevsky et al., 2000; Steele-Macinnis et al., 2011) and, in the case of H_2O, re-equilibration with their host melt (e.g. Qin et al., 1992; Hauri, 2002; Portnyagin et al., 2008; Gaetani et al., 2012).

Rare examples of glasses quenched from undersaturated melts have been reported in the literature: Saal et al. (2002) describe a positive correlation between CO_2 and Nb in matrix glasses and melt inclusions from the Siqueiros fracture zone on the East Pacific Rise that is indicative of vapour undersaturation, where both CO_2 and Nb behave incompatibly during fractionation. CO_2 fluxes have been calculated from Nb concentrations in a number of magmatic settings using CO_2/Nb values assumed to be representative of undegassed primary melts (e.g. Workman et al., 2006; Cartigny et al., 2008; Shaw et al., 2010). However, estimates of

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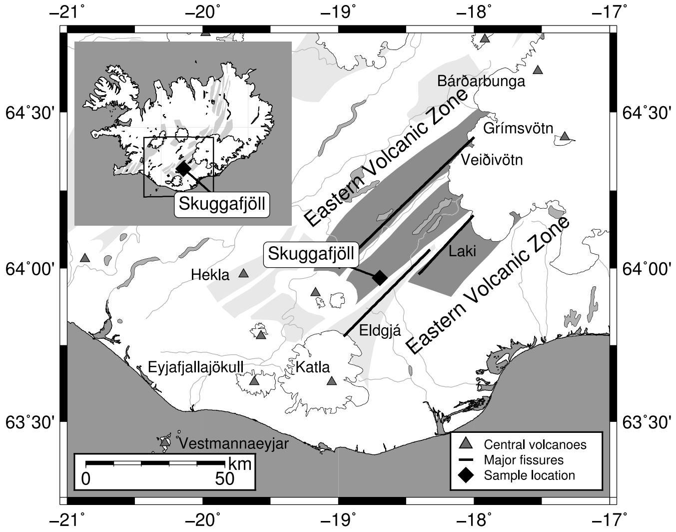

Fig. 1. Map showing the location of Skuggafjöll within the Eastern Volcanic Zone (EVZ) of Iceland. Central volcanoes and major fissure eruptions are labelled. Fissure swarms in the northeastern region of the EVZ associated with tholeiitic volcanism are shown as dark shaded regions (Thordarson and Larsen, 2007, and references therein). Fissure swarms associated with alkalic or transitional volcanism are shown as pale shaded regions.

primary CO_2/Nb vary depending on location and measurement method: the value of 239 ± 46 for Siqueiros determined from direct analysis of glass by Saal et al. (2002) lies at the lower end of the global range, whereas values of ∼570 and ∼730 for 14°N and 34°N on the Mid-Atlantic Ridge reconstructed from lava δ^{13}C contents by Cartigny et al. (2008) lie towards the upper end. The only estimate of undegassed CO_2/Nb from an Icelandic magma is 314 ± 125 from the Borgarhraun lava flow (Hauri et al., 2002).

Calculations using CO_2/Nb to determine initial CO_2 contents generally assume that magmas evolve along a single liquid line of descent from a primary melt with a specific Nb content. However, it is well known from melt inclusion studies of single eruptions in Iceland that primary melts are highly heterogeneous in terms of their trace element and isotope compositions (e.g. Gurenko and Chaussidon, 1995; Slater et al., 2001; Maclennan et al., 2003; Maclennan, 2008b). Whether primary melt heterogeneity results from the melting process or from mantle source variability, it is expected that undegassed, enriched melts with high Nb contents would also have high CO_2 contents (Cartigny et al., 2008). In this case, a positive correlation between CO_2, Nb and the degree of melt enrichment recorded by trace element ratios such Ce/Y would be predicted. In order to use CO_2/Nb to quantify magmatic carbon budgets, a good understanding of what controls CO_2/Nb during magmatic evolution and melt mixing is required. Iceland is an ideal location to investigate the behaviour of CO_2 in primitive melts, because magma may be stored at depths where vapour saturation is unlikely (e.g. Winpenny and Maclennan, 2011).

We present major element, trace element and volatile data from 110 olivine-hosted melt inclusions from the primitive Skuggafjöll eruption in the Eastern Volcanic Zone (EVZ) of Iceland (Fig. 1). By considering trace element data alongside volatile data, we demonstrate that the CO_2 content of melt inclusions is controlled by mixing between geochemically distinct parental melts that have experienced different extents of CO_2 exsolution prior to melt inclusion entrapment. Our results also highlight the risks of interpreting melt inclusion volatile data without the corresponding trace element data. In the absence of trace element data, the volatile systematics we have observed might have been interpreted erroneously using models involving open-system degassing, conduit convection or gas flushing processes.

2. Sample collection and analytical methods

Skuggafjöll is an ∼820 m high mountain in the EVZ between the Vatnajökull and Mýrdalsjökull glaciers (Fig. 1; 63.968°N, 18.695°W). The mountain forms part of a northeast–southwest-striking hyaloclastite ridge (or tindar), and is likely to have formed during the last glacial period (Jakobsson and Gudmundsson, 2008). The lower flanks of the mountain are composed of vesicular, highly phyric, glassy pillow basalts, whereas the upper portions are composed of hyaloclastite, containing up to fist-sized lithics of pillow basalt and individual macrocrysts in a palagonite matrix.

Olivine macrocrysts in the size range 0.25 mm to 3 mm were picked from crushed pillow glasses collected from three localities at the base of the mountain. Care was taken to select pale green, unaltered olivine macrocrysts that contained glassy melt inclusions without post-entrapment daughter crystals. Macrocrysts were individually mounted in CrystalBond™ and polished to expose melt inclusions before being re-mounted in Buehler EpoThin™ resin and re-polished for analysis.

Melt inclusions were analysed for trace elements, H_2O, F and CO_2 by secondary ion mass spectrometry (SIMS). Major elements and S were determined by electron probe microanalysis (EPMA). SIMS analyses were performed using a Cameca ims-4f instrument at the NERC Ion Microprobe Facility at the University of Edinburgh, UK. CO_2 analyses were performed first, with a high mass resolution configuration, in order to enable good separation of ^{12}C and $^{24}Mg^{2+}$ peaks. H_2O, F and trace elements were then measured with a lower mass resolution configuration. CO_2, H_2O, F and trace elements of low abundance, such as Yb and Lu, were measured with a 1σ precision of ±10%. Trace elements of high abundance, such as Zr and Sr, were measured with a 1σ precision of ±5%. Errors in CO_2 and H_2O were determined using repeat analyses of a suite of basaltic glass standards with compositions given by Shishkina et al. (2010). Errors in F and trace elements were determined using repeat analyses of international standards, ML3B-G, BCR-2G and GOR132-G. EPMA analyses were performed using a Cameca SX100 instrument at the Department of Earth Sciences at the University of Cambridge, UK. Full details of analytical procedures, as well as SIMS and EPMA data, are provided in the supplementary material.

Raman spectroscopy (e.g. Frezzotti et al., 2012) and heating/cooling stage experiments (e.g. Hansteen and Klugel, 2008) were undertaken prior to SIMS analyses in order to determine the CO_2 content of inclusion-hosted bubbles. If CO_2 is present in inclusion-hosted bubbles, it must be accounted for when calculating the total CO_2 content of melt inclusions (e.g. Hartley et al., 2014). More than 200 olivine grains containing bubble-bearing inclusions were mounted in CrystalBond™ for analysis by Raman spectroscopy using a Horiba LabRam™ instrument at the University of Cambridge, UK. The detection limit of CO_2 in inclusion-hosted bubbles is better than 0.04 g/cm^3 based analysis of CO_2-bearing samples on the same instrument (Hartley et al., 2014). Ten olivine grains containing bubble-bearing inclusions were individually polished and investigated using a Linkham THMS650 heating/cooling stage interfaced with a Zeiss Axioscope™ microscope. Olivine grains were cooled to −90 °C before being heated slowly to 35 °C, in order to observe of phase change temperatures within bubbles (Hansteen and Klugel, 2008). The detection limit of CO_2 is similar to that estimated for Raman spectroscopy by Hartley et al. (2014) (e.g. Rosso and Bodnar, 1995).