Halogen degassing during ascent and eruption of water-poor basaltic magma

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ABSTRACT

A study of volcanic gas composition and matrix glass volatile concentrations has allowed a model for halogen degassing to be formulated for Kīlauea Volcano, Hawai i. Volcanic gases emitted during 2004–2005 were characterised by a molar SO_2/HCl of 10–64, with a mean of 33; and a molar HF/HCl of 0–5, with a mean of 1.0 (from approximately 2500 measurements). The HF/HCl ratio was more variable than the SO_2/HCl ratio, and the two correlate weakly. Variations in ratio took place over rapid timescales (seconds). Matrix glasses of Pele's tears erupted in 2006 have a mean S, Cl and F content of 67, 85 and 173 ppm respectively, but are associated with a large range in S/F. A model is developed that describes the open system degassing of halogens from parental magmas, using the glass data from this study, previously published results and parameterisation of sulphur degassing from previous work. The results illustrate that halogen degassing takes place at pressures of <1 MPa, equivalent to <~35 m in the conduit. Fluid–melt partition coefficients for Cl and F are low (<1.5); F only degasses appreciably at <0.1 MPa above atmospheric pressure, virtually at the top of the magma column. This model reproduces the volcanic gas data and other observations of volcanic activity well and is consistent with other studies of halogen degassing from basaltic magmas. The model suggests that variation in volcanic gas halogen ratios is caused by exsolution and gas–melt separation at low pressures in the conduit. There is no evidence that either diffusive fractionation or near-vent chemical reactions involving halogens is important in the system, although these processes cannot be ruled out. The fluxes of HCl and HF from Kīlauea during 2004–5 were ~25 and 12 t/d respectively.

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1. Introduction

At Kīlauea and most other volcanoes, halogens are much less abundant than the three primary volatile species H_2O, CO_2 and S in magmatic vapour and contribute little to magma buoyancy and eruptive processes. Halogens do, however, play an important role in magmatic systems. Chlorine abundance in magma is controlled by fractional crystallisation, H_2O degassing, melt-vapour partitioning and vapour separation and loss, making it a useful tracer for magmatic processes (*e.g.* Sun et al., 2007) and volcanic degassing (*e.g.* Villemant et al., 2008). When Cl degasses into the atmosphere as a relatively minor constituent of volcanic gases, it has disproportionate atmospheric effects: Cl radicals act to destroy ozone (*e.g.* Rose et al., 2006). Hydrogen fluoride is much less reactive, but is a strong acid when dissociated in water: it has been linked to fluorosis (Cronin and Sharp, 2002) and will etch the surface of silicate ash particles (Delmelle et al., 2007). At Kīlauea Volcano, F becomes highly enriched in residual melts, and becomes the most significant volatile in slowly-cooled shallow magma bodies and lava lakes (Helz, 1980).

Halogens typically occur in volcanic gases as hydrogen chloride (HCl) and hydrogen fluoride (HF), with trace amounts of the species hydrogen bromide (HBr) and hydrogen iodide (HI; Aiuppa et al., 2005). In the mantle, halogens are accommodated in the mineral structures of phlogopite, pargasite and apatite, where they occupy hydroxyl ion sites (*e.g.* Aoki et al., 1981). Like other volatiles, their distribution in the mantle is heterogeneous and related to tectonic setting. Chlorine, in particular, is enriched in subduction settings owing to contributions from subducted sediments and hydrous minerals in altered basalts (*e.g.* Kent et al., 2002). Major enrichments in halogen concentrations have been documented for ocean island settings such as the Azores and Iceland, relative to Mid-Atlantic Ridge basalts (Schilling et al., 1980; Thordarson and Self, 2003) but the degree of enrichment varies widely between ocean islands (Stroncik and Haase, 2004).

Chlorine and fluorine rarely reach saturation in magmas; instead, they either behave as non-volatile, relatively incompatible elements (F and Cl are incorporated into apatite and amphiboles respectively at low pressures; *e.g.* Brenan, 1993) in water-poor melts, or they partition into a vapour phase (*e.g.* Webster, 2004). Very little is known about the partitioning behaviour of Cl between melt and vapour in basaltic melts; even less is known about the degassing behavior of F. Fluorine tends to behave as an incompatible, nonvolatile

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element for a large part of magma evolution, and increases in concentration in the melt with decreasing extents of melting (Dixon et al., 1997) and/or increasing degrees of fractionation (*e.g.* Byers et al., 1984). A suite of Ko olau (Oahu) melt inclusions analysed by Hauri (2002) show a trend of decreasing F with H_2O, suggesting that F is degassed at low pressure. Degassing of halogens has been modeled empirically at Mount Etna, based on field measurements (Aiuppa et al., 2002, 2004), which has confirmed that Cl and F partition into a vapour phase to a greater extent at low pressures.

Halogens have only rarely been quantified in volcanic gases emitted from Kīlauea because they are relatively minor components of the gas phase and are thus difficult to measure. There are a few studies that quantify HF in condensates (Murata et al., 1963) and volcanic gases near to the beginning of the current eruption (Gerlach and Graeber, 1985; Greenland, 1988). A filter pack study in 1985 observed large variability in gaseous F/Cl, which was ascribed qualitatively to changes in magma supply and residence time beneath Pu u Ō ō (Miller et al., 1990). Open path Fourier transform infra red (OP FTIR) measurements of halogens in volcanic gases were carried out during 2004–2005 and the concentrations of Cl, F and S were measured in glasses in Pele's tears erupted from Pu u Ō ō in 2006; these data are used to formulate a quantitative model to describe halogen degassing at Kīlauea Volcano.

2. Geological setting

Kīlauea Volcano is the youngest and most active subaerial volcano of the Hawaiian Volcanic Chain. Kīlauea makes up the south-eastern portion of the island of Hawai i, abutting the southern flank of Mauna Loa. Kīlauea has been active semi-continuously throughout historical times; the current eruption began in January 1983 on the East Rift Zone. Between 1983 and 1986 the eruption was characterised by regular intervals of lava fountaining activity, interspersed with repose periods averaging 24 days in length (Heliker and Mattox, 2003). Effusion rates reached 390 m^3/s and fountains reached heights of >450 m (Heliker and Mattox, 2003). From 1986, the eruption entered a phase of continuous, effusive activity, characterised by eruption rates of around 0.13 km^3/year (Heliker and Mattox, 2003). During 2004–2005, the eruption was characterised by effusion of lava from vents on the south flank of Pu u Ō ō, whilst much of the degassing took place from vents inside the crater (Fig. 1). Lava spattering, low fountaining and gas pistoning activity took place from time to time at the crater and south flank vents during this period (Edmonds and Gerlach, 2007) and Pele's tears and hair were typical eruptive products.

Basaltic magma is generated at depths of several tens of kilometres beneath the summit of Kīlauea; degassing is dominated by CO_2 during magma ascent and prior to residence in a magma chamber (Dixon et al., 1991). Gerlach and Graeber (1985) proposed that magma degasses in two distinct stages, based on suites of gas samples collected and analysed in 1983 from the East Rift Zone, and from a lava lake at the summit in the early-20th century by T. A. Jaggar. The first stage of degassing occurs in the magma storage area beneath the summit, giving rise to a CO_2-rich plume that escapes through the caldera floor; the second stage of degassing occurs as the magma migrates along the East Rift and nears the surface at Pu u Ō ō, where the more soluble gases H_2O and SO_2 exsolve. This model explains observations of a high CO_2 emission rate and high molar C/S at the summit of Kīlauea (type 1 gas) and a high SO_2 emission rate and a lower molar C/S at Pu u Ō ō (type 2 gas; Gerlach and Graeber, 1985). Degassing is thought to proceed in equilibrium during lava effusion, with continuous bubble nucleation and growth and minor bubble coalescence, based on vesicle size distributions (VSDs; Mangan et al., 1993; Cashman et al., 1994). Corresponding VSD studies of Pele's tears (erupted during lava spattering or weak strombolian activity) have not been published. Recently, distinct degassing regimes have been recognised, based on gas compositions measured by spectroscopic methods during differ-
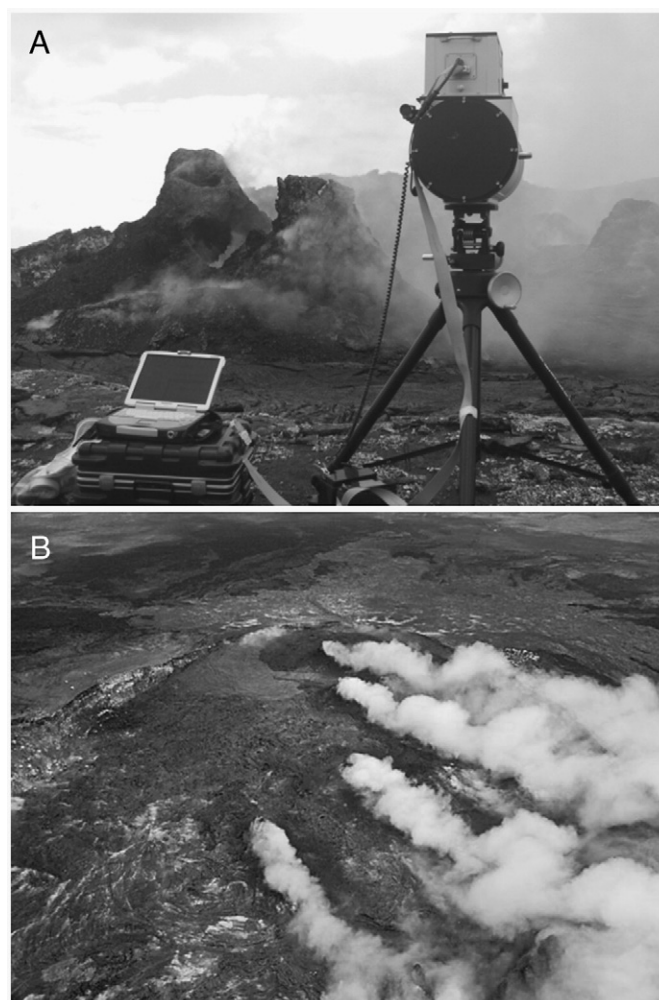
Fig. 1. Photographs to show (top) the FTIR spectrometer and telescope, mounted on a tripod, receiving IR from an incandescent vent, with cooler volcanic gases passing in front of the source and absorbing radiation. The spectrometer is connected to a portable acquisition computer system; (bottom) the crater of Pu u Ō ō, showing the degassing vents measured in this study.

ent kinds of eruptive activity at Pu u Ō ō: persistent degassing (equilibrium degassing and limited melt-gas separation), lava spattering (bubble rise from a few tens of metres depth) and gas pistoning (gas slug ascent from >100–500 m depth; Edmonds and Gerlach, 2007). The former is the most common mode of degassing and was prevalent during the measurements presented here.

3. Methods

3.1. Volcanic gas measurements

Open path Fourier transform infra red (OP FTIR) spectroscopy is a technique used to measure the composition of gases in open air. The method has been applied successfully to basaltic volcanic gases previously (Mori et al., 1993; Francis et al., 1995). OP FTIR relies on a spectrometer receiving infra red radiation (IR) from a source through a cloud of cooler gas. Under these conditions, IR is absorbed by the gases and concentration-pathlengths can be quantified precisely for various gas species simultaneously. In practice, a variety of IR sources can be utilized; for this study, incandescent vents were used (Fig. 1). In general, the signal-to-noise ratio (and hence the accuracy and precision of the measurements) is inversely proportional to the pathlength and directly proportional to the strength of the IR source and the concentration of gas in the pathlength. Pu u Ō ō provides high