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Chlorine variations in the magma of Soufrière Hills Volcano, Montserrat: Insights from Cl in hornblende and melt inclusions

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Abstract

The Soufrière Hills Volcano in Montserrat erupts a Cl-rich, porphyritic andesite. HCl degassing accompanies eruption and is dependent on the growth rate of the lava dome. The magma contains hornblende phenocrysts that show repetitive zoning in most elements, including Cl. On the basis of the zoning data, (Cl/OH) ratios in the melt, calculated from partitioning data, increase rimward through each zone, indicating that the phenocrysts formed under conditions of varying $(Cl/OH)_m$. An empirical relationship between A-site occupancy in the hornblende and temperature implies that crystallisation of each zone is also accompanied by increasing temperature. Each zone ends at a resorption horizon, and crystallisation recommences at lower temperature and $(Cl/OH)_m$. Melt inclusion H_2O and Cl contents for the 8th January 2007 explosive eruption can be explained by closed-system degassing with $D_{Cl}^{fl\text{-}m}$ between 5 and 30, or by open-system degassing accompanied by a small amount of crystallisation. However, neither simple closed-system degassing nor convective circulation of magma can explain the positive correlation of $(Cl/OH)_m$ with temperature. We suggest that the zoning can be caused by accumulation of CO_2-rich vapour in the andesite, probably as a result of mafic magma injection into the chamber. Decreasing H_2O fugacity and/or increasing Cl_m result in increasing $(Cl/OH)_m$ while heat transferred with the volatiles causes the rise in temperature. Intermittently, the accumulated fluid is lost to the surface, possibly as a result of renewed eruptive activity. This model requires the CO_2-rich fluid to be decoupled from the magma, consistent with previous observations of continuous CO_2 emissions at the surface.

1. INTRODUCTION

The behaviour of magmatic volatiles is one of the primary influences on the eruptive activity of arc volcanoes. Closed-system degassing leads to the build-up of gas pressure beneath the vent and can result in explosive behaviour. In contrast, open-system degassing can cause almost complete degassing of the magma and results in the build-up of a highly viscous lava dome during effusive eruptions. Despite its much lower abundance than some volatile species (e.g. H_2O, CO_2; Wallace, 2005), Cl is an important volatile and a good source of information about the degassing regime. It is incompatible in the melt and is partitioned strongly into an exsolved vapour phase (e.g. Kilinc and Burnham, 1972; Webster and Holloway, 1988; Webster, 1992); thus it can help to constrain the nature and extent of magmatic degassing. Cl is a particularly significant volatile component in arc systems; Cl contents of evolved arc magmas are high (typically 1500–3000 ppm, Wallace, 2005). The Soufrière Hills Volcano, Montserrat has particularly high Cl concentrations in both the magma and emitted gas phase (e.g. Hammouya et al., 1998; Oppenheimer et al., 1998; Edmonds et al., 2001, 2002; Harford et al., 2003). Higher Cl concentrations have been reported only for Augustine Volcano (Symonds et al., 1990). Combined

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use of melt inclusion and gas emissions data has previously allowed interpretation of Cl degassing processes. For Soufrière Hills Volcano, experimental and petrological studies have previously determined that surface HCl emissions are the result of syn-eruptive degassing of Cl from the andesite (Edmonds et al., 2001; Signorelli and Carroll, 2001; Edmonds et al., 2002; Villemant et al., 2008) as it undergoes decompression crystallisation (e.g. Sparks et al., 2000; Harford et al., 2003; Couch et al., 2003). In contrast, SO_2 is thought to originate in the mafic magma; SO_2 emissions are therefore related to permeability of the magma system and changes in SO_2 supply from the mafic magma at depth (e.g. Young et al., 1998; Edmonds et al., 2001; Oppenheimer et al., 2002). The main source of CO_2 emissions is also thought to be the deep mafic magma (Edmonds et al., in review).

Cl can also be taken into some phenocryst phases (e.g. hornblende, biotite) along with other volatiles (e.g. F, Li, Rowe et al., 2008). Hornblende is a useful mineral for tracking magma conditions, because its composition responds to external parameters including oxygen fugacity (Scaillet and Evans, 1999), temperature and pressure (e.g. Holland and Blundy, 1994; Rutherford and Devine, 2003; Johnson and Rutherford, 1989). Soufrière Hills Volcano typically erupts a porphyritic andesite with hornblende phenocrysts that show wide cyclic or repetitive zoning. Similar, but finer-scale zoning has been observed in the Unzen dacite and was interpreted as the result of volatile transfer from mafic material ponding near the base of the chamber, and consequent degassing and crystallisation of the andesite (Sato et al., 2005). Rutherford and Devine (2003) studied zoning in hornblende phenocrysts erupted at Soufrière Hills Volcano during 1995–2002, and concluded that it represented major-element change associated with magma mixing; however no Cl data were available. Magma mixing is an important process at Soufrière Hills Volcano (e.g. Murphy et al., 2000; Couch et al., 2001; Devine et al., 2003), and recent work has shown that phenocrystic amphiboles and those from mafic inclusions can be distinguished on the basis of minor-element compositional differences (Humphreys et al., 2009).

Here, we report new measurements of H_2O and Cl in matrix glass and plagioclase-hosted melt inclusions from a small explosive event at Soufrière Hills Volcano in January 2007, as well as major- and minor-element data from zoned hornblendes erupted between 2001 and 2007. These data are combined with the H_2O/Cl ratio of gases emitted at the surface, as well as Cl concentrations from the zoned hornblendes. We present a quantitative degassing model for the recently erupted magma, and interpret the hornblende zoning as a result of transfer of hot, CO_2-rich vapour from mafic material into the andesite.

2. SAMPLES AND METHODS

This study focuses on material from the second and third phases of dome growth at Soufrière Hills Volcano, erupted between July 2001 and January 2007. 14 samples were studied, including 13 samples of hornblende–plagioclase andesite and one macroscopic mafic inclusion (see Table 1 of Humphreys et al., 2009 for samples and modal compositions). The samples include dome rocks and pumiceous pyroclastic flow material.

2.1. Electron probe microanalysis (EPMA)

Mineral compositions were analysed using a Cameca SX-100 5-spectrometer electron microprobe at the University of Cambridge. Major elements were analysed with a 15 kV, 10 nA beam; a 15 kV, 100 nA beam was used for minor elements. The beam was focused to a 2 μm spot. Glasses were analysed using a 15 μm, 15 kV beam with 2–4 nA beam current for major elements and 10 nA beam for minor elements. Na and Si were analysed first with short counting times in order to reduce migration of alkalis (following Devine et al., 1995; Blundy and Cashman, 2005; Humphreys et al., 2006). Typical peak counting times were 20 s for major elements and 30 s for minor elements.

2.2. Secondary ion mass spectrometry (SIMS)

Plagioclase crystals containing melt inclusions were mounted in resin and prepared using diamond polishing techniques to reveal the inclusions. Following major-element analysis, the grain mounts were coated in gold for SIMS analysis. Matrix glasses and melt inclusions in plagioclase were analysed for $^{1}H^{+}$, $^{7}Li^{+}$, $^{23}Na^{+}$, $^{35}Cl^{+}$ and $^{42}Ca^{+}$ using a Cameca ims-4f ion microprobe at the University of Edinburgh, controlled by Charles Evans and Associates PXT interface and software. A 5 nA primary beam of O^{-} ions was accelerated onto the sample surface with a net impact energy of 14.5 keV. The surface was cleaned using a 2 min pre-sputter with the beam rastered over a 10 μm square area. The beam size was approximately 14 × 17 μm. Counts were collected over 10 cycles. Mass 0.7 was used to monitor the background count rate of the electron multiplier detector. The mass spectrometer was calibrated for the secondary ions prior to each analysis. ^{30}Si was used as the internal standard, and the NIST standard SRM610 was used as the primary calibration standard. For smaller inclusions, an aperture was introduced that effectively reduced the beam current to ~1.5 nA, and the beam size to approximately 10 × 13 μm. This gave slightly higher analytical uncertainties, of $\leqslant$4% relative for Cl and $\leqslant$1% relative for Li (compared with $\leqslant$2% and $\leqslant$0.6% relative respectively for the larger beam). H_2O contents were calculated from a daily working curve of H/Si vs. H_2O (Blundy and Cashman, 2005), which gives a straight line with R^2 0.98 or better for a set of well-characterised standard glasses, following the procedure described in Humphreys et al. (2006) and Blundy and Cashman (2005). This method gave typical errors in determining H_2O of 5–15% relative. For Cl and F, two standards were used with 1550 ppm Cl and 2230 ppm F, and 530 ppm Cl, 770 ppm F, respectively.

Major-element analyses that had analytical totals outside the range 98–102% (when including H_2O measured by SIMS) were discarded, as were those with poor correlation between H_2O from SIMS and volatiles by difference