

New geochemical insights into volcanic degassing

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Magma degassing plays a fundamental role in controlling the style of volcanic eruptions. Whether a volcanic eruption is explosive, or effusive, is of crucial importance to approximately 500 million people living in the shadow of hazardous volcanoes worldwide. Studies of how gases exsolve and separate from magma prior to and during eruptions have been given new impetus by the emergence of more accurate and automated methods to measure volatile species both as volcanic gases and dissolved in the glasses of erupted products. The composition of volcanic gases is dependent on a number of factors, the most important being magma composition and the depth of gas–melt segregation prior to eruption; this latter parameter has proved difficult to constrain in the past, yet is arguably the most critical for controlling eruptive style. Spectroscopic techniques operating in the infrared have proved to be of great value in measuring the composition of gases at high temporal resolution. Such methods, when used in tandem with microanalytical geochemical investigations of erupted products, are leading to better constraints on the depth at which gases are generated and separated from magma. A number of recent studies have focused on transitions between explosive and effusive activity and have led to a better understanding of gas–melt segregation at basaltic volcanoes. Other studies have focused on degassing during intermediate and silicic eruptions. Important new results include the recognition of fluxing by deep-derived gases, which buffer the amount of dissolved volatiles in the melt at shallow depths, and the observation of gas flow up permeable conduit wall shear zones, which may be the primary mechanism for gas loss at the cusp of the most explosive and unpredictable volcanic eruptions. In this paper, I review current and future directions in the field of geochemical studies of volcanic degassing processes and illustrate how the new insights are beginning to change the way in which we understand and classify volcanic eruptions.

Keywords: magma degassing; geochemistry; volcanic gases

1. Introduction

Volatiles make up only a few weight per cent of magma, yet have an important role in controlling eruption style and duration (Woods & Huppert 2003). Transitions from effusive to explosive styles of volcanic eruption are caused by changes in magma ascent rate (e.g. Woods & Koyaguchi 1994; Sparks 2003),

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which have implications for gas loss through the development of magma permeability (Eichelberger *et al.* 1986; Burton *et al.* 2007a) and through the conduit walls (Jaupart & Allegre 1991). Explosive activity can take place with little warning, putting people at risk from the hazards of pyroclastic flows and surges. The geochemical study of volcanic magma degassing aims to describe and quantify volatile exsolution, magma fragmentation and gas–melt segregation processes, as these are key to understanding the triggering, development and style of volcanic eruptions.

Geochemical quantification of magmatic volatiles and degassing is usually approached from two angles: the first aims at quantification of volatile concentration in magma prior to significant degassing; this is usually accomplished by analysing melt inclusions inside phenocrysts (e.g. Anderson & Brown 1993) or quenched submarine lavas (e.g. Dixon *et al.* 1991); or by phase equilibrium experiments at high pressures and temperatures (e.g. Pichavant *et al.* 2002), designed to recreate the mineral assemblage of a volcanic rock. This approach is rarely able to capture pre-degassing volatile concentrations, as highly insoluble species such as CO₂ exsolve largely before the onset of significant crystallization in deep crustal magma chambers. It is therefore believed that magmas in crustal storage regions commonly exist in equilibrium with a significant exsolved gas phase, which melt inclusions will not record.

The second, complementary approach targets volcanic gases: the exsolved, integrated products of magma degassing. Volcanic gas studies can provide information on the composition of gases, which is sensitive to gas–melt segregation depth (e.g. Burton *et al.* 2007b) and on the flux of gases, which is sensitive to pressure and magma volume. In order to make sense of gas flux data, it is necessary to quantify the recharge, crystallization and eruption history of magma, which is only possible by detailed petrographic study. The ideal approach entails all of these complementary methods, which allows a detailed picture of the bulk volatile content of a magma system to be generated.

Volcanic gas measurements are not straightforward. Of the multitude of problems to contend with in the interpretation of volcanic gas compositions and fluxes, scrubbing of acidic gases by groundwater or a hydrothermal system is potentially the most serious (Symonds *et al.* 2001). Direct sampling of volcanic gases requires close access to vents and fumaroles, which can be hazardous. The measurement of gases emitted during explosive activity, critical for an understanding of transitions between eruption styles, requires a remote approach, which is offered by Fourier transform infrared spectroscopy (OP FTIR; Oppenheimer 2003). The advantage of this method, which has only been fully exploited in recent years, is that the composition of gases emitted during explosive activity can be measured remotely at a high temporal resolution.

The degassing regime may be evaluated using gas ratios, typically made up of one species that is highly insoluble and one that is more soluble in magma, such as CO₂/H₂O, SO₂/HCl and CO₂/SO₂. The gas ratios evolve during magma decompression according to their solubilities; the gas ratio will be preserved at the point of gas–melt segregation, if the gas phase is not modified further during ascent to the surface. In basaltic systems, gas–melt segregation usually corresponds to the onset of gas slug ascent, or the development and isolation of a foam layer at the roof of a magma storage area or sill (Jaupart & Vergnolle 1989; Menand & Philips 2007). In silicic systems, gas–melt segregation may occur when magma

permeability is established through bubble networks (Eichelberger *et al.* 1986), when permeable shear zones develop at the conduit walls (Gonnerman & Manga 2003; Rust *et al.* 2004), or at near-solidus magma temperatures, gas flows through a system of fractures. When the results of such studies are combined with petro-geochemical investigations of erupted products, a powerful tool emerges that can be used to describe the physics and chemistry of magma degassing during volcanic eruptions. In this paper, I will review the state of the art in gas geochemical studies of active volcanic degassing processes and how these new, direct observations are changing the way volcanic eruptions are classified.

2. Geochemical measurements of volcanic degassing

There are three aspects of technique development that, taken together, have allowed rapid improvements of our understanding of volcanic degassing processes: volcanic gas measurements; microanalysis of quenched melts; and multi-species volatile solution models. Volcanic gas measurements have benefited from developments in spectroscopy and field portable, low cost electrochemical sensors. OP FTIR relies on quantifying the unique absorption signature of gases in the infrared region of the electromagnetic spectrum. The unique absorptivity of a particular gas is used to evaluate the measured absorbance in terms of concentration and pathlength. OP FTIR requires an infrared source, which can be the Sun, a lamp or an incandescent lava flow or vent. Spectra collected over short pathlengths (up to of the order of a few hundred metres), using a lamp or active source allows the quantification of H₂O and CO₂ gases, under certain conditions. Errors are mainly due to a high background concentration (in the case of H₂O and CO₂), spectral interference between species and changes in temperature of the volcanic gases. Details of the retrieval technique are given elsewhere (Allard *et al.* 2005; Oppenheimer *et al.* 2006) and the methodology is reviewed by Oppenheimer & McGonigle (2004) and summarized in figure 1.

High temporal resolution measurements of the primary volcanic gas species are also possible using closed path and electrochemical sensor techniques. A portable, multi-sensor instrument pack has recently been developed, called the Multi-component gas analyser system (Multi-Gas), to measure CO₂ and H₂O (using a LI-840 non-dispersive IR (NDIR) spectrometer), and SO₂ (by electrochemical sensor) concentrations (using a humidity sensor; Shinohara 2005; Aiuppa *et al.* 2007; Shinohara *et al.* 2008), with an associated error of 10–30% on the measurements. Alkaline filter pack techniques can measure HCl, HF and SO₂ in the plume, and other electrochemical sensors can be deployed for H₂S and H₂.

Total fluxes of volcanic gases may also be measured using spectroscopic techniques. Sulphur dioxide (SO₂) flux can be measured at a high temporal resolution using differential optical absorption spectroscopy with small, portable UV spectrometers (reviewed by Oppenheimer & McGonigle 2004). The gas ratios provided by OP FTIR can be combined with flux data in order to generate fluxes of the other volcanic gas species in a well-mixed plume. CO₂ fluxes are commonly quantified using NDIR spectrometers, which are usually dual wavelength, closed-path analysers. The NDIR spectrometers can be used to measure fluxes of CO₂ from the soil and in the plume by flying traverses through it (Gerlach *et al.* 1998).

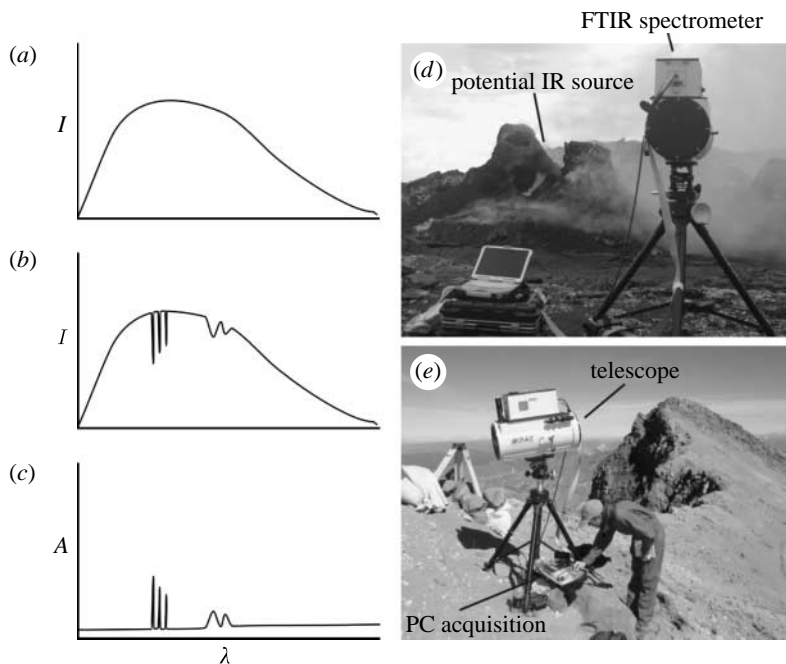


Figure 1. (a–c) Absorbance spectra are generated using measured spectra (intensity, I , plotted against wavelength, λ) normalized by a background spectrum, which does not contain absorption features due to volcanic gases. The absorbance (A) is used to calculate concentration pathlength for multiple gas species using their unique absorptivity. (d) FTIR at Pu'u 'O'o, Kilauea Volcano Hawai'i, using incandescent vents as an IR source; (e) FTIR at Mount St. Helens, USA, using the lava dome (out of sight) as an IR source.

Microanalysis techniques to measure volatiles in quenched melts have improved immensely in recent years, largely due to the development of methodologies to quantify the major volatile species H_2O and CO_2 (Hauri *et al.* 2002; Wallace 2005). Closed-path FTIR permits direct, non-destructive measurement of the major volatile elements (including H- and C-bearing species) in silicate glasses, with a fine-scale spatial resolution (10–20 μm) and single ppm detection limits (e.g. Stolper 1982). Until recently, ion probes were not suitable for the analysis of H_2O and CO_2 (mainly due to high detection limits; Ihinger *et al.* 1994). Recent improvements in secondary ion mass spectrometry, however, has permitted rapid and accurate analysis of the volatile elements H, C, F, S and Cl at the 5–10 μm scale (e.g. Hauri *et al.* 2002) in singly polished samples; this has greatly increased the published database for these volatiles in volcanic glasses and melt inclusions. The analysis of melt inclusions themselves has associated difficulties and uncertainties (most important of which is post-entrapment modification, by crystallization and/or leakage), which are reviewed by Lowenstern (1995) and Baker (2008).

The third major development, which has direct implications for the ways in which volatile data are interpreted, is the emergence of sophisticated and accessible multi-species solution models, based on thermodynamical modelling and experimental data (Papale 1999; Newman & Lowenstern 2002; Moretti & Papale 2004), which allow the prediction of gas composition with pressure, temperature,

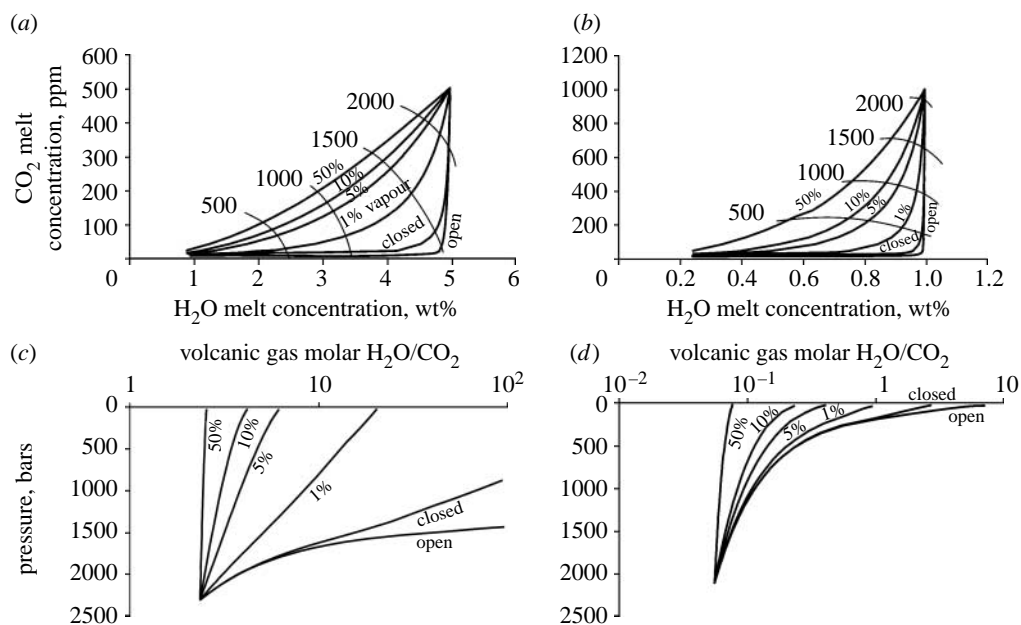


Figure 2. Plots to show the evolution of (a, b) melt and (c, d) volcanic gas compositions with degassing of (a, c) rhyolite (850°C, 5 wt% H₂O, 500 ppm CO₂) and (b, d) basalt (1150°C, 1 wt% H₂O, 1000 ppm CO₂). Isobars are marked, labelled with pressure in bars. Curves are labelled with proportion of exsolved gas in equilibrium with the melt, from open (gas phase removed incrementally during every degassing step), closed (starting with 0% gas with no removal of vapour) and 1–50 wt% excess vapour. Curves calculated using VOLATILECALC (Newman & Lowenstern 2002).

fugacities of oxygen and other components, and with varying gas–melt ratios. The gas–melt ratio is generally a consequence of closed, open or ‘excess vapour’ regimes of degassing. Closed-system degassing describes the vesiculation of magma where gas bubbles remain in physical contact and equilibrium with their host melt; open-system degassing involves differential gas movement through magma (bubble rise or vapour loss through permeable magma). The excess vapour regime of degassing involves a free vapour phase fluxing through the magma, derived from deeper in the system; this vapour buffers the volatile concentration in the magma. Figure 2 illustrates the importance of measuring both melts and gas compositions in order to characterize fully the degassing regime. For rhyolites with coexisting vapour, the maximum range in melt CO₂ concentrations are approximately 1–300%, while the corresponding range in volcanic gas composition is approximately 1–1000%, showing that gas composition is more sensitive to gas–melt ratio than melt composition (figure 2a, c). For water-poor basalts, the degassing regime is constrained by only very small changes in measured melt H₂O content at pressures above 500 bars; volcanic gas composition, however, ranges over two orders of magnitude (figure 2b, d). Conversely, if the degassing regime can be constrained with the melt volatile content, it may be possible to evaluate the melt–gas segregation pressure using the volcanic gas composition. Empirical solution models for sulphur and chlorine are well constrained for a number of systems (Dixon *et al.* 1991), which enable similar degassing trends to be identified for the interpretation of CO₂/SO₂ and S/Cl in volcanic gases (e.g. Aiuppa *et al.* 2007).

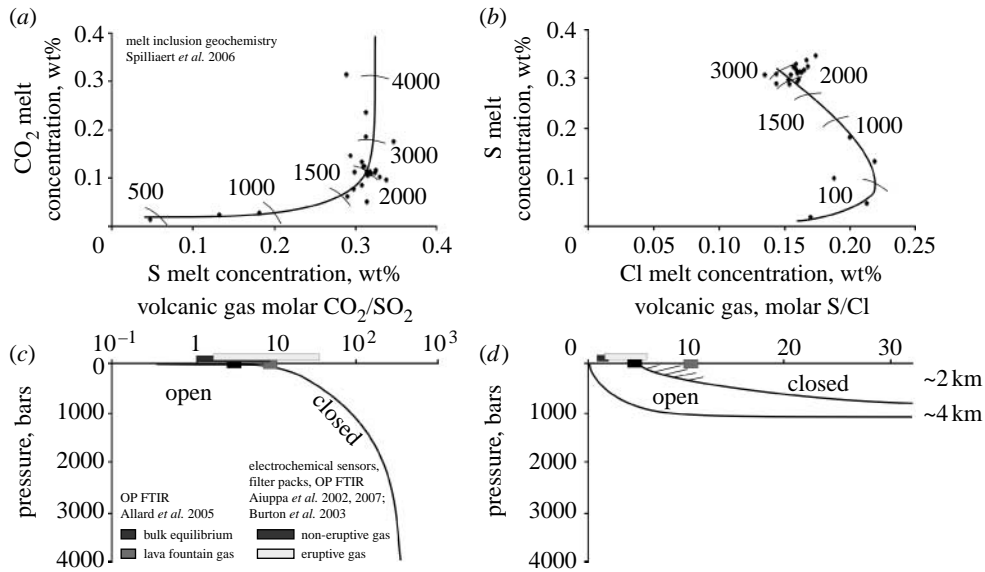


Figure 3. (a, b) Melt inclusion and (c, d) volcanic gas data from Mount Etna, Italy, from Aiuppa *et al.* (2002, 2007), Allard *et al.* (2005) and table 1, Spilliaert *et al.* 2006. Melt inclusion plots show CO₂ against S concentrations (a) and S against Cl concentrations (b). Isobars are calculated from H₂O and CO₂ equilibria (from Spilliaert *et al.* 2006); solid lines are fitted polynomials. (c, d) The volcanic gas trends are calculated directly from the melt inclusion data, and are from Spilliaert *et al.* (2006) and Aiuppa *et al.* (2007). Ranges in volcanic gas compositions are shown for a variety of methods and for eruptive (light grey box) and non-eruptive (black box) activity (effusive and explosive activity) and for gas emitted during lava fountaining. The cross-hatched area on the S/Cl gas plot (d) is a range in expected gas S/Cl, arising from the variable Cl degassing recorded in glasses (Spilliaert *et al.* 2006).

3. Volatile degassing during basaltic volcanic eruptions

Basaltic volcanoes are ideal targets for integrated volatile degassing studies for two reasons: (i) basaltic magmas are relatively unmodified from parental melts (by fractional crystallization, assimilation and mixing) and are more likely to preserve original volatile concentrations in melt inclusions and (ii) their low viscosity allows two phase flow, raising the possibility that gases which have equilibrated at depth can reach the surface in relatively unmodified form as gas slugs or foam (reviewed by Parfitt 2004). A number of basaltic volcanoes have been studied intensively using OP FTIR, which has led to significant insights into degassing mechanisms; these include: Etna, Italy (Allard *et al.* 2005); Stromboli, Italy (Burton *et al.* 2007b); Nyiragongo, Republic of Congo (Sawyer *et al.* 2008); Kilauea, USA (Edmonds & Gerlach 2007); and Yasur, Vanuatu (Oppenheimer *et al.* 2006).

Mount Etna has been the focus of significant gas geochemistry studies (Allard *et al.* 2005; Aiuppa *et al.* 2007), which have been coupled with melt volatile geochemistry. S and CO₂ concentrations in olivine-hosted melt inclusions are shown in figure 3 (from Spilliaert *et al.* 2006); pressure is constrained by H₂O/CO₂ equilibria (Moretti & Papale 2004). Cl degassing does not begin until pressures of 400 bars or less; melt inclusions record a trend of Cl incompatibility

in the melt synchronous with S degassing, up to low pressures. The data also illustrate that S degasses at lower pressures than CO₂, such that magmas at above 1000 bars are expected to be in equilibrium with volcanic gases with CO₂/SO₂ more than 100, while at lower pressures, the gas phase will become progressively enriched in SO₂ (figure 3). Measurements of volcanic gases using an IR spectrometer (for CO₂) and an electrochemical sensor (for SO₂; Aiuppa *et al.* 2007) show large increases in CO₂/SO₂ prior to strombolian activity, interpreted to represent the pre-eruptive degassing of volatile-rich rising magma (figure 3).

Molar CO₂/S and S/Cl were measured in the volcanic gases emitted synchronous with lava fountaining in June 2000, using the incandescence of the fountain as an IR source (Allard *et al.* 2005). The fountain gas was richer in insoluble gases (CO₂/S approx. 7–10 and S/Cl approx. 10) than the bulk equilibrium gas (CO₂/S approx. 3 and S/Cl approx. 3; figure 3), interpreted as indicating a deep origin for the gases driving the lava fountain (approx. 1.5–1.8 km based on S/Cl; Allard *et al.* 2005). Volcanic gases emitted at Etna both prior to and during explosive activity, both Strombolian (discrete explosions) and Hawaiian (sustained fountains), therefore consistently display higher CO₂/SO₂ and S/Cl than effusive and non-eruptive activity for a particular crater. There are various possible causes for these changes in gas ratios, which include non-equilibrium degassing due to high magma ascent rates in the case of fountaining or an influx of volatile-rich magma and gas–melt segregation at depth.

Recent analogue experiments using shock tube apparatus have shed new light on the kinetic limitations of degassing during lava fountaining (Namiki & Manga 2008), which may allow a more informed interpretation of volcanic gas data. It was observed that magma ascent rate is the fundamental control on the degassing style. The gas inside the decompressing bubbles cannot expand instantaneously in response to pressure changes; there is an upper limit to the expansion velocity. If the decompression is sufficiently fast, the required expansion velocity for the gas pressure to remain in equilibrium will be too large and the bubbles will develop an overpressure, leading to fragmentation (Namiki & Manga 2008). The inability of gas bubbles to equilibrate with respect to pressure implies that the bubbles will not be in geochemical equilibrium upon eruption, and gas compositions will show a ‘deep’ signature that is not necessarily a consequence of gas segregation and/or accumulation at depth. Gas compositions observed synchronous with lava fountaining (Allard *et al.* 2005) are consistent with this model for basaltic fragmentation.

Measurements of volcanic gases at Kilauea Volcano also show consistent changes in erupted gas ratios corresponding to different degassing regimes. The volatile mass budget for the ongoing east rift eruption of Kilauea Volcano (1983–2008) is well characterized (Gerlach & Graeber 1985). A model for degassing was formulated by Dixon *et al.* (1991), based on a suite of submarine glasses, which preserved pre-eruptive H₂O and S contents, but were largely degassed of CO₂ (figure 4). The glasses exhibit a range in volatile concentrations, and these variations are probably controlled by: the presence of an immiscible sulphide phase, which may buffer S (Wallace & Carmichael 1992); multiple stages of isobaric vapour-saturated fractional crystallization, which will tend to increase the concentration of H₂O over CO₂ (e.g. Wallace *et al.* 1995); and the presence of excess CO₂-rich vapour, which would elevate melt CO₂ concentration. Sulphur degassing follows H₂O degassing closely (Gerlach 1986).

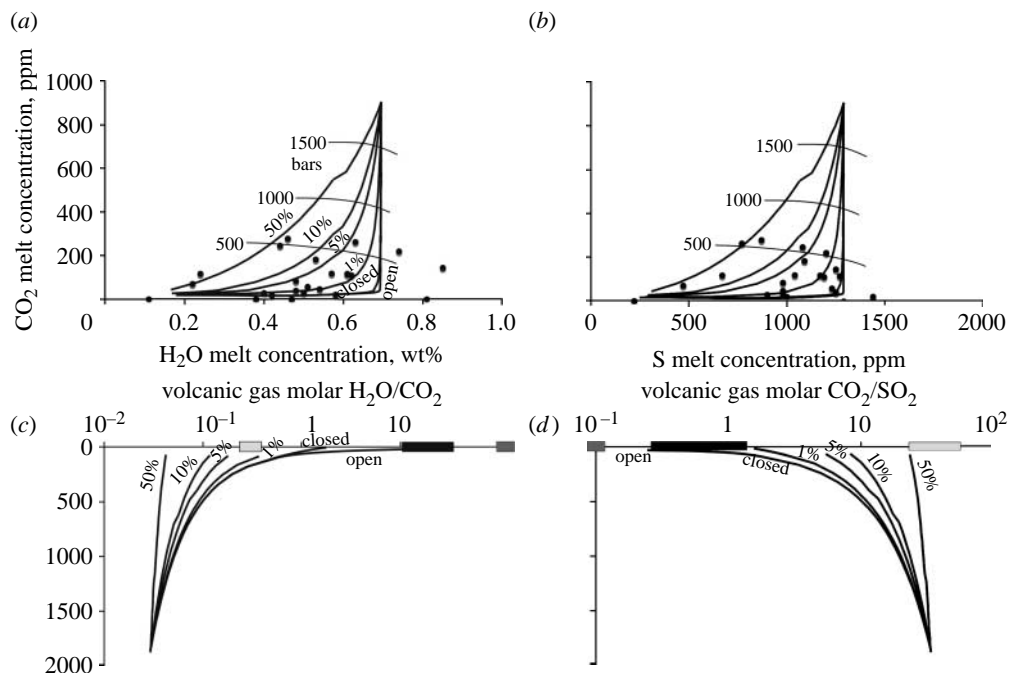


Figure 4. Melt volatile concentrations measured in submarine quenched glasses dredged along the Puna Ridge, Kilauea Volcano (Dixon *et al.* 1991). (a,b) Plots of CO_2 against (a) H_2O and (b) sulphur. The degassing behaviour of sulphur is assumed to mirror that of H_2O (Gerlach & Graeber 1985; Dixon *et al.* 1991). Isobars and curves are calculated from $\text{H}_2\text{O}/\text{CO}_2$ equilibria using Volatilecalc (Newman & Lowenstern 2002). (c,d) Volcanic gas compositions (molar ratios) with pressure, calculated using the degassing curves above, labelled with the proportions of exsolved vapour. The results of OP FTIR measurements during effusive degassing (black box), lava spattering (dark grey box) and gas pistoning (light grey box) activity are marked (from Edmonds & Gerlach 2007).

Recent OP FTIR measurements of $\text{H}_2\text{O}/\text{CO}_2$ and CO_2/SO_2 have been carried out at Pu'u 'O'o, Kilauea Volcano, during lava effusion, lava spattering and 'gas pistoning' (cyclic rise of the magma column, culminating in low fountaining). The measured gas ratios span three orders of magnitude as a consequence of variable melt–vapour separation at depth (figure 4). Gases emitted during lava effusion are consistent with open-system degassing of magma. Lava spattering is accompanied by the emission of H_2O and S-rich gases, consistent with open-system degassing of a stagnant magma column, with bubbles in equilibrium with melt at shallow depths in the conduit. The gas erupted during gas pistoning, however, has a much higher CO_2 concentration (Edmonds & Gerlach 2007), which could be due to either accumulation of CO_2 -rich gases at depth, followed by bubble rise, or kinetically-limited degassing during rapid magma ascent. Alternatively, there may be a decoupled, excess CO_2 vapour fluxing through the system from depth, which may accumulate in a shallow sill, then sporadically erupt in the form of a gas slug. The observation of a large, CO_2 -rich plume at the summit of Kilauea (Gerlach *et al.* 2002) lends support to a system rich in CO_2 , and efficient melt–gas segregation.

Further detailed gas composition measurements have been carried out during basaltic volcanic eruptions elsewhere. Gases emitted from the lava lake at Nyiragongo, Republic of Congo, are remarkably stable, despite minor strombolian and lava fountaining activity on the surface of the lake (Sawyer *et al.* 2008). Degassing at the surface of the lava lake is thought to occur through a combination of closed-system degassing during magma ascent, followed by open-system degassing near to the surface; dense, degassed magma then sinks to be replenished by volatile-rich magma in a self-sustaining convective regime (Sawyer *et al.* 2008). Short-lived changes in the ratios between S, Cl and F gases were ascribed to variability in shallow gas–melt segregation processes, as bubbles became large enough to accelerate and separate from their host melt. Similar changes in the relative proportions of S, Cl and F in volcanic gases at Etna have been modelled using an open-system Rayleigh distillation model to describe the fractionation that occurs between these species during magma ascent and bubble separation, which reproduces the range in observed gas compositions (Aiuppa *et al.* 2002).

Strombolian explosions at Yasur, a basaltic volcano in Vanuatu, were accompanied by marked increases in SO₂/HCl, ascribed to melt–gas segregation at greater pressures than during passive gas emissions between explosions. Recent measurements of gases emitted during strombolian eruptions at Stromboli (Italy) have shown clear differences from gas emissions between explosions and they correspond to modelled gas compositions in equilibrium with melt at a pressure of 70–80 MPa, at approximately 3 km depth (Burton *et al.* 2007*b*). These observations are consistent with the prevalent view that strombolian explosions are driven by the ascent of large bubbles or gas slugs from depth, which burst at the top of the magma column.

In summary, integrated studies of volatile degassing have been advanced considerably by observations of rapid changes in gas composition synchronous with different styles of basaltic eruptive activity. These observations have allowed more precise models of degassing processes to be developed which, in particular, are able to define a range of pressures at which melt and bubbles segregate in the conduit/magma chamber system. These results have far-reaching consequences for eruption forecasting and hazard assessment when these measurements are used for volcano monitoring purposes.

4. Degassing during silicic volcanic eruptions

Degassing at silicic arc systems is much less well studied in terms of integrated geochemical gas and melt volatile data; the reasons are linked to the complexity of petrogenesis for intermediate and silicic magmas, which often mean that only the very latest stages of melt development and evolution are recorded in melt inclusions (e.g. Wallace 2005). Silicic volcanic systems are also inherently more hazardous, which limits close approach to make detailed gas composition measurements. The degassing processes that take place in silicic systems are summarized in figure 5 and discussed below.

It has been proposed, on the basis of a wealth of evidence, such as (i) the ‘excess sulphur’ emitted by silicic eruptions and (ii) the observation, from melt inclusion volatile data, that most intermediate–silicic arc magmas are volatile-saturated during crystallization, that arc magmas coexist with a substantial vapour phase in

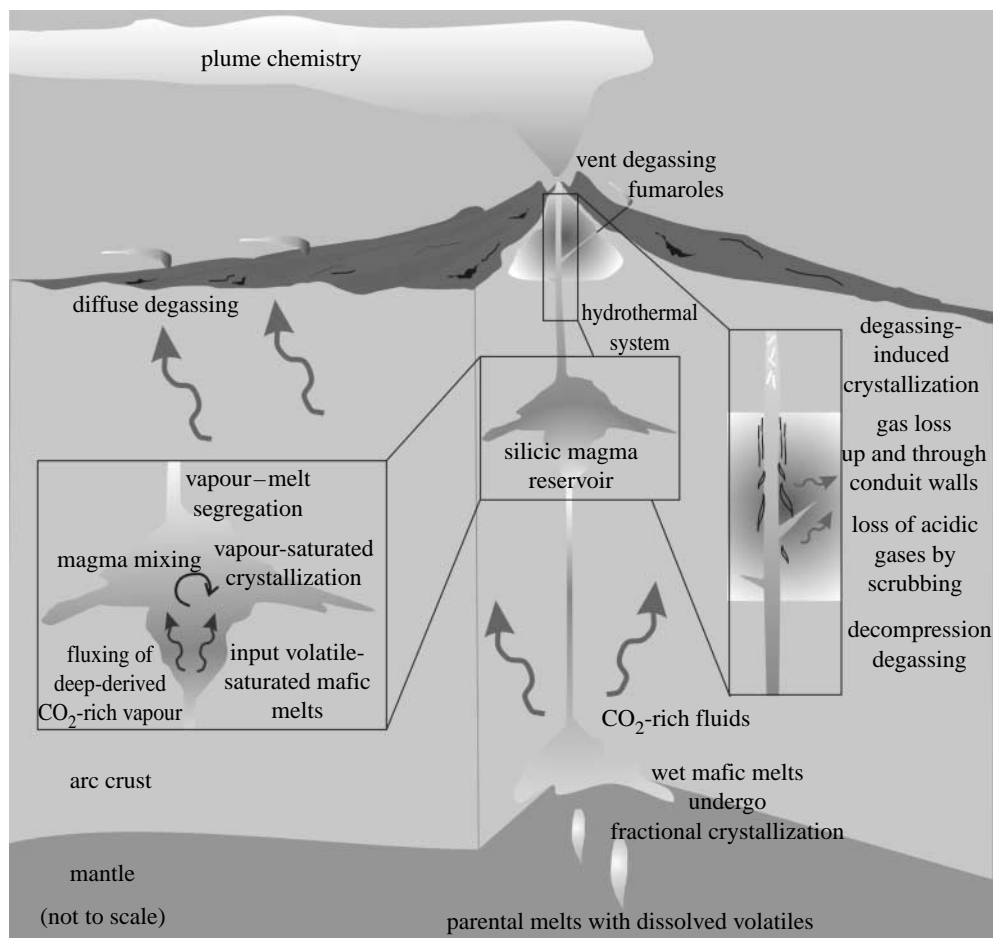


Figure 5. Processes acting to modify melt and vapour composition at an arc volcano that have been wholly or partly inferred from studies of volatiles in melts and volcanic gases.

crustal storage regions (Wallace & Gerlach 1994). Andesitic arc volcanoes may be regarded as vents that allow subducted volatiles to be returned to the surface, with a magmatic fluid phase present all the way down to the zone of magma generation. Shallow silicic magma chambers are recharged with volatiles supplied by mafic magmas that have differentiated in a lower crustal ‘hot zone’ (Annen *et al.* 2006). Implicit in the fractional crystallization of vapour-saturated melts is the exsolution of up to a few wt% H₂O, CO₂ and other associated volatiles, which together form a high pressure, supercritical fluid that either coexists with the mafic melts or segregates from it and moves independently through the crust (figure 5). Good evidence for deep degassing beneath arc volcanoes comes from melt inclusions hosted by olivine phenocrysts in mafic magmas at Popocatepetl, Mexico (Roberge *et al.* 2007), which show very high concentrations of CO₂ and S (above 1000 and 2000 ppm, respectively) and indicate, by their H₂O and CO₂ concentrations, that degassing begins at depths of at least 25 km; this clearly illustrates the role of wet mafic magma in supplying volatiles, in the form of a vapour phase, to silicic arc systems.

Many studies of melt inclusions in silicic arc systems have documented elevated CO₂ over that expected from saturation models (figure 2); this has been ascribed to fluxing by CO₂-rich vapour derived from deeper crustal vapour-saturated magma differentiation (Rust *et al.* 2004; Blundy & Cashman 2006; Johnson *et al.* 2008). The observation of large fluxes of mantle-derived CO₂ through the flanks of arc volcanoes (e.g. Allard *et al.* 1991) may support the existence of a deep-derived, decoupled vapour phase. Multiple stages of magma storage and volatile fluxing were recorded by melt inclusions in the erupted products of the 18 May 1980 eruption of Mount St. Helens (USA), where the concentrations of Li, short-lived radiogenic isotopes and CO₂ in the melt suggest that a deep-derived vapour phase was able to ascend through the system on a time scale of months (Berlo *et al.* 2004). The mechanism of permeability development throughout the conduit and magma reservoir, where porosities are expected to be low, remains unclear.

In addition, mafic magma underplates shallow magma chambers and mixes with resident silicic magmas, thereby transferring heat and volatiles directly to the melt. High fluxes of SO₂ from silicic arc volcanoes have been attributed to degassing of unerupted mafic magma (Wallace 2001). The SO₂ flux from Soufriere Hills Volcano, Montserrat, has been attributed to a vapour phase supplied by mafic magma (Edmonds *et al.* 2001); however, the relative importance of a deep-derived vapour phase over the degassing of mafic magma in a shallow storage reservoir to supply this S flux is unknown. The emission rate of SO₂ remains high (greater than 1000 t d⁻¹) during 12–24-month long pauses in the eruption, suggesting that there is efficient melt–gas segregation and a high bulk permeability, which allows the SO₂-rich vapour to ascend to the surface while magma is stagnant in the system.

Satsuma-Iwo-jima Volcano, Japan, is a geochemically well-characterized system that illustrates these degassing processes (Saito *et al.* 2001). Evolution of magma volatile composition was studied in melt inclusions collected from ejecta from various eruptions, from its caldera-forming eruption of 6300 kyr BP to a recent rhyolitic effusive eruption. Basaltic andesite scoria erupted at approximately 3 kyr BP shows evidence of isobaric, vapour-saturated degassing processes. An inverse correlation between CO₂ and H₂O in the melt indicates fractional crystallization at approximately 3–5 km, as well as the addition of excess CO₂ vapour from depth, from a degassing, recharging mafic magma. Rhyolitic pumices erupted approximately 1.3 kyr BP show high H₂O contents (up to 4.8 wt%) and low CO₂, which records magma decompression and degassing from approximately 8–9 to approximately 3–5 km, suggesting the existence of a shallow magma storage area where basaltic andesites underplate and mix with overlying silicic magmas. Recent rhyolitic lavas have shown low H₂O and elevated CO₂, which indicates decompressional degassing to low pressures, combined with fluxing by deep-derived CO₂-rich gases from depth, supplied by mafic melts. The rhyolite therefore acts as a *transporter* (sic) of volatile components from the underlying basaltic magma to the surface (Saito *et al.* 2001).

Decompressional degassing takes place in the magma chamber and conduit as magma ascends and erupts; evidence for this comes from melt inclusions in low-pressure phases (Wallace 2001; Blundy & Cashman 2005), albite-rich microlites and phenocryst rims (Murphy *et al.* 2000) and an increase in gas emissions during magma ascent and eruption (e.g. Edmonds *et al.* 2003). There is now also

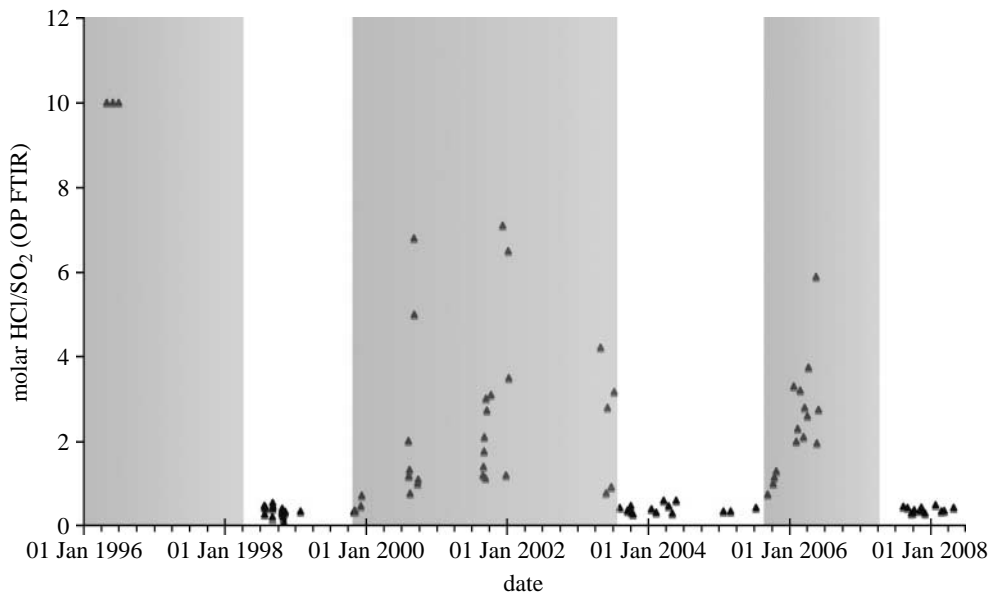


Figure 6. Molar HCl/SO₂, measured by OP FTIR, with time in the plume of Soufriere Hills Volcano, Montserrat, with periods of lava dome growth shown qualitatively (shaded grey). Data from 1996 to 2003: Edmonds *et al.* (2001, 2002) and Oppenheimer *et al.* (2002) and data from 2004–2008: the Montserrat Volcano Observatory web page www.mvo.ms, by permission of T. Christopher, Montserrat Volcano Observatory.

abundant empirical and theoretical evidence for extensive, shallow, melt–gas segregation in conduits. Highly permeable shear zones form at the conduit walls due to brittle failure of viscous melts at relatively low rates of magma ascent, which allows the upward flow of a gas phase (Gonnerman & Manga 2003; Rust *et al.* 2004). Large emissions of gases (up to a few kilotonnes of SO₂) emitted in a single pulse during lava dome collapses at Soufriere Hills Volcano (Edmonds *et al.* 2003; Carn *et al.* 2007) provides empirical evidence for a shallow conduit gas storage area, which might result from the accumulation of this segregated gas beneath a relatively impermeable large lava dome.

Gas geochemistry OP FTIR data from Soufriere Hills Volcano illustrates shallow decompressional degassing of Cl (Edmonds *et al.* 2002; Oppenheimer *et al.* 2002). Unlike S, HCl gas is only present in the plume during periods of lava extrusion (up to 13 000 t d^{−1} in 2000; Edmonds *et al.* 2002). When magma ascent ceases, HCl flux decreases rapidly to very low levels (less than 50 t d^{−1}). These variations in HCl flux, which are distinct from the degassing of SO₂, are illustrated clearly in a plot of HCl/SO₂ against time (figure 6). It has therefore been proposed that Cl partitions into a H₂O-rich vapour during magma ascent and degassing, generating a Cl-rich plume (Edmonds *et al.* 2002). Further, this partitioning must occur at low pressures, as very little magma–gas segregation is observed (the HCl and lava fluxes ‘shut off’ in tandem).

In summary, studies of degassing in silicic systems using a geochemical approach illustrate processes of mafic replenishment, gas transfer between crustal reservoirs independently of magma, and volatile fractionation during magma ascent and vesiculation. Gas composition can be used to monitor the

ascent and eruption of magma, although the measurements are far more challenging than for their basaltic counterparts. Many of the inferences made concerning gas fluxing require substantial permeability in the system such that gas can be transferred to the surface through stagnant magma bodies, which is not well understood.

5. Classification of eruptions based on vapour–melt segregation

A generic classification of volcanic eruptions is based on vapour–melt flow regimes (Slezin 2005 and references therein). Eruptions are separated into three classes: (i) eruption of melt with separated bubbles that can move independently, (ii) eruption of gas and pyroclasts, which includes high intensity, sustained and transient explosive eruptions, and (iii) eruption of a two-phase flow in which both phases are continuous but move with different velocities; this corresponds to extrusive eruptions and is possible only at slow ascent rates. Models for the generation of explosive basaltic volcanism were developed further by studies of gas segregation at the roof of magma chambers and in horizontal sills (Jaupart & Vergnolle 1989; Menand & Philips 2007), which show that gases can separate from magma at depth, to give rise to regions of gas-rich and gas-poor magma. These models may apply to episodes of strombolian activity, driven by the ascent of large gas slugs, and may explain persistent degassing, which requires gas–melt separation and continuous magma recharge.

These ideas are developed further by recent volatile geochemistry studies. In basaltic systems, regimes of gas pistonning, lava spattering and strombolian eruptions form an end member representing separated two-phase flow at low magma ascent rates and high degrees of melt–gas segregation. Studies of gas composition and petro-geochemical data from Mount Etna have allowed a model for the development of shallow gas percolation (the onset of open-system degassing and melt–gas segregation in the conduit) to be developed that highlights the mechanisms behind transitions between explosive and effusive activity (Burton *et al.* 2007a). Gas geochemistry measurements, combined with petro-geochemical studies of erupted products, have shown that gas–melt segregation can occur up to a few km depth for some eruption types and settings. While the conclusions drawn from these studies reproduce the generally accepted broad interpretation of these eruption types, they are, in addition, yielding a more accurate picture of the details of the degassing process, in particular the pressure at which gas loss from the magma occurs and how efficient this process is. The prevalence of one particular eruptive style over another is controlled by magma properties (total volatile content, viscosity, temperature). Lava fountaining and basaltic plinian eruptions are generally accepted to represent the closed-system degassing end member at high magma ascent rates (figure 7), although gas compositions measured during lava fountaining remain ambiguous as the role of accumulated gas at depth in driving the activity, and this requires further observation.

For silicic systems, gas fluxing and lava dome collapse both liberate large quantities of vapour and little magma; these are manifestations of deep and shallow accumulations of vapour, respectively, from the gas composition. The placement of vulcanian explosions on this classification is more complex.

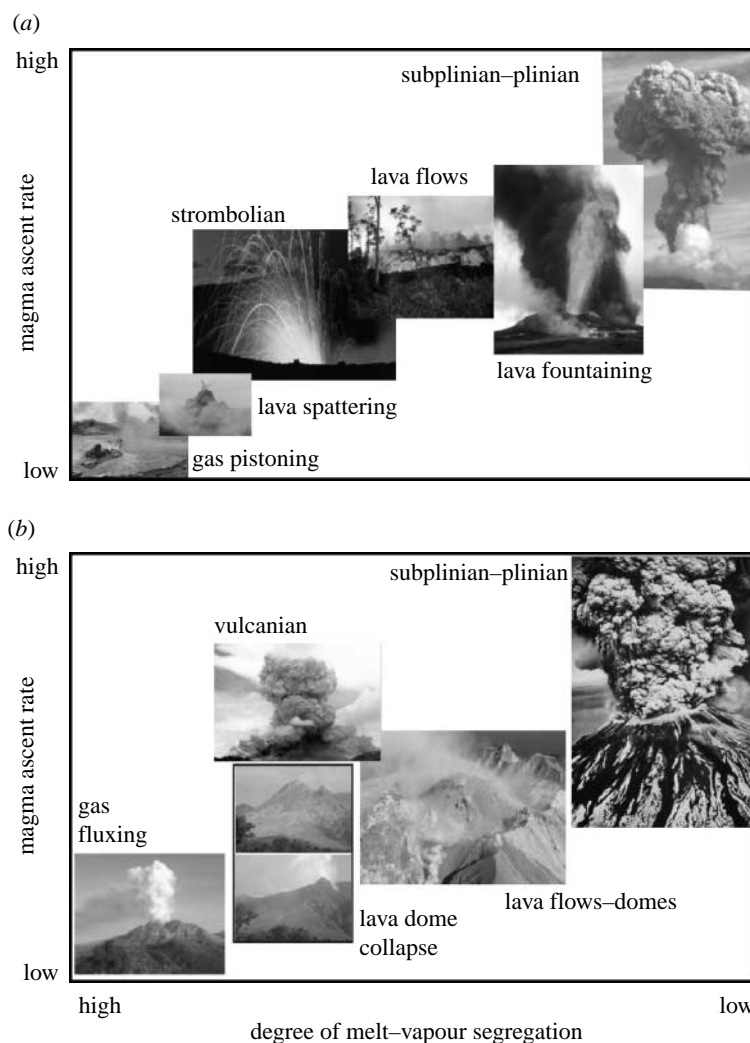


Figure 7. Volatile geochemistry studies support the existence of a wide range of gas–melt segregation regimes during volcanic degassing; these are shown in this illustrative diagram in terms of the degree of gas–melt segregation and magma ascent rate for (a) basaltic systems and (b) intermediate–silicic systems.

Detailed petrological studies of the products of vulcanian explosions at Soufriere Hills Volcano indicate that they occur in response to overpressure caused by magma degassing beneath a relatively impermeable ‘degassed cap’ (Melnik & Sparks 2002; Clarke *et al.* 2007). Eventually, overpressure beneath the cap exceeds the tensile strength of the melt and causes brittle failure of the magma and rapid decompression and vesiculation of the underlying magma (Melnik & Sparks 2002). Evidence for gas–melt segregation beneath a degassed cap comes from the observation of a large pulse of gas released during a ‘failed’ vulcanian explosion at the end of a series of explosions at Soufriere Hills Volcano in 2003 (Edmonds & Herd 2007); this was interpreted as the escape of vapour through shear zones around a degassed plug, which relieved overpressure and prevented

the explosion. Lava domes and flows occur at intermediate degrees of melt–gas segregation and ascent rate. Transitions between lava dome growth and vulcanian explosions occur in response to changes in magma ascent rate (driven by changes in magma pressure at depth; Melnik & Sparks 2002), which has implications for the development of permeability and gas loss. It has been observed that conduits and lava domes can become progressively ‘sealed’, preventing gas loss and building shallow overpressure, which can cause transitions to explosive activity (e.g. Fischer *et al.* 1996). Plinian explosions occur in response to rapidly ascending magma degassing in a closed system (figure 7) and are usually mutually exclusive of vulcanian activity during a particular eruption owing to the requirement that magma ascent keeps pace with fragmentation in the conduit, which yields sustained explosivity, in contrast to transient vulcanian explosions. Gas composition measurements have not been carried out during plinian activity owing to the logistical difficulties of making measurements, primarily the high ash content of the column, which precludes remote spectroscopic measurements.

6. The future

Future developments in the field of geochemical studies of magma degassing will focus on improvements in instrumentation to measure volcanic gases (H_2O and CO_2 in particular) on a variety of spatial and temporal scales, combined with more sophisticated microanalytical methods to measure volatile and light elements in glass and phenocryst phases, which will allow a more detailed interpretation of how magma and vapour interact over a range of pressures in the crust prior to and during eruption. An improved understanding of degassing processes will feed into the development of more successful forecasting of eruptions and changes in eruptive style, and more accurate assessments of hazard and risk.

As well as the more traditional measurements of SO_2 , the future will bring improved ground and aircraft-based spectroscopic methods to measure H_2O and CO_2 gases, which will allow integrated petro-geochemical degassing studies of the most important volatile species in driving volcanic activity. Our interpretation of volcanic gas data at present is hampered by the difficulties involved in measuring these species, mainly due to their high concentrations in air. Recently, volcanic CO_2 has been detected for the first time using an unmanned aerial vehicle (McGonigle *et al.* 2008), which holds promise for volcano-monitoring and degassing studies. The accurate measurement of H_2O and CO_2 in gases from basaltic volcanoes will advance our understanding of mechanisms of explosive activity, as the ratio between these species is highly sensitive to pressure, which makes it a useful tool for assessing the depth of melt–gas segregation. For silicic volcanoes, the measurement of CO_2 , along with other gases, will elucidate the role of excess vapour in magma chambers and volatile fluxing, which has important implications for transitions between effusive and explosive activity, as well as understanding magma and volatile budgets in volcanic settings.

While degassing mechanisms are becoming well constrained, time scales of degassing are generally still elusive; the advent of methods such as portable mass spectroscopy (Diaz *et al.* 2002), which could be used to measure the short-lived

radioactive isotopic compositions of volcanic gases, raise the possibility of assessing time scales of degassing, although this has yet to be exploited fully for many volcanic centres by combination with microanalysis of the same components in erupted rocks, critical for mass balance. Portable mass and laser spectroscopies (Richter *et al.* 2002) may also be used to measure the stable isotopes of carbon, sulphur and oxygen in volcanic gases, to assess the role of hydrothermal systems and to discriminate between open and closed styles of degassing when combined with analysis of volcanic glasses.

It is clear that, as well as measuring gas emissions, it is crucial to have an understanding of the geochemical evolution of magma prior to eruption in order to achieve an unambiguous interpretation of volatile data. There are a number of recent studies using the composition (and texture) and zoning in phenocrysts of amphibole, apatite and plagioclase and microlites (Humphreys *et al.* 2008) and concentrations of light elements such as Li in melt inclusions to infer degassing processes (Berlo *et al.* 2004) that provide a valuable complement to volcanic gas measurements and, when combined with studies of volatile short-lived radioactive isotopes, will allow both spatial and temporal understanding of volcanic degassing processes. Techniques for assessing the post-entrapment modification of melt inclusions are becoming more sophisticated (e.g. Baker 2008). These developments might allow correction for processes such as boundary-layer enrichment in volatile species such as sulphur, which leads to overestimation of the pre-eruptive volatile concentration. This will greatly advance our ability to model degassing using geochemical data. This paper has not touched on the many other complementary petrological techniques that lend insight into magma degassing processes, such as phase equilibrium experiments (e.g. Pichavant *et al.* 2002) and textural analysis of erupted products (e.g. Lautze & Houghton 2007). As more insight is gained into degassing processes at a wide range of volcano types and magma compositions, generic models relating degassing behaviour to eruption style will evolve.

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