A model for degassing at the Soufrière Hills Volcano, Montserrat, West Indies, based on geochemical data

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Abstract

A model is presented to describe the degassing behaviour of sulphur and chlorine at the Soufrière Hills Volcano, Montserrat, using both geochemical analyses of glass and remote sensing data (correlation spectroscopy and open-path Fourier transform infrared spectroscopy). Constraints on total SO2 emitted at the surface (1.2 Mt up to September 2000) and petrological data indicate that the andesite was not the sulphur source. Mafic magma that intruded into the andesite magma chamber to trigger eruption at 5–7 km depth recharged the sulphur contents of the shallow volcanic system. Sulphur is removed from the mafic melt to enter a water-dominated vapour phase at depths of 5–7 km or greater. The passage of SO2 to the surface is sporadic and discontinuous in time and is governed by the permeability of the conduit and wallrock and the supply of mafic magma from depth. Chlorine is derived from the andesite magma and degasses on magma ascent, shown by the melt evolution recorded in the matrix glasses and the apparent link between extrusion rate and HCl flux at the surface. Petrological estimates of chlorine loss agree with measurements of total chlorine emission at the surface. The chlorine content of the matrix glass may be explained by fractional crystallisation combined with the partitioning of chlorine into a water-rich fluid phase with a partition coefficient of the order of 50. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: degassing; sulphur; chlorine; Soufrière; Montserrat; Fourier transform infrared spectroscopy; inclusions; melts

1. Introduction

The Soufrière Hills Volcano, Montserrat, has been in active eruption since mid-1995 [1]. The first phase of andesite lava extrusion ceased in March 1998 and, from then until November 1999, activity was characterised by intermittent dome collapse (as portions of the dome became increasingly unstable) and shallow-level explosions caused by the build-up of fluid pressures in the upper conduit region. During this phase, seismicity levels were low, with a low frequency of long period and hybrid events. A hybrid swarm from 5 to 8 November 1999, culminating in a series of explosions from 8 to 11 November, heralded the ascent of fresh magma that reached the surface on or around 16 November and began the second phase of dome-building. Extrusion has continued up to the time of writing, with extru-
sion rates thought to be varying from 1 to 5 m$^3$ s$^{-1}$. The present mass of new material at the time of writing (September 2000) is estimated at $70 \times 10^6$ m$^3$.

The petrology and geochemistry of the dome lava and pumice have been monitored throughout the eruption [2,3], and have been homogeneous with time. They are coarse-grained, porphyritic, crystal-rich, hornblende–hypersthene andesite [4]. The andesite phenocryst assemblage constitutes 45–55% by volume of the bulk rock and consists of plagioclase (30–35%), amphibole (6–10%), orthopyroxene (2–5%), titanomagnetite (2–4%), quartz (<0.5%), clinopyroxene microphenocrysts (<0.5%) and accessory apatite and ilmenite [2,4,5]. The groundmass is made up of microphenocrysts and microlites of the phases above (plus clinopyroxene) and rhyolite glass (75–79 wt% SiO$_2$), which comprises 5–35% by volume of the groundmass. The petrology of the andesite has been interpreted as that of a long-lived, crystallising magma body residing in a magma chamber at 5–7 km depth [2,4,5]. Periodically, the magma chamber is invaded by mafic magma that may trigger eruption. It has been suggested that the similar bulk compositions, the narrow range in mineral compositions and the evidence for a long cooling history indicate that all of the eruptions over the past 24 kyr have been tapping the same magma body [2,4]. Mafic inclusions within the andesite lava and pyroclastic products are interpreted as evidence of ‘magma mingling’ [4] of hotter, more mafic magma with a relatively cool (850°C) andesite body. Disequilibrium textures are prevalent within the andesite: sieve-textured plagioclase, resorption of quartz and reverse zoning of orthopyroxene and plagioclase. These features all indicate a recent heating event (sieve-texture may develop within a few years in hydrous systems [6]). The seismic episode beginning in 1992 may have been related to this intrusion event that caused this heating and triggered the eruption. Replenishment of a magma chamber with hotter magma rich in volatiles can trigger eruption by creating an over-pressure due to the increase in magma volume, exsolution of volatiles, convective upwelling of the resident magma or a transfer of volatiles from mafic to andesite magmas [4]. Whole rock compositions of the mafic magma inclusions are basaltic to basaltic andesite in composition (XRF analysis [2,4]).

Understanding degassing processes is of key importance in volcanic systems. At Soufrière Hills, Montserrat, there is an extensive record of gas emissions at the surface. Correlation spectrometer (COSPEC) measurements provide SO$_2$ emission rates from July 1995 up to the present (September 2000), except for interruptions due to instrument failure and unfavourable weather conditions. Open-path Fourier transform infrared spectroscopy (FTIR) has yielded ratios between HCl and SO$_2$ concentrations using absorptions in the infrared spectrum of the sun viewed through the volcanic plume. Coupled with this, geochemical analysis of the melt inclusions and matrix glass of the erupted products for rare earth and other trace elements provides information regarding the loss of volatiles from the melt at various stages during the melt evolution, pre- and syn-eruption. The exsolution, migration and expansion of volatiles through the shallow volcanic system are key parameters in eruption dynamics. Understanding mechanisms of gas loss is of particular importance in subduction zone settings as these are characterised by dome-building and explosive eruptions, with transitions between the two types of activity thought to be caused by fluctuations between conduit systems that are ‘closed’ and ‘open’ to gas movement [7,8].

An important aspect of the routine monitoring of active volcanoes is the recognition of changes in the degassing regime. Changes in gas emission rate or composition may indicate changes in magma supply or the ability of the edifice to transmit gases to the atmosphere. This paper aims to relate the gas output at the surface, measured using a COSPEC and by open-path FTIR, to pre- and syn-eruption melt volatile compositions (sulphur and chlorine). Melt inclusions in plagioclase and the matrix glass of the andesite were analysed for volatile, major and trace elements in order to build a picture of progressive degassing of the melt. This was achieved using laser ablation inductively coupled mass spectroscopy (LA ICP-MS) to analyse the glasses for trace elements deemed incompatible with the crystallising assem-
blage. These may be used to develop a model of melt evolution by crystallisation in the magma chamber and during ascent. Calculated and observed models of the evolution of the melt in terms of volatile elements, as a function of crystallisation, indicate different stages of degassing that took place between the magma chamber and the surface at various stages of pre- and syn-eruption. Degassing may occur by partitioning into a vapour phase or during decompression during magma ascent and eruption. The relative importance of these processes will greatly influence patterns of gas output into the atmosphere, with different types of volcanic activity associated with different gas signatures.

2. Methodology

2.1. Remote sensing techniques

2.1.1. The correlation spectrometer

The COSPEC has been used to measure SO$_2$ gas fluxes at the Soufrière Hills Volcano, Montserrat, relatively continuously throughout the 1995–1999 eruption. The record begins in the early stages of the eruption (29 July to 28 August 1995), resumes from 28 April 1996 until 4 July 1997, continues from 7 July 1998. Since then COSPEC has been deployed regularly (2–6 traverses per day, 2–5 times per week), up to the present.

The COSPEC detects the column mass of SO$_2$ in the atmosphere by recording the absorption of solar ultraviolet radiation after passing through the plume, utilising a strong SO$_2$ absorption band at 0.18–0.32 μm [9,10]. COSPEC data have been obtained from a variety of platforms at the Soufrière Hills Volcano. Road traverses have been successfully used here [11] and at many other volcanoes (e.g. Etna, Sicily [12]; Galeras, Colombia [13]). The COSPEC has also been regularly operated on the helicopter and from a boat offshore. Details of the ground-based traverse technique are given elsewhere [11,14]. The instrument is connected to a chart recorder and 12 V battery in the field, and used in conjunction with a hand-held GPS system, to record the position every 60 or 30 s, simultaneously marking the chart.

The COSPEC output, effectively a concentration-pathlength product, is multiplied by the plume width and the speed at which the plume moves through the traverse, which can be assumed to be equivalent to the wind speed. The data are also corrected for the obliquity of the traverse to the plume azimuth. This gives a concentration volume per time (ppm m$^3$/s) that is converted into metric tonnes per day. Typically 2–6 traverses are carried out per day. The wind speed is measured from St Georges Hill using a hand-held anemometer (elevation approximately 300 m) or estimated from the helicopter at plume height (approximately 350 m). Wind speed variation and measurement inaccuracies are the main source of error in COSPEC measurements, leading to an estimated error of ±30% at Soufrière Hills volcano [14].

2.1.2. FTIR spectroscopy

Open-path FTIR spectroscopy detects gases (SO$_2$ and HCl, among others) through their absorptions in the infrared region. Both artificial and natural volcanic (the dome) infrared sources of radiation have been used as well as the sun. Measurements have been carried out on Montserrat during July and August 1996, July, September, October and November 1998, January, November and December 1999 and August 2000. All measurements after 1996 have utilised the sun as a source of infrared radiation, having the advantage of improving the signal to noise ratio in the regions of interest and being a safer and more straightforward way to deploy the instrument in the field [15,16].

A MIDAC brand FTIR spectrometer is used which incorporates a Michelson-type interferometer, a 1 mm$^2$ mercury–cadmium–telluride detector and an additional indium–antimonide detector, attached to a 25 cm Newtonian telescope. Gas column amounts are determined using a forward model and HITRAN [15].

2.2. Analytical techniques

2.2.1. Sample description

The samples analysed in this study are from pyroclastic flow deposits from April and Septem-
ber 1996 and 21 September 1997. They are dense andesite dome blocks and vesiculated pumice-type material (21 September deposits). Some of the samples have mafic enclaves, thought to be representative of the mafic magma intruded into the chamber that may have triggered eruption [2]. Plagioclase-hosted melt inclusions (Fig. 1) and the matrix glass of the andesite were analysed, first by electron microprobe and then by LA ICP-MS analysis. Over 150 glass compositions were analysed from 25 samples.

2.2.2. Electron probe microanalysis

Glass compositions were analysed in the Department of Earth Sciences in Cambridge on a CAMECA SX-50 electron microprobe with Oxford Instruments ZAF4-FLS software for quantitative analysis. Major elements were analysed using energy dispersive methods; chlorine and sulphur were determined by wavelength dispersive spectrometry. A 1–3 μm beam was used with a beam current of 3 nA (to minimise sodium loss), a 20 kV accelerating voltage and a counting time of 50–200 s per analysis. Accuracy for major elements is 1% relative, detection limits 0.1 wt% and precision 0.1% for concentrations near detection limits (0.2 wt% for sodium).

2.2.3. LA ICP-MS

LA ICP-MS analysis was performed at the Institute of Geography and Earth Sciences, University of Wales, Aberystwyth using a VG Elemental PlasmaQuad PQII+. This was coupled to a 500 mJ Nd:YAG laser operating at 266 nm. Individual melt inclusions were located on the optical system for trace element analysis. A relatively low energy (0.5–1 mJ) and repetition rate (5 Hz) was used to avoid shattering of the glass and ablating through the inclusion. The sample was moved in 2.5 mm steps under the laser beam during the analysis, using a resolution of 15 μm for the laser beam. The minor 44Ca isotope was used as the internal standard for the analysis, using a concentration determined from electron microprobe analysis. The NIST 610 glass reference material was used for calibration [17]. Detection limits for many elements were in the sub-ppm range [18]. For homogeneous materials, the precision of LA ICP-MS analyses is typically better than ±10% and accuracy ±10% [18].

2.3. Trace element modelling

We use selected trace element concentrations determined by LA ICP-MS analysis to assess the
extent of crystallisation required to relate individual melt inclusions in plagioclase phenocrysts and microphenocrysts or matrix glasses back to the least evolved glass composition analysed. For this we use the Rayleigh fractional crystallisation equation. We note that for the largest phenocrysts equilibrium crystallisation is likely to have been more important, but for their rims and the microphenocrysts, we assert that fractional crystallisation must have played a large role. We use:

$$C_{L_i}/C_{O_{ir}} = f^{(D_{crystals}^i-1)}$$

where $C_{L_i}$ is the concentration of the element $i$ in the glass (melt), $C_{O_{ir}}$ the concentration in the original liquid, $f$ the remaining melt fraction and $D_{crystals}^i$ the bulk partition coefficient for element $i$ for partition between the melt and the crystallising assemblage. We use a selection of trace elements whose melt compositions are highly correlated and that are incompatible. From our analyses, Pr is considered representative of the most incompatible elements in this crystallising assemblage. La, Ce and Nd are also considered suitable for use in determining $f$ values for the range of melt compositions analysed. Bivariate plots of these elements with Pr allow calculation of their apparent bulk partition coefficients, assuming that Pr has a mineral–melt partition value of 0 (Fig. 2). The slope of the plots is equal to $(1-D_{melt}^i)$, where $D_{crystals}^i$ is the bulk partition coefficient for the partitioning of element $i$ between the melt and the crystallising assemblage:

$$\log\left( C_{L_i}/C_{O_{ir}} \right) = \left( 1-D_{melt}^i \right) \left( \log\left( C_{L_{Pr}}/C_{O_{Pr}} \right) \right)$$

From Fig. 2 $D_{melt}^{La} = 0.2$, $D_{melt}^{Cr} = 0.1$ and $D_{melt}^{Nd} = 0.1$. From these derived partition coefficients we calculate $f$ values (melt fraction remain-
ing) from Eq. 1 above for each analysis performed on the matrix and melt inclusion glasses. This yields average \( f \) (melt fraction remaining, or inversely amount of crystallisation) for each glass analysis.

We assume that sulphur and chlorine are incompatible in the crystallising assemblage and their bulk partition coefficients are equal to zero. However, the authors recognise that chlorine partitions into amphibole with a melt–crystal partition coefficient of approximately 1 in the temperature and pressure range in which amphibole is stable (at pressures greater than 100 MPa at 800–850°C). Using the modal proportions of

<table>
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<td>bd</td>
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<td>bd</td>
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<td>94.95</td>
<td>95.09</td>
<td>94.68</td>
<td>94.28</td>
<td>&gt; 95.29</td>
<td>95.74</td>
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<td>75.84</td>
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<td>12.7</td>
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<td>2.7</td>
<td>1.4</td>
<td>2.3</td>
<td>0.3</td>
<td>1.2</td>
<td>1.4</td>
<td>2.0 (0.9)</td>
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<td>MnO</td>
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<td>0.05</td>
<td>0.01</td>
<td>0.12</td>
<td>bd</td>
<td>0.01</td>
<td>0.07</td>
<td>0.07 (0.06)</td>
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<td>MgO</td>
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<td>bd</td>
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<td>0.03</td>
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<td>1.5</td>
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<td>Na₂O</td>
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<tr>
<td>Cl ppm</td>
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<td>828</td>
<td>3244</td>
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<tr>
<td>F ppm</td>
<td>bd</td>
<td>196</td>
<td>583</td>
<td>0</td>
<td>833</td>
<td>211</td>
<td>bd</td>
<td>341 (300)</td>
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<td>97.82</td>
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<td>98.11</td>
<td>97.62</td>
<td>99.05 (1.70)</td>
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Table 1
Major and volatile element composition of the glasses analysed


B: 1: Murphy et al. [2] andesite matrix glass, normalised to volatile-free. 3–9: A range of andesite matrix glass compositions from this work. 10: Mean andesite matrix glass composition from this work (standard deviation in brackets). bd: below detection. The authors note that the Na content is probably too low by 5–10% due to volatilisation.

Fig. 3. Plot to show \( f \), melt fraction remaining as derived from trace element concentrations in plagioclase melt inclusion glass and andesite matrix glass, against glass chlorine content in parts per million. Solid lines are calculated lines of melt chlorine concentration evolution for melt–crystal partition coefficients of 0, 1 and 2. These are derived from the Rayleigh fractional crystallisation equation.
A

\[ f_{\text{melt fraction remaining}} \]

\( D = 0 \)

\( D = 1 \)

\( D = 2 \)

Sulphur

B

\[ f_{\text{melt fraction remaining}} \]

\( D = 0 \)

\( D = 1 \)

\( D = 2 \)

Chlorine
minerals in the assemblage, this translates to a bulk partition coefficient of approximately 0.1. Subsequent crystallisation at shallower depths will not involve chlorine being incorporated into any crystallising phase. These melt–crystal partition coefficients for chlorine and sulphur were affirmed by analysing phenocrysts for these elements using the electron microprobe and they were found to be below detection in all of the crystallising phases with the exception of amphibole. Hence for shallow-level (less than 4 or 5 km) crystallisation, any loss of chlorine or sulphur from the melt may be ascribed to the exsolution of gas rather than incorporation into phenocrysts.

![SO$_2$ and HCl emission rates time series for Soufrière Hills Volcano, Montserrat.](image)

Fig. 4. SO$_2$ and HCl emission rates time series for Soufrière Hills Volcano, Montserrat. For SO$_2$, each point represents one measurement obtained by a horizontal traverse perpendicular to the plume direction. Typically 2–6 traverses are carried out in one day. Error bars are 30%. HCl emission rates are derived from COSPEC and HCl:SO$_2$ mass ratios derived from open-path FTIR spectroscopy measurements. Error bars are 35% (error in ratio determination combined with error on COSPEC measurements). Solid diverging black lines represent changes in extrusion rate schematically.

| Table 2 | Mean sulphur and chlorine concentrations of plagioclase-hosted melt inclusions and andesite matrix glass, measured by electron microanalysis |
|-----------------|------------------|-----------------|-----------------|-----------------|
|                | Sulphur (ppm)    | S.D.            | Chlorine (ppm)  | S.D.            |
| Plagioclase MI  | 46               | 40 (35)         | 3265            | 1058 (35)       |
| Most primitive plagioclase MI | 35               | 0 (1)           | 2070            | 0 (1)           |
| Andesite matrix glass | 70               | 61 (36)         | 985             | 750 (36)        |

S.D. is the standard deviation and the number in parentheses denotes the number of analyses. Sulphur and chlorine concentration of the most primitive melt inclusion analysed is also given.
3. Results

3.1. Trace element modelling

Major and volatile element data for the glass types analysed are given in Table 1. The $f$ values calculated using the trace element data are plotted against glass volatile content (Fig. 3). The calculated lines of melt evolution represent how concentrations of chlorine and sulphur in the melt (starting from their pre-eruption concentrations) would evolve corresponding to $D_{\text{crystals}}^\text{melt} = 0$, 1 and 2. We would of course expect, with no degassing, chlorine and sulphur to be enriched in the melt during crystallisation corresponding to $D_{\text{crystals}}^\text{melt} = 0$ up to their solubility limits as this provides an upper limit to the concentration of these volatile species in the melt. It has been experimentally determined that the solubility limits for the Soufrière Hills magma chlorine range from 0.48 to 0.68 wt% at 860–890°C and 25–250 MPa [26]. Initial sulphur and chlorine content at $f = 1$ is the concentration of these species in the most primitive plagioclase melt inclusion sampled (the melt is still of rhyolite composition). Volatile compositions of the most primitive melt inclusion and the other glass types analysed are given in Table 2.

3.2. Remote sensing data

Sulphur output to the surface has been measured using the COSPEC for periods of passive gas release to the atmosphere during both syn- and post-extrusive periods (Fig. 4). During short-lived, large, explosive emissions of SO$_2$, when logistical problems of access, safety and light conditions make COSPEC impossible, SO$_2$ emissions are picked up by the satellite-based total ozone mapping spectrometer (TOMS). TOMS data are available for two of the large collapse events, 3 July 1998, when 11 kt ± 30% SO$_2$ were recorded in one day; and on 26 December 1997, when 33 kt ± 30% SO$_2$ were present in the plume between 60 and 57°W at 1543Z [20]. The 26 December 1997 event involved a sector collapse followed by a volcanic blast relating to this unloading, a large dome collapse and pyroclastic flow activity down the south-west flank of the volcano.

We can make a first order approximation of the

<table>
<thead>
<tr>
<th>Method</th>
<th>Date</th>
<th>SO$_2$ flux, Mt</th>
</tr>
</thead>
<tbody>
<tr>
<td>COSPEC:</td>
<td>Jul 95 to Nov 99</td>
<td>0.77–0.88$^b$</td>
</tr>
<tr>
<td>TOMS:</td>
<td>26 Dec 97</td>
<td>0.033</td>
</tr>
<tr>
<td></td>
<td>3 Jul 98</td>
<td>0.011</td>
</tr>
<tr>
<td>Scaling factor$^c$</td>
<td>17 Sep 96</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>25 Jun 97</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>21 Sep 97</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.86–0.97$^d$</td>
</tr>
<tr>
<td>COSPEC</td>
<td>Nov 99–Sep 00</td>
<td>0.30</td>
</tr>
<tr>
<td>Scaling factor$^c$</td>
<td>20 Mar 00</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.35$^e$</td>
</tr>
</tbody>
</table>

Total: 1.17–1.26

Phase I refers to the first phase of dome-building, from November 1995 up to mid-March 1998, the residual period from mid-March 1998 up to the beginning of November 1999 and phase II from the onset of the second phase of dome-building (mid-November 1999) up the time of writing (September 2000). The lack of data between July 1997 and July 1998 is accounted for.

$^a$Using extrusion rate as a proxy [1].

$^b$Using diffusion tube data as a proxy.

$^c$Scaling factor based on mass material collapsed, using the mean SO$_2$ per tonne material collapsed away from the TOMS data for 26 December 1997 and 3 July 1998 (33 kt for 90×10$^6$ m$^3$ on 26 December 1997 and 11 kt for the collapse of 25×10$^6$ m$^3$ on 3 July 1998).

$^d$Estimate of total SO$_2$ emission for July 1995 to October 1999.

$^e$Estimate of total SO$_2$ emission for November 1999 to September 2000.
total SO$_2$ emitted during the other large, single events by scaling these emissions by mass of material collapsed away: $90 \times 10^6$ m$^3$ on 26 December 1997 and $25 \times 10^6$ m$^3$ on 3 July 1998. This approximation may be applied to collapses on 17 September 1996, 25 June 1997 and 21 September 1997. Integrating beneath the COSPEC SO$_2$ emission time series curve gives an approximate SO$_2$ emission from the Soufrière Hills Volcano during passive degassing between eruptive or collapse events. The year gap in data from July 1997 to July 1998 may be treated in one of two ways:

1. by using a scaling factor derived from mass of sulphur dioxide emitted per tonne of magma [21],

2. by using a scaling factor based on diffusion tube data collected every 2 weeks in Plymouth. Together, these records enable us to make an estimate that approximately 1.2 Mt SO$_2$ has been emitted between July 1995 and September 2000 (Table 3).

Open-path FTIR has yielded HCl:SO$_2$ mass ratios (Table 4). The spectra collected in 1996, using artificial and volcanic sources of infrared energy, were lacking in sulphur dioxide absorptions above detection limits. These detection limits suggest that the HCl:SO$_2$ mass ratio exceeded 10. This time series of HCl:SO$_2$ mass ratios may be combined with the COSPEC data to give an approximate HCl emission rate time series (Fig. 4).

4. Discussion

Up to September 1999, the volume of erupted magma is assumed to be of the order of 0.3 km$^3$ (of which 50–35% by volume is melt prior to ascent), equivalent to 240–345 Mt melt (assuming a melt density of 2300 kg/m$^3$). In order to account for the SO$_2$ flux seen at the surface during phase I of dome-building (a total emission of approximately 1 Mt), an original sulphur content of 1400–2100 ppm sulphur in the melt is necessary. The glass inclusions contain less than 50 ppm sulphur and sulphur is clearly not lost from the melt at any stage during the sequence of glasses analysed here (Fig. 3). The source of this excess sulphur is a common subject for debate and has been attributed to various processes, including the degassing of unerupted magma, sulphur released from the breakdown of sulphur-bearing phases such as anhydrite and pyrrhotite [22], sulphur released on mixing between reduced and more oxidised magmas [23] and the presence of a fluid phase at depth prior to eruption [24]. The mafic magma input into the andesite system and an associated vapour phase may have been the source of this sulphur. Sulphur fluid–melt partition coefficients have been found to be strongly dependent on redox conditions [25]. The presence of pyrrhotite in the mafic inclusion glass suggests that sulphur is locked up in this phase on saturation in

<table>
<thead>
<tr>
<th>Date</th>
<th>HCl:SO$_2$ mass ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 Jul 98</td>
<td>0.49</td>
</tr>
<tr>
<td>26 Jul 98</td>
<td>0.48</td>
</tr>
<tr>
<td>27 Jul 98</td>
<td>0.27</td>
</tr>
<tr>
<td>28 Jul 98</td>
<td>0.39</td>
</tr>
<tr>
<td>29 Jul 98</td>
<td>0.47</td>
</tr>
<tr>
<td>30 Jul 98</td>
<td>0.44</td>
</tr>
<tr>
<td>31 Jul 98</td>
<td>0.51</td>
</tr>
<tr>
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<tr>
<td>6 Sep 98</td>
<td>0.40</td>
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<tr>
<td>7 Sep 98</td>
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</tr>
<tr>
<td>25 Oct 98</td>
<td>0.48</td>
</tr>
<tr>
<td>26 Oct 98</td>
<td>0.23</td>
</tr>
<tr>
<td>27 Oct 98</td>
<td>0.22</td>
</tr>
<tr>
<td>31 Oct 98</td>
<td>0.22</td>
</tr>
<tr>
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<td>0.26</td>
</tr>
<tr>
<td>8 Nov 98</td>
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<tr>
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</tr>
<tr>
<td>8 Nov 99</td>
<td>0.35</td>
</tr>
<tr>
<td>7 Dec 99</td>
<td>0.47</td>
</tr>
<tr>
<td>11 Dec 99</td>
<td>0.72</td>
</tr>
<tr>
<td>21 Dec 99</td>
<td>2.01</td>
</tr>
<tr>
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<td>1.18</td>
</tr>
<tr>
<td>11 Aug 00</td>
<td>1.19</td>
</tr>
<tr>
<td>14 Aug 00</td>
<td>1.33</td>
</tr>
<tr>
<td>17 Aug 00</td>
<td>0.77</td>
</tr>
<tr>
<td>30 Aug 00</td>
<td>2.05</td>
</tr>
</tbody>
</table>

Uncertainties in these ratios are $\pm 5\%$.  

EPSL 5758 13-3-01
the mafic melt, and hence prior to contact with the andesite magma at 5–7 km, the fluid–melt partition coefficient for this melt was low [25]. At a low $f_{O_2}$, increasing the amount of sulphur in the melt will tend to increase the amount of pyrrhotite crystallising and will not increase the proportion of sulphur entering a coexisting vapour phase [25]. It is possible, then, that the relatively oxidising conditions of the andesite-bearing magma chamber induced the formation of a vapour phase at the time of intrusion, which effectively stripped the mafic melt of its sulphur at an early stage.

After extrusion of the andesite dome ceased in March 1998, SO$_2$ emission rates remained high and variable. The source of this SO$_2$ could have been the progressive degassing of the trapped reservoir of a sulphur-rich vapour phase in the conduit system, or from the ‘second boiling’ of the existing cooling and solidifying dome and upper conduit material. We can calculate whether the mass of sulphur remaining in the cooling 1995–1998 dome and conduit melt, on complete crystallisation, was enough to sustain SO$_2$ fluxes from March 1998 to November 1999. The volume of material remaining in the upper conduit and dome, cooling and crystallising anhydrous phenocrysts was approximately 0.06 km$^3$ in September 1999, with 65–95% crystallinity, i.e. 7–50 Mt of melt (assuming a melt density of 2300 kg/m$^3$). This implies a maximum further 1200–7000 tonnes of sulphur dioxide output (assuming a mean sulphur content of 70 ppm in the glass), which, at the mean rates of SO$_2$ emission throughout the post-extrusion phase (a mean of 150 tonne/day in August to October 1999), would sustain observed degassing rates for a mere 1–5 weeks. This suggests that the residual period SO$_2$ emission was the result of the continued supply of a fluid phase (derived from the mafic magma), migrating upwards with some aspects of the volcano’s activity reflecting permeability and fluid pressure build up in shallow levels of the dome.

Analyses of the glasses in this study show that a wide range of chlorine contents is recorded in matrix and inclusion glass (the chlorine contents of some of the plagioclase melt inclusion glasses are greater than 3500 ppm, reaching up to 4500 ppm, whilst the matrix glass chlorine contents range from 100 up to 2400 ppm). In order to interpret these observations fully, in terms of what processes cause loss of chlorine from the melt, we should consider the processes of crystallisation, which will increase the chlorine content of the melt, and degassing, which will counteract this increase. The chlorine contents of the matrix glasses in Fig. 3 may be explained by fractional crystallisation offset by the degassing of chlorine on magma ascent.

Melt inclusions inside plagioclase phenocrysts appear to indicate that significant amounts of chlorine were already dissolved within the andesite prior to mafic input. It is unlikely, due to viscosity and thermal contrasts, that the two magmas mixed significantly, and diffusion rates are thought to be too low [26] for efficient transfer of volatiles. Therefore the chlorine output as seen by the FTIR monitoring would most likely have been derived from the andesite, as it ascended to the surface.

Fig. 3 shows a clear kink where the crystallisation-induced increase in concentration of chlorine in the melt in the magma chamber was interrupted. The later glasses (lower $f$ value) lose chlorine, grading into and overlapping the field of the matrix glass chlorine concentrations. This implies that chlorine is being lost on magma ascent, when these matrix glasses were quenched. The change in trace element concentration of these glasses is likely to be the result of crystallisation on ascent, during syn-eruptive degassing of chlorine. The assumption of fractional crystallisation for the change on trace element abundances in the melt can therefore be justified as we seem to have mainly sampled melt that has evolved to its present composition through late-stage syn-eruptive crystallisation.

For a water-saturated rhyolite melt at 830°C and 100 MPa pressure, the solubility of chlorine in high-SiO$_2$ melts increases rapidly with chlorine molality in the aqueous fluid [27–29]. A solubility limit range for chlorine in the Soufrière Hills magma of 0.48–0.68 wt% for 860–890°C and 25–250 MPa has been determined from experimental work [19]. With decreasing pressure, chlorine solubility increases [28]. This implies that chlorine
should not degas on decompression at all, rather
that it is transported to the surface by the magma
and there eventually reaches the atmosphere by
second boiling as the melt cools and concentrates
chlorine to its solubility limits. However, the af-
finity of chlorine for a water-rich vapour phase
has been well documented [28,29] and provides
the means for chlorine to leave the melt on ascent
and crystallisation of the magma. The loss of
chlorine from the melt therefore depends on the
initial chlorine content of the melt, whether the
vapour phase is free to escape to the atmosphere
(i.e. a ‘closed’ or an ‘open’ system) and the rela-
tive rates of water and chlorine fluid–melt equili-
bration [29]. We can use the mass balance equa-
tion below for closed-system degassing
incorporating crystallisation to illustrate this argu-
ment:

\[
C_{\text{Cl}}^{\text{melt}} = \frac{C_{\text{Cl}}^{\text{melt}} M_{\text{melt}}}{M_{\text{melt}}(1 - \chi) + D_{\text{fluid/melt}}^{\text{fluid}} M_{\text{fluid}}}
\]  

(3)

where \(C_{\text{Cl}}^{\text{melt}}\) is the concentration of chlorine in the
melt; \(C_{\text{Cl}}^{\text{melt0}}\) is the initial chlorine content of the
melt (2070 ppm; this work); \(M_{\text{melt}}\) is the mass
of melt; \(M_{\text{fluid}}\) is the mass of fluid exsolved;
\(D_{\text{fluid/melt}}^{\text{fluid}}\) is the fluid–melt partition coefficient for
chlorine and \(\chi\) is the fraction crystallised. We
find that the effects of crystallisation and degass-
ing into a fluid phase effectively cancel out when
we assume a partition coefficient of around 10 for
closed-system degassing. We propose a higher fluid–melt partition coefficient of the order of 50, to
account for the loss of chlorine observed in the
matrix glasses after 95% crystallisation. Similarly,
open-system degassing, with chlorine entering a
fluid phase according to a Rayleigh distillation
process, is able to reduce chlorine contents suffi-
ciently with a fluid–melt partition coefficient of 50
or less.

We can calculate a total chlorine emission from
the petrological data for the first phase of dome-
building. The total volume of erupted material
during the first phase of activity (November
1995 to March 1998) was 0.3 km³. The propor-
tion of melt prior to ascent was 35–50% by vol-
ume, implying 240–345 Mt of melt using a density
of 2300 kg/m³. We can calculate the total chlorine
degassed using the difference between the chlorine
content of the most primitive plagioclase melt in-
clusions after 50% crystallisation (4500 ppm) and
the matrix glass chlorine content (800 ppm), and
scaling this to the total melt erupted. This implies
a total syn-eruptive degassing of 0.9–1.3 Mt HCl.

We can compare this with observations of HCl
emission at the surface (Fig. 4). If we assume a
similar ratio of HCl to SO₂ to that in 1996 pre-
valued during 1997 we can estimate the total HCl
release up to September 1999. This suggests a
minimum figure of 0.70 Mt HCl ± 35%, not ac-
counting for possible spikes during explosive peri-
ods, which is within error of that calculated by
the petrological method. The peak in chlorine
emission occurred at the peak of volcanic activity
and extrusion rate of andesite magma. This sub-
stantiates the idea that chlorine exsolves from the
melt on ascent at shallow levels in the system.

We can calculate whether the amount of chlor-
ine emitted to the surface as HCl during the re-
sidual period (non-extrusional) could potentially
be derived through the ‘second boiling’ of the ex-
isting original dome and conduit material, i.e.
during the crystallisation of chlorine-free pheno-
crys. With 7–50 Mt melt containing an average
of 800 ppm chlorine, 6–41 kt of HCl could ex-
solve on complete crystallisation. This, at emis-
sion rates of 80 tonne/day (the mean flux of
HCl during the residual period), could sustain de-
gassing for up to a year and a half.

The HCl emissions during the residual period
(between dome-building phases I and II) from
March 1998 up to November 1999 could therefore
be accounted for solely by second boiling of the
existing dome and conduit material. This is in
contrast to the behaviour of sulphur, which enters
a vapour phase at a greater depth, thereafter mi-
grating upwards slowly and discontinuously, sub-
ject to processes of sealing and permeability fluc-
tuations of the magma and edifice. We are
suggesting, therefore, the presence of a gas phase
that changes in composition with depth during erup-
tive periods. At magma chamber depths
\(X_S > X_{\text{Cl}}\) in the gas phase (where \(X_S\) and \(X_{\text{Cl}}\)
are the mass fractions of sulphur and chlorine
in the fluid phase), whilst at shallower depths
\(< 2 \text{ or } 3 \text{ km}), X_{\text{Cl}} > X_S\), with the change in these
mass fractions being a function of pressure, water fluid–melt equilibration and melt composition. During non-eruptive periods the concentration profile of this fluid phase will change as the chlorine source becomes shallower (second boiling in the upper conduit and dome).

4.1. How we may recognise 'the end of the eruption'

A decrease of the SO$_2$ flux down to low levels (< 200 tonne/day) does not necessarily indicate the waning of an eruption. SO$_2$ emission from June 1999 until October 1999 was generally less than 200 tonne/day, interrupted sporadically by higher values (1200 tonne/day following a small collapse on 4 September 1999). These higher values clearly indicate the production of a volatile phase in the deeper conduit or magma chamber system. It seems that whilst low HCl and SO$_2$ emission rates are an indication of a decrease in activity, SO$_2$ emission rates may be more influenced by the permeability of the edifice and conduit region. A stored gas phase at depth may be released into the atmosphere slowly and discontinuously, representing a considerable hazard in terms of explosions and fluid pressure-driven collapse. It remains to be seen how long the SO$_2$ vapour phase will take to dissipate fully, but it seems likely that SO$_2$ emission rates will eventually reach levels of < 150 tonne/day, after a period of some months to years. Gravitational collapses of the dome after this period should have little effect on gas emissions and this may be a criterion for assessing whether an eruption may be over. HCl fluxes, as we have seen, may be sustained for periods of years at low levels driven only by cooling and crystallisation of the existing dome material. The emission rate of HCl is likely to be low whilst there is no magma ascending to the surface. Therefore a very low HCl flux (< 100 tonne/day) is indicative of an absence of gas-rich magma near the surface. A high flux of HCl (> 100–200 tonne/day) may indicate magma degassing at intermediate to shallow depths, and a low HCl flux (< 100 tonne/day) may be the result of a low extrusion rate or the degassing of existing emplaced dome and conduit material.

5. Conclusions

SO$_2$:HCl ratios and absolute fluxes of these gas species form signatures characteristic of distinct features of volcanic activity. At Souffrière Hills Volcano we have seen that effusive dome-building episodes are associated with both high SO$_2$ (400–3000 tonne/day) and HCl fluxes (800–2000 tonne/day) and HCl:SO$_2$ of 1–5. HCl flux appears to be associated with periods of high extrusion rate and derived from the andesite magma, actively exsolving on ascent from the magma chamber. SO$_2$, in contrast, appears to be a constituent of a deep-seated (magma chamber depths) hydrous gas phase that is derived from the intruded mafic magma and released to the atmosphere in a discontinuous way, dependent on the permeability of the conduit and conduit wallrock. Periods of non-extrusion are associated with low HCl flux and a variable SO$_2$ flux, from < 50 tonne/day up to > 4000 tonne/day. During these periods HCl:SO$_2$ reaches values as low as 0.1 (January 1999).

It is proposed that HCl flux is a proxy for extrusion rate of the andesite lava at Soufrière Hills Volcano, whilst the variation in SO$_2$ emission rate is closely related to changes in the permeability of the system and the supply of sulphur from the mafic source at depth, and this may remain high many months to years after extrusion of andesite lava has ceased. We may define gas-based criteria to distinguish between episodes of ‘stasis’ between dome-building episodes and the ‘end of the eruption’. For example, a SO$_2$ flux of 150 tonne/day can only be sustained for a few weeks through crystallisation of the existing material at the surface. Therefore at any period, for the same volume of material, 2–3 weeks after the last extrusive event, if SO$_2$ emission rate is greater than or equal to 150 tonne/day even for a short period of time, then the eruption must be thought of as continuing. If SO$_2$ emission rates remain consistently low for a period of time over and beyond this time period, HCl emission rates are less than 100 tonne/day and the HCl:SO$_2$ ratio is less than 0.1, then the eruption is finishing.
Acknowledgements

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