1. Introduction

The Soufrière Hills Volcano (SHV) on Montserrat in the West Indies has been erupting episodically since 1995 [Sparks and Young, 2002; Loughlin et al., 2010; Wade et al., 2010]. The lava is a hornblende-hypersthene-normative andesite containing mafic enclaves of basaltic andesite composition [e.g., Murphy et al., 2000; Devine et al., 1998; Humphreys et al., 2009]. The activity to date has exhibited five eruptive phases, separated by pauses, typically of less than two years in duration until the latest pause, which began in 2010 and continues at the time of writing (July 2014). The sustained emission of SO$_2$ during these otherwise quiescent periods has been an important indicator of ongoing volcanic unrest [Edmonds et al., 2001; Oppenheimer et al., 2002; Christopher et al., 2010]. The Montserrat Volcano Observatory operationally measures SO$_2$ flux from the volcano during daylight hours, with a network of scanning UV spectrometers [Edmonds et al., 2003a, 2003b; Christopher et al., 2010] using Differential Optical Absorption Spectroscopy (DOAS), combined with meteorological information (wind velocity). Open-path Fourier-Transform Infrared (FTIR) spectroscopy is used to measure the molar ratio HCl/SO$_2$ in the volcanic plume [Oppenheimer et al., 2002; Edmonds et al., 2002; Christopher et al., 2010]. A key observation is that the ratio HCl/SO$_2$ decreases by a factor of around 10 during quiescent periods compared with periods of lava extrusion, and decreased steadily during a quiescent period [Oppenheimer et al., 2002]. The rise in HCl/SO$_2$ has been generally synchronous with the onset of lava extrusion and is a valuable monitoring tool [Edmonds et al., 2002; Christopher et al., 2010]. The trends have been interpreted in terms of chlorine partitioning into a hydrous vapor phase during ascent and degassing of the andesite; during pauses, little degassing of water and chlorine occurs and the plume is instead dominated by “deep-derived” SO$_2$ and CO$_2$ [Edmonds et al., 2002, 2010].

Subduction zone magmas are, in general, enriched in halogens due to the devolatilization of chlorine-bearing minerals in the subducting slab [e.g., Poli and Schmidt, 2002; Wallace, 2005; Pyle and Mather, 2009; Baker and Balcone-Boissard, 2009]. The abundance of chlorine in typical arc-related rhyolite melts may reach 0.85 wt% (although more typically ranges up to around 0.45 wt%) [Wallace, 2005]. The concentration of bromine in rhyolitic melts has been reported in the range 0.0001–0.03 wt%, based on published melt inclusion and matrix glass data [Aiuppa et al., 2009; see also Gerlach, 2004; Aiuppa et al., 2005; Bureau et al., 2010;
Table 1. Halogen and Sulfur Gas Ratios From the Literature, Measured Spectroscopically (Either by FTIR for HCl/SO$_2$ or by DOAS)$^{a}$

<table>
<thead>
<tr>
<th>Volcano</th>
<th>Magma Composition</th>
<th>Tectonic Setting</th>
<th>Date of Measurement</th>
<th>HCl/SO$_2$ (mol/mol)</th>
<th>BrO/SO$_2$ (mol/mol)</th>
<th>OCIO/SO$_2$ (mol/mol)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambrym</td>
<td>Basalt</td>
<td>Subduction zone</td>
<td>Mar 2003</td>
<td>$2.3 \times 10^{-4}$</td>
<td>$1.4 \times 10^{-3}$</td>
<td></td>
<td>Bani et al. [2009]</td>
</tr>
<tr>
<td>Etna</td>
<td>Basalt</td>
<td>Subduction related</td>
<td>Jul 2001, Oct 2000</td>
<td>$2.5 \times 10^{-4}$</td>
<td>$5.7 \times 10^{-1}$</td>
<td></td>
<td>Burton et al. [2003], Louban et al. [2009], Allard et al. [2005], Bobrowski and Platt [2007], Bobrowski et al. [2007]</td>
</tr>
<tr>
<td>Eyjafjallajökull</td>
<td>Dacite mixed</td>
<td>Mantle plume</td>
<td>Mar 1999, May 2001</td>
<td>$1.1 \times 10^{-4}$</td>
<td>$3 \times 10^{-4}$</td>
<td></td>
<td>Heur et al. [2011]</td>
</tr>
</tbody>
</table>

$^{a}$Passive" denotes studies where a distinction was made between explosive release of gas and quiescent degassing. All HCl/SO$_2$ ratios have been recalculated to molecular ratios where necessary. Where the volcano was not erupting at the time that the gas measurements were made, magma composition is taken as that of the most recent eruption prior to the measurements.

Kutterolf et al., 2013). The SHV is notable in comparison to other arc volcanoes for the relative chlorine enrichment observed in its gas emissions, in apatite and in melt inclusions [Edmonds et al., 2002; Oppenheimer et al., 2002; Villemant et al., 2008; Humphreys et al., 2009]. It has been inferred that volatiles in the atmospheric plume are sourced from both the mafic magma at depth and from andesite degassing during decompression and eruption [Edmonds et al., 2001].

Plagioclase-hosted melt inclusions in SHV lavas contain up to 0.45 wt% chlorine [Edmonds et al., 2001; Humphreys et al., 2009]; the concentration of bromine in melt inclusions has not been measured. Signorelli and Carroll [2001] determined experimentally that the SHV magma could contain up to 0.68 wt% Cl before an immiscible brine phase would form. The exsolution of chlorine from melt takes place via partitioning into an aqueous phase, which depends primarily on melt composition [Webster et al., 1999; Shinohara et al., 1989; Shinohara, 1994]. A fraction of the chlorine degassing from the rhyolitic melt likely also occurs at magma reservoir pressures, and may be controlled by the activity of H$_2$O in the coexisting vapor. Zonation in the Cl/OH content of hornblende phenocrysts may be explained by the addition to the andesite of a hot CO$_2$-rich vapor from basaltic magma, thereby changing the activity of H$_2$O and Cl partitioning behavior [Humphreys et al., 2009]. The mass flux of chlorine-bearing gases is dependent on the degassing flux of water and on crystallization, which will drive CI out of the melt during degassing-induced undercooling [Villemant and Boudon, 1999; Edmonds et al., 2002; Villemant et al., 2005, 2008]. This mechanism for chlorine degassing provides an explanation for high HCl/SO$_2$ ratios in the volcanic gases during lava extrusion, when chlorine is actively partitioning into the vapor exsolved on magma ascent, promoted by rapid crystallization of microlites in the rhyolitic melt. Changes in the ratio of sulfur to chlorine in volcanic gases may also be caused by second boiling during prolonged cooling and crystallization of shallow-emplaced or erupted magmas [Symonds et al., 1996]. Very little is understood, in contrast, about the behavior of bromine during degassing.
In 2002, the bromine monoxide (BrO) content of a volcanic plume was measured for the first time using a miniature ultraviolet spectrometer at SHV [Bobrowski et al., 2003]. These were the first observations of reactive bromine associated with volcanic degassing, and they were made during a period of eruption. BrO is thought to form from magmatic hydrogen bromide (HBr) via two mechanisms. In the very early plume, HBr can react with OH radicals to form Br [Roberts et al., 2009]. Alternatively and more prominently, HBr can react with HOBr on aerosol particles to form Br2, which photolyses to Br [von Glasow, 2010]. Br then reacts with ozone (O3) to form BrO.

It has been observed at a number of volcanoes (Table 1), but not previously interpreted with respect to bromine partitioning at depth. The abundance of BrO relative to SO2 has been observed to increase rapidly in the first few minutes after release from the vent [Bobrowski et al., 2007]. The ratio has also been shown to vary with volcanic activity at Etna [Bobrowski and Giuffrida, 2012]. However, the behavior of bromine in melts is very poorly understood. Under experimental conditions, synthetic melts suggest a higher fluid-melt partition coefficient for Br than for Cl [Bureau et al., 2000]. However, Villemant et al. [2008], based on studies of SHV, posit that the ratio of fluid-melt partition coefficients is closer to 1.

Recent experiments by Louvel [2011] demonstrate that, at upper crustal pressures, there is still considerable uncertainty regarding bromine behavior, and this is further demonstrated in the data presented by Kutterolf et al. [2013]. There are thus outstanding questions concerning the partitioning behavior of Br between melt and its source.
and hydrous vapor in relation to that of Cl. There are also resulting questions concerning the potential use of BrO as a monitoring tool [Bobrowski and Giuffrida, 2012].

In 2011, a series of spectra were acquired at SHV using a UV spectrometer and analyzed by DOAS in order to quantify the relative abundances of SO2, BrO and any other reactive gas species. Our principal aim was to identify whether or not BrO was still being generated in the plume during a quiescent period, i.e., during an interval of no lava dome growth when we might expect the proportion of halogens to be reduced. The relative abundances of Cl and Br, given our understanding of the degassing budget at SHV, might yield insight into the degassing behavior of these volatiles from the andesite. Our findings have implications for the utility of measuring BrO/SO2 for volcano monitoring purposes. Given the high levels of halogens recorded at SHV by previous authors [Bobrowski et al., 2003; Edmonds et al., 2001, 2002; Christopher et al., 2010], we also analyzed spectra for the presence of OClO and report for the first time measurements of this species at SHV, which has important implications for understanding reactive halogen chemistry in volcanic plumes.

2. Methods

2.1. Measurements

Measurements were made on seven days over three weeks during April 2011, on days when conditions were close to optimal for minimizing the impact of scattering effects on DOAS retrieval results (see "Field conditions" below). Field locations are shown in Figure 1. Efforts were made to estimate the evolution of the plume chemistry with distance from the vent. The measurement locations varied depending on meteorological conditions and plume direction. While the dominant plume direction on Montserrat is to the west, over the former capital city Plymouth, on several of our measurement days the plume was transported to the west-north-west.

An Ocean Optics 2000 UV spectrometer attached to a single lens telescope via a solar-resistant optical fibre bundle and assembled in a thermostabilized box was used. The resulting field of view was 8 mrad. The spectrometer acquires spectra with a wavelength range of 285–430 nm and a resolution of 0.47 nm (full-width-at-half-maximum), which excludes under-sampling effects [Roscoe et al., 1996; Chance et al., 2005]. A Hoya U-330 ultraviolet filter was placed in front of the lens to reduce the amount of stray light in the spectrometer. The device was mounted on a tripod. Wavelength calibration and instrumental function of the spectrometer were determined by means of mercury and cadmium calibration lamps. These results were tested using the calibration approach of QDOAS [Danckaert et al., 2012]. The solar spectrum reported by Chance and Kurucz [2010], convolved to spectrometer’s resolution, was compared with spectra measured outside the plume.

Spectra were recorded using Ocean Optics Spectrasuite software and DOASIS [Kraus, 2006]. The telescope elevation was fixed so as to point at the plume centre, as judged visually. The angle of elevation varied from day to day between 15° and 45°. The azimuth of the observation direction varied depending on the desired plume age. Total integration time (exposure time multiplied by the number of coadded spectra acquired) for the individual measurements was maintained at 10 s, and the exposure time varied automatically depending on the light conditions in order to avoid saturation effects. Plume-free background spectra were measured before and after every measurement period. The background spectra were recorded at comparable elevation angles and azimuths to the measurements, usually above the plume, toward the zenith and also toward the north. Background spectra were examined in the field to check that they were registered outside of the plume. This involved retrieval of SO2, ozone and fitting of the Ring effect, but with the convolved solar spectrum used as a reference [Salerno et al., 2009]. In addition, dark (10 s integration time without coadds) and offset (3 ms integration time 10,000 coadds) spectra were recorded before and after every measurement period.

2.2. Field Conditions

Montserrat is subject to strong easterly winds, which dispersed the plume rapidly off the island on most of the measurement days, such that the plume transport was turbulent rather than laminar. The plume was largely transparent, but varied in opacity. Measurements were performed only when plume transmittance was \( \leq 0.75 \) (estimated by using background and plume spectra at 370 nm) and horizontal visibility was at least 20 km. The plume width at locations where spectra were collected was about 2 km (based on airborne traverses performed during 2012). Thus the extinction of plume aerosols is less than 0.14 km\(^{-1}\) whilst the
Table 2. Summary of Data Sets Collected During the Measurement Perioda

<table>
<thead>
<tr>
<th>Data Set</th>
<th>Date in April 2011</th>
<th>Telescope Elevation (°)</th>
<th>Telescope Azimuth (°)</th>
<th>Wind Speed (Standard Deviation) (Average m/s)</th>
<th>Wind Direction (Standard Deviation) (°)</th>
<th>Approximate Plume Age (min)</th>
<th>Approx distance to plume centre (km)</th>
<th>No. Spectra before average</th>
<th>Local Start Time</th>
<th>Local End Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>2M1B</td>
<td>2</td>
<td>18</td>
<td>240</td>
<td>11.8 (2.1)</td>
<td>99.2 (9.4)</td>
<td>18</td>
<td>4</td>
<td>410</td>
<td>12:40</td>
<td>15:08</td>
</tr>
<tr>
<td>2M2A</td>
<td>2</td>
<td>23</td>
<td>150</td>
<td>11.4 (1.5)</td>
<td>98.5 (7.2)</td>
<td>5</td>
<td>3</td>
<td>110</td>
<td>16:10</td>
<td>16:45</td>
</tr>
<tr>
<td>3M1C</td>
<td>3</td>
<td>28</td>
<td>120</td>
<td>10.4 (1.3)</td>
<td>94.3 (8.3)</td>
<td>4</td>
<td>5</td>
<td>153</td>
<td>15:34</td>
<td>16:23</td>
</tr>
<tr>
<td>9M1A</td>
<td>9</td>
<td>45</td>
<td>185</td>
<td>11.0 (1.5)</td>
<td>99.9 (8.8)</td>
<td>11</td>
<td>3</td>
<td>221</td>
<td>12:08</td>
<td>13:22</td>
</tr>
<tr>
<td>9M4A</td>
<td>9</td>
<td>20</td>
<td>165</td>
<td>10.3 (1.3)</td>
<td>101.1 (8.2)</td>
<td>8</td>
<td>2</td>
<td>250</td>
<td>15:54</td>
<td>17:09</td>
</tr>
<tr>
<td>10M1A</td>
<td>10</td>
<td>25</td>
<td>150</td>
<td>8.2 (1.2)</td>
<td>98.9 (9.2)</td>
<td>11</td>
<td>4</td>
<td>165</td>
<td>13:26</td>
<td>14:20</td>
</tr>
<tr>
<td>10M4A</td>
<td>10</td>
<td>20</td>
<td>195</td>
<td>8.4 (1.1)</td>
<td>97.4 (8.0)</td>
<td>13</td>
<td>2</td>
<td>292</td>
<td>16:11</td>
<td>17:35</td>
</tr>
<tr>
<td>17M4A</td>
<td>17</td>
<td>15</td>
<td>230</td>
<td>4.5 (1.1)</td>
<td>77.5 (14.2)</td>
<td>60</td>
<td>12</td>
<td>202</td>
<td>13:05</td>
<td>14:15</td>
</tr>
<tr>
<td>17M4B</td>
<td>17</td>
<td>15</td>
<td>205</td>
<td>5.3 (1.1)</td>
<td>68.5 (10.6)</td>
<td>28</td>
<td>4</td>
<td>214</td>
<td>14:34</td>
<td>15:51</td>
</tr>
<tr>
<td>17M4C</td>
<td>17</td>
<td>20</td>
<td>170</td>
<td>5.7 (1.2)</td>
<td>73.4 (9.4)</td>
<td>14</td>
<td>3</td>
<td>201</td>
<td>16:11</td>
<td>17:38</td>
</tr>
<tr>
<td>18M4B</td>
<td>18</td>
<td>25</td>
<td>125</td>
<td>4.4 (0.8)</td>
<td>91.6 (9.4)</td>
<td>12</td>
<td>3</td>
<td>405</td>
<td>15:18</td>
<td>17:37</td>
</tr>
<tr>
<td>19M1A</td>
<td>19</td>
<td>30</td>
<td>130</td>
<td>3.5 (1.4)</td>
<td>88.5 (17.2)</td>
<td>12</td>
<td>5</td>
<td>263</td>
<td>11:18</td>
<td>12:50</td>
</tr>
</tbody>
</table>

Table 3. Absorption Cross Sections Used in the Fitting Process.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Reference Cross Section</th>
<th>Temperature/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO2</td>
<td>Bogumil et al. [2003]a</td>
<td>293</td>
</tr>
<tr>
<td>O3</td>
<td>Burrows et al. [1999]</td>
<td>273</td>
</tr>
<tr>
<td>O2</td>
<td>Greenblatt et al. [1990]</td>
<td>296</td>
</tr>
<tr>
<td>BrO</td>
<td>Fleischmann et al. [2004]</td>
<td>293</td>
</tr>
<tr>
<td>OCIO</td>
<td>Kromminga et al. [2003]</td>
<td>293</td>
</tr>
<tr>
<td>NO2</td>
<td>Vandaee et al. [1998]</td>
<td>293</td>
</tr>
<tr>
<td>HCHO</td>
<td>Meller and Moorgat [2000]</td>
<td>298</td>
</tr>
</tbody>
</table>

aThe choice of cross section was made because Bogumil et al. [2003] measured temperature-dependent cross sections. Their data were collected at a resolution of 0.2 nm using SCIAMACHY, and therefore we deconvolved the cross section to 0.1 nm for our retrievals.
Figure 2. Example of a fit for BrO and OClO in the range 331–357 nm. Column amounts are stated for each gas, with error in brackets. Units are intensity (arbitrary units). All shifts < 0.2 in magnitude; squeeze = 1 except for SO$_2$ (0.985) and Ring (0.988).
3. Results

Table 4 shows the average column amounts of SO2 retrieved in each of the data sets. We applied a detection limit of three times the retrieval error in selecting the data. This allows for small errors due to scattering and laser effects. Table 4 also shows average ratios obtained for each data set. All ratios are based on molar proportions. BrO/SO2 was lowest (down to 5.0 $\times 10^{-2}$) in young plume, with higher values (>1.0 $\times 10^{-2}$) occurring for plume ages exceeding 8 min, in general. However, after the first 20 min, there seems to be little impact of plume age on BrO/SO2. This is consistent with results from other studies [e.g., Bobrowski and Giuffrida, 2012]. The BrO/SO2 molar ratio was consistently around 2 $\times 10^{-2}$ for a plume of similar age to that measured by Bobrowski et al. [2003]. OClO was identified conclusively in three of the data sets.

Figure 3 shows correlations between SO2 and BrO for six of the measurement days. The BrO/SO2 ratio is consistent across the period, though there is some variation in slant column densities.

The final week of measurements was characterized by lower wind speeds and clearer skies. Attempts to measure the ageing plume offshore on 17 April 2011 had limited success due to attenuation and the angle at which the measurements had to take place (over the ocean, with a long path through the plume). Successful measurements demonstrate that the ratio of BrO to SO2 remained relatively constant through the different plume ages on 17 April (Figure 4a). On 9 and 10 April, higher ratios of BrO/SO2 were found later in the day (Figure 4a; compare Table 3). There is no discernable relationship between SO2 column amount and the BrO/SO2 ratio (Figure 4b).

It was possible to detect both BrO and OClO on 18 April (Figure 5). While the correlation between BrO and OClO is relatively good, the relationship between SO2 and OCIO is less so but still apparent. Note that correlation between SO2 and OCIO is weaker than that between SO2 and BrO. While OCIO was detected on 2 April, it was not present at sufficient levels for reliable retrievals during the second week of measurements (9–16 April). BrO abundance was lower relative to SO2 in the first week of measurements, coincident with a higher SO2 flux [MVO, 2011].

4. Discussion

4.1. Bromine in the Soufrière Hills Magmas

Our results suggest that the ratio of BrO/SO2 was almost an order of magnitude lower at the time of our measurements compared with those of Bobrowski et al. [2003] (Figure 6). Measuring the plume during eruptive activity in May 2002, Bobrowski et al. [2003] obtained an average BrO/SO2 ratio of 8.2 $\times 10^{-4}$ (and also quote 1.0 $\times 10^{-3}$ as representative), while our average ratio is 1.75 $\times 10^{-4}$ and our highest is 3.1 $\times 10^{-4}$ (Table 3 and Figure 3). While Bobrowski et al. [2003] measured slant column amounts (SCA) of BrO up to 2.0 $\times 10^{15}$ molecules cm$^{-2}$, our highest BrO SCA is 5.78 $\times 10^{14}$ molecules cm$^{-2}$. There are several possible explanations for this. Initially, we consider the possibility that the differences are within error of the measurement technique. We then examine two further possibilities – a change in the rate of HBr oxidation to...

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Table 4. Summary of Data Sets Obtained, and the Detection of Reactive Halogens in the Plume

<table>
<thead>
<tr>
<th>Data Set</th>
<th>Average SO2 CA $\times 10^{18}$ Molecules/cm$^2$</th>
<th>Average BrO/SO2 mol/mol $\times 10^{-4}$</th>
<th>Average OCIO/SO2 mol/mol $\times 10^{-4}$</th>
<th>Average BrO/OClO mol/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>2M1B</td>
<td>1.4</td>
<td>1.1</td>
<td>5.8</td>
<td>0.2</td>
</tr>
<tr>
<td>2M2A</td>
<td>3.1</td>
<td>1.0</td>
<td>n.d.</td>
<td>0.2</td>
</tr>
<tr>
<td>3M1C</td>
<td>0.8</td>
<td>1.5</td>
<td>n.d.</td>
<td>0.2</td>
</tr>
<tr>
<td>9M1A</td>
<td>0.6</td>
<td>2.6</td>
<td>d.l.</td>
<td></td>
</tr>
<tr>
<td>9M4A</td>
<td>0.8</td>
<td>3.7</td>
<td>d.l.</td>
<td></td>
</tr>
<tr>
<td>10M1A</td>
<td>1.4</td>
<td>1.8</td>
<td>d.l.</td>
<td></td>
</tr>
<tr>
<td>10M4A</td>
<td>1.4</td>
<td>2.4</td>
<td>d.l.</td>
<td></td>
</tr>
<tr>
<td>17M4A</td>
<td>0.4</td>
<td>2.0</td>
<td>n.d.</td>
<td></td>
</tr>
<tr>
<td>17M4B</td>
<td>0.7</td>
<td>2.5</td>
<td>n.d.</td>
<td></td>
</tr>
<tr>
<td>17M4C</td>
<td>0.4</td>
<td>2.5</td>
<td>n.d.</td>
<td></td>
</tr>
<tr>
<td>18M4B</td>
<td>1.0</td>
<td>3.1</td>
<td>4.2</td>
<td>0.7</td>
</tr>
<tr>
<td>19M1A</td>
<td>0.9</td>
<td>1.3</td>
<td>5.2</td>
<td>0.2</td>
</tr>
</tbody>
</table>

The abbreviation d.l. means that although the species was detected, it was very close to the detection limit. M1–M4 represent the location of the measurements, as shown in Figure 1. Times are local (equivalent to Eastern Standard Time, UTC—5 h). Plume age was calculated from the wind speed and distance of measured light path from the volcano.
BrO (with the implication that the flux of bromine from the volcano might not have changed), and a change in the partitioning behavior of Br from the melt into the gas phase.

The DOAS technique and retrievals are subject to instrumental and analytical error. The instrumental setup for this project and the locations of the measurements were different to that of Bobrowski et al. [2003]. Bobrowski et al. [2003] and Bobrowski and Platt [2007] do not provide details about the meteorological conditions and transparency of the plume during their measurements. They also used a different wavelength range for the evaluation of SO2 (307.5–316 nm), while we used 310–323.67 nm to improve the signal-to-noise ratio. It is possible, too, that the turbulence of the plume due to varying wind velocities could impact the results. However, our ratios are relatively constant in spite of significant variations in weather conditions within our measurement period.

The SO2 flux at the time of the measurements by Bobrowski et al. [2003] was slightly lower than that during our measurements, which might imply that the changes in the ratio in part relate to SO2 not BrO. Errors on the SO2 measurements are also high (10–30%; Edmonds et al., 2003a, 2003b; Christopher et al., 2010).

Figure 3. Results for BrO for several days during April 2011, including all data recorded on each day. Typical errors are $3 \times 10^{13}$ molecules cm$^{-2}$ for BrO and $2.5 \times 10^{16}$ molecules cm$^{-2}$ for SO2; all data shown are above the detection limit of three times the retrieval error.
However, the column amounts for SO2 measured by Bobrowski et al. [2003] are comparable to ours (with the exception of the 2M2A data set on 2 April, which represents very young plume with a higher SCA of SO2). We also obtain a lower ratio regardless of time of day and plume age, encompassing the possible ranges of measurements by Bobrowski et al. [2003] and therefore excluding the possibility of significant influence from processing artefacts. While Bobrowski et al. [2003] may have underestimated SO2 due to saturation effects, this is not consistent with the lower flux and similar column amounts in 2002. Our observation that most of the change in BrO/SO2 occurs in the first few minutes is consistent with the results of Bobrowski et al. [2007] and Bobrowski and Giuffrida [2012]. While some of the difference might be attributable to error, its magnitude is large enough that other mechanisms should be explored. Therefore, bearing in mind the changing volcanic activity, it is probable that there is less BrO relative to SO2 (the flux of which remains relatively high and constant; Figure 7) in the plume at SHV during eruptive pauses. If the difference in measured BrO/SO2 between periods of dome growth and hiatus is real, it suggests that, for our measurement period either (i) lower reaction rates to convert HBr to BrO in the plume or (ii) less HBr in the magmatic gas phase relative to SO2. We will discuss these possibilities in turn.
4.1.1. Plume Processes: Reaction Rates for HBr to BrO

In this section, we assume, as is well documented [e.g., Gerlach, 2004; Oppenheimer et al., 2006a; Bobrowski et al., 2007; Roberts et al., 2009], that BrO is not a primary magmatic gas. The formation of BrO in volcanic plumes via conversion of HBr initially occurs due to reaction with OH radicals:

\[ \text{HBr} + \text{OH} \rightarrow \text{Br} + \text{H}_2\text{O} \] (R1)

\[ \text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2 \] (R2)

This reaction occurs in the earliest plume. Reaction of BrO with HO2 and NO2 may then occur [but see von Glasow, 2010], generating HOBr and BrONO2. These are highly reactive in acidic aerosols [Oppenheimer et al., 2006a, 2006b], generating BrCl and Br2—Br2 being favored under volcanic conditions [Roberts et al., 2009]. This reaction rapidly increases the Br2 abundance in the plume. Br2 preferentially partitions back into the gas phase, and it is rapidly photolysed:

\[ \text{Br}_2 \rightarrow \text{h}_\text{m} \rightarrow 2\text{Br} \] (R3)

Br then reacts with ozone (R2). The rapid acceleration of BrO formation in the early volcanic plume is well documented by both observations and models [Bobrowski and Platt, 2007; Oppenheimer et al., 2006a, 2006b; Bobrowski and Giufrida, 2012; Bobrowski et al., 2007; Afe et al., 2004]. It is dependent on the availability of OH, O3 and aerosols — and on the mixing ratio of atmospheric and volcanic gas [Martin et al., 2006]. The availability of photons for reaction with Br2 is clearly also important. This could vary seasonally, with time of day and with cloud cover. Initially we will discuss variability in environmental factors, and then use HCl and SO2 data to calculate the potential difference in oxidation rates.

Bobrowski et al. [2003] measured the plume in May 2002; our measurements were carried out in April 2011. It is unlikely that seasonal variation in actinic flux affected the difference in measurements [e.g., Madronich, 1987; Dlugokencky et al. 1996]. Our measurements spanned a 3 week period, and were made at a range of times of day. The volcanic plume may have been smaller during our measurements and was potentially...
more transparent due to a lack of ash/condensation, both of which should facilitate, not inhibit, BrO formation (by promoting both mixing with ambient air and photolysis).

At the time of the measurements, fumarole temperatures on the lava dome measured remotely by MVO exceeded 500°C [MVO, 2011]. This suggests that temperatures in the shallow system were close to magmatic and that there has been little change in gas temperature that might affect HBr reactions [Gerlach, 2004; Martin et al., 2006, 2012; Roberts et al., 2009]. However, other factors in the plume may still contribute to changing rates of conversion of HBr to BrO (e.g. atmospheric effects and aerosol processes; see for example Martin et al., 2012), and we investigate this further using published data from petrological studies of SHV.

Pumiceous clasts with high vesicularity at SHV have higher Cl and Br content than dome rocks, and both species appear to have similar degassing behaviors [Villemant et al., 2008] (using whole-rock Br content corrected for the small amount in hornblende phenocrysts). Open-system degassing promotes halogen exsolution. Both species have fluid-melt partition coefficients $>1$ in water-rich systems [Villemant et al., 2008; Bureau et al., 2000]. Halogens are enriched in the melt by crystallization whilst also being depleted due to H$_2$O degassing and partitioning into the gas phase. While experimental data from Bureau et al. [2000] suggest that gas-melt partition coefficients between the halogens increase from Cl to Br, these data are based on synthetic albitic melts. The modeling of Villemant et al. [2008] suggests that the halogens (other than F) in fact have similar vapor-melt partition coefficients in natural systems. They further report that the Cl/Br ratio in the SHV andesite is anomalously low (of the order of 160 by mass) and suggest that this relates to shallow contamination of the melt. The Cl/Br mass ratio in the basalt, on the other hand, is $\sim 300$ [Villemant et al., 2008].

The mass ratio of Cl in HCl gas to Br in BrO (Cl/Br*) has been estimated as $\sim 500$ [Villemant et al., 2008], based on measurements obtained via infrared and ultraviolet spectroscopy of the plume [Oppenheimer et al., 1998; Bobrowski et al., 2003; Edmonds et al., 2002]. The inferred high rate of oxidation of HBr to BrO is contrasted with an inferred scavenging of Cl into aerosols and particulate surfaces, as suggested by leachate [Edmonds et al., 2003a, 2003b] and aerosol data [Allen et al., 2000]. Using the data obtained in all our measurements with an estimated SO$_2$ flux and HCl/SO$_2$ ratio (see Table S), we obtain a Cl/Br* mass ratio of 1300:500. This suggests that not only has BrO/SO$_2$ decreased but that BrO has decreased relative to HCl.

Following Villemant et al. [2008] and taking the ratio of the fluid-melt partition coefficients as unity, the mass of bromine in the fluid phase can be calculated from the mass of chlorine (based on the HCl/SO$_2$ mass ratio and an estimated SO$_2$ flux) and the concentration of both elements in the melt (Cl/Br = 160). This suggests that for 175 Mg of chlorine in the gas phase, there are 1.09 Mg of bromine (Br$_{total}$). We would thus expect a BrO/SO$_2$ mass ratio of $7.3 \times 10^{-4}$ for andesite degassing and $3.8 \times 10^{-4}$ for basalt degassing—if all the bromine and chlorine in the melt is degassed in an open system and a third of the Br is oxidized to BrO. Our average BrO/SO$_2$ mass ratio is $3.2 \times 10^{-4}$. This suggests either that the ratio of the partition coefficients is not unity in our case, or that the amount of HBr being oxidized is lower than at the time of the measurements made by Bobrowski et al. [2003]. If the latter is the case, then we calculate that $\sim 15\%$ of the total bromine emission from the volcano was being oxidized during our measurement period. This is roughly half the mass of HBr that was being oxidized during the 2002 measurements.

4.1.2. Magma Processes: Changes in the Relative Partitioning of Halogens

Another plausible scenario based on the evidence presented here is that the HBr/SO$_2$ ratio of gas emitted from the volcano is lower during times of eruptive hiatus. This has implications both for Br partitioning...
between fluid and melt, and also potentially for volcano monitoring. If the rate of atmospheric oxidation of HBr to BrO is the same for our observation period as for that of Bobrowski et al. [2003], then the Br emission relative to Cl and SO2 has decreased. Bromine may be more “soluble” than sulfur in basaltic magmas at Mount Etna [Bobrowski and Giuffrida, 2012]. However, there are several critical differences between Etna and SHV that might affect bromine degassing. It is known that Cl partitioning, for example, is affected by pressure, temperature and composition of the melt and vapor phases [Webster, 1992; Metrich and Rutherford, 1992; Bureau and Metrich, 2003; Louvel, 2011], and is inhibited during closed-relative to open-system degassing [Villemant et al., 2008]. Bromine may have a higher partitioning coefficient than chlorine in synthetic albite melts [Bureau et al., 2000], but this may not apply at SHV because of the lower polymerization of natural rhyolitic melts [Villemant et al., 2008; Balcone-Boissard et al., 2010; Louvel, 2011]: there are unresolved questions about the partitioning behavior of the halogens relative to each other in diverse systems. In this section, we speculate on a possible interpretation of our data in combination with measurements from Montserrat reported by the MVO, the work of Bobrowski et al. [2003] and that of Villemant et al. [2008], and compare this with results from the experimental petrology literature.

The decrease of Br relative to Cl suggests that the relative partitioning of Cl and Br into the fluid phase has changed. If we take the SO2 fluxes reported by MVO during the period (Table 5), the relatively constant mass ratio of HCl/SO2 during measurements [Villemant et al., 2008] calculated from Table 4, this relationship can be modeled. Figure 8 shows a plot of Cl/Br in the gas phase (HCl and BrO) against the Br in BrO for our data and those of Bobrowski et al. [2003]. This suggests a power law upon which the ratio of partition coefficients may depend.

The partition coefficient of chlorine in rhyolitic melts varies with melt chlorine content [Villemant et al., 2008]. Figure 8 suggests that the ratio between the fluid-melt

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**Table 5. Pertinent Quantities From the Literature, used in the Modeling**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Data Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO2 flux average wk 1</td>
<td>696 tonnes per day</td>
<td>MVO Weekly Reports</td>
</tr>
<tr>
<td>SO2 flux average wk 2</td>
<td>514 tonnes per day</td>
<td>MVO Weekly Reports</td>
</tr>
<tr>
<td>SO2 flux average wk 3</td>
<td>596 tonnes per day</td>
<td>MVO Weekly Reports</td>
</tr>
<tr>
<td>SO2 flux during measurements of Bobrowski et al. [2003]</td>
<td>400 tonnes per day</td>
<td>Villemant et al. [2008]</td>
</tr>
<tr>
<td>Cl in melt inclusions</td>
<td>1500–4500 ppm</td>
<td>Humphreys et al. [2009]</td>
</tr>
<tr>
<td>HCl/SO2 mass ratio during measurements</td>
<td>0.3 ± 0.06</td>
<td>SAC Report 16, Appendix 2 [SAC, 2011]</td>
</tr>
<tr>
<td>HCl/SO2 mass ratio in measurements of Bobrowski et al. [2003]</td>
<td>0.5 ± 0.1</td>
<td>Villemant et al. [2008]</td>
</tr>
<tr>
<td>Cl/Br mass ratio (andesite)</td>
<td>160</td>
<td>Villemant et al. [2008]</td>
</tr>
<tr>
<td>Cl/Br mass ratio (basalt)</td>
<td>300</td>
<td>Villemant et al. [2008]</td>
</tr>
<tr>
<td>D_Cl/D_Br (experimental)</td>
<td>0.46</td>
<td>Bureau et al. [2000]</td>
</tr>
<tr>
<td>D_Cl/D_Br (modeled)</td>
<td>1</td>
<td>Villemant et al. [2008]</td>
</tr>
</tbody>
</table>

*Partition coefficients from Bureau et al. [2000] are for their experimental conditions at 200 MPa, 900°C.*
partition coefficients for Cl and Br, \( \frac{D_{\text{Cl}}}{D_{\text{Br}}} \), varies with gas Br content. We can quantify this relationship using the following equation:

\[
\frac{D_{\text{Cl}}}{D_{\text{Br}}} = \left( \frac{x_{\text{Cl}}}{x_{\text{Br}}} \right) \left( \frac{x_{\text{M}}}{x_{\text{F}}} \right)
\]

In this equation, \( D \) represents the fluid-melt partition coefficients and \( X \) the concentrations in fluid and melt. This assumes that the original mass ratio of Cl/Br in the melt was 160 (Villemant et al., 2008) (all Br being sourced from the andesite). From Figure 8, we obtain the relationship \( \frac{x_{\text{Cl}}}{x_{\text{Br}}} = 19(Br^*)^{-1.8} + 285 \). This gives a ratio of partition coefficients of \( \sim 0.05(Br^*)^{-1.8} + 0.8 \), suggesting that the ratio of partition coefficients, \( \frac{D_{\text{Cl}}}{D_{\text{Br}}} \), ranges from 1 for Bobrowski et al. (2003) to 8 for our lowest BrO/SO\(_2\) ratio in the entire data set, and 5 for the lowest average ratio: it is lower during eruptive activity. The ratio of \( \sim 1 \) suggested by Villemant et al. (2008) is an asymptote on Figure 8 and is therefore more likely to be achieved during eruptive activity. This may be due to changes in the magmatic system when fresh magma is not being supplied to shallow depths. This result may aid the reconciliation of the differing values of \( \frac{D_{\text{Cl}}}{D_{\text{Br}}} \) so far provided in the literature (Table 6). We suggest, therefore, that while some HBr can exsolve from the melt at depth, the primary source of the previously recorded high Br emission at SHV is shallow and dependent upon eruptive activity. However, further work is necessary to constrain possible variations in HBr oxidation rate and the magnitude of errors associated with plume dispersion, aerosol processes and spectroscopic methods. This would enable assessment of the relative contributions of these factors in determining BrO/SO\(_2\) ratios.

The reasons for a decrease in the ratio of partition coefficients may relate to degassing processes in the shallow magmatic system. HCl degassing is strongly coupled with melt water content, whereas this relationship has not been investigated for HBr. It is possible that the relative importance of the basaltic magma source compared to the andesite also shifts during pauses. It has been shown that the partitioning of Br and Cl in silicic melts varies with pressure [e.g., Bureau et al., 2000; Louvel, 2011; Bureau and Metrich, 2003], and thus while at shallow pressures \( D_{\text{Br}} > D_{\text{Cl}} \), this relationship may be reversed at higher pressures. Therefore, our results might indicate that there is no magma in the shallow system; HCl is lower in pauses because it is degassing at depth, and HBr is lower still because the Br partition coefficient at magma chamber pressures is lower than that of Cl. This is consistent with recent studies by Louvel [2011], which showed a decrease in Br partitioning with increasing temperature. Additionally, there are indications from the experimental literature that the use of synthetic melts rich in Na may not be appropriate in simulating magmatic conditions [Louvel, 2011; Villemant et al., 2008; Baker and Alletti, 2012]. This strongly suggests the need for additional experimental research into the behavior of Br relative to H\(_2\)O and other halogens in natural melts under magmatic conditions.

### 4.2. OCIO in the Volcanic Plume

Volcanic plumes are chemically reactive, due both to the presence of a large range of compounds and to the availability of surfaces (ash and nonsilicate aerosol) on which reactions can occur [Mather et al., 2003]. The abundance of thermal energy close to the vent, the humidity of the plume, the sudden exposure of a comparatively reduced magmatic gas mixture to atmospheric oxygen, and the incidence of sunlight also enhance its reactivity. Recent studies have reported detection of several reactive halogen oxides in volcanic plumes—BrO, OCIO and ClO [Bobrowski et al., 2003, 2007; Kern et al., 2009, 2010; Lee et al., 2005; Sawyer et al., 2011; Salerno et al., 2009; Theys et al., 2014]. Models and calculations suggest that these are not primary magmatic gases, but are produced in the plume due to aqueous phase oxidation of hydrogen halides.
and subsequent photolysis of BrCl and Br₂ [Oppenheimer et al., 2006a, 2006b; Bobrowski et al., 2007; Gerlach, 2004; Aiuppa et al., 2005; Roberts et al., 2009]. This has been corroborated by observations that the abundance of BrO in the plume increases with distance from the vent [Bobrowski et al., 2007; Oppenheimer et al., 2006a, 2006b]. As BrO formation in volcanic plumes occurs as a result of the photodissociation of Br₂ followed by reaction with ozone, it has been observed to reach a maximum at midday [Kern et al., 2009]. However, this was not clear in our data, with some of the later afternoon measurements being higher – this is consistent with models [e.g., von Glasow et al., 2002]. BrO abundance has been observed to correlate with that of SO₂ during daylight [Bobrowski et al., 2003; Kern et al., 2009].

OCIO is formed from the reaction between ClO and BrO:

\[
\text{ClO} + \text{BrO} \rightarrow \text{OCIO} + \text{Br} \tag{R4}
\]

This reaction is therefore dependent on the formation of ClO, which is formed from photolysis of BrCl and reaction of Cl and ozone. While ClO has been reportedly detected in volcanic plumes [Lee et al., 2005; Bobrowski et al., 2007], the reliability of the measurements could be called into question because the ClO absorption in the ultraviolet coincides with that of SO₂ (which is typically very strong), and also due to the effects of stray light in the spectrometer in this wavelength interval [Kern, 2009]. ClO also reacts with NO₂ to form ClONO₂, which may then be hydrolyzed on sulfate aerosols to form HOCI and HNO₃, and HOCI photolyses to OH + Cl.

Two other reactions occur between BrO and ClO:

\[
\begin{align*}
\text{BrO} + \text{ClO} & \rightarrow \text{O}_2 + \text{Br} + \text{Cl} \\
\text{BrO} + \text{ClO} & \rightarrow \text{BrCl} + \text{O}_2
\end{align*} \tag{R5, R6}
\]

BrCl may also photodissociate to form Br and Cl. This ultimately increases the formation of BrO. Equation (R4) suggests that there should be a positive correlation between BrO and OCIO, and thus between SO₂ and OCIO. However, OCIO has a very short half-life in the atmosphere due to the following reaction:

\[
\text{OCIO} + \text{hv} \rightarrow \text{ClO} + \text{O} \tag{R7}
\]
OCIO formation also requires high levels of BrO and ClO in the plume. Since it can only be formed by the reaction of these two molecules, OCIO is a good indicator both of chlorine activation and of high BrO concentrations. OCIO concentrations in the atmosphere were observed to increase following the 1991 Pinatubo eruption, probably as a result of chlorine nitrate activation on aerosol surfaces [Solomon et al., 1993].

Several factors affect halogen oxide formation [Gerlach, 2004; Wayne, 2000; Bobrowski et al., 2007; Oppenheimer et al., 2006a, 2006b; von Glasow et al., 2009]. These include gas temperature (high temperature facilitates the direct release of Br and Cl from HBr and HCl); aerosol formation (which significantly increases the surface area for heterogeneous chemical reactions forming Br2 and Cl2 and acidity; time of day (due to the role of photolysis) and mixing between ambient air and the plume (since this facilitates the availability of ozone to form the halogen oxides).

In addition, OCIO detection was challenging because of some overlap between the BrO and OCIO cross sections and because of the relatively low column amounts of this gas on several days. OCIO was more challenging to retrieve in data sets collected during strong winds, or under conditions of substantial cloud cover (e.g., on 9 and 10 April). It also requires high levels of both ClO and BrO in order to form, suggesting that it might be sensitive to both halogen emission rates and to a stable plume with clear light path.

Using MVO’s measurement of the HCl/SO2 ratio in the gas phase (0.3 ± 0.06), we can also calculate the extent of HCl oxidation in the plume, if we assume that all OCIO in the plume is derived from HCl. Our OCIO/SO2 ratios suggest that < 0.01% of the total Cl in HCl in the plume was converted to OCIO. This is consistent with the complexity of chlorine reactions in the plume, and the instability of OCIO (estimated to have a half-life of around 9 s) [Kern, 2009]. It is likely that HCl remains the dominant Cl-phase in the plume for much longer than HBr [e.g., Kern, 2009; Bobrowski et al., 2007], and much of the HCl may be scavenged by aerosols. In general, the correlation between SO2 and OCIO was relatively poor. BrO and OCIO SCAs show a stronger correlation. This is expected, since OCIO formation is dependent on BrO and ClO. The high OCIO/SO2 ratios during the day on 2 and 19 April 2011 are indicative of the highly dynamic environment of the tropospheric volcanic plume, the abundance of BrO and continuous formation of OCIO. Figure 9 summarizes the implications of the results from this study and those on which it builds.

5. Conclusions

BrO/SO2 ratios at the Soufrière Hills Volcano on Montserrat decreased by almost an order of magnitude during an eruptive hiatus, and the ratio of Cl/Br in the gas phase increased. We suggest that this increase can be modeled by changes in the partitioning of these elements into the hydrous vapor phase in the absence of magma ascent. We suggest that the partitioning of the elements Cl and Br may vary relative to one another with degree of degassing. During magma ascent, vigorous water degassing and partitioning of halogens into vapor, the two halogen species partition into fluids to the same degree. At lower rates of degassing, however, when magma ascent and/or water degassing is sluggish, bromine degasses much less relative to chlorine. However, there are likely to be a number of factors affecting the difference in BrO/SO2 ratios between phases of lava extrusion and eruptive pauses. Other possible causes include the quantity of Br in HBr that is oxidized and the uncertainties on spectroscopic measurements of volcanic gases.

The use of miniature UV spectrometers for SO2 monitoring has proliferated over the past decade [Galle et al., 2010]. SO2 detection is relatively straightforward due to its high abundance in the plume. BrO and OCIO, however, are present in much lower quantities and the retrieval process can be technically challenging. This renders them unlikely candidates for operational monitoring at active volcanoes. In addition, Kern et al. [2009] confirmed that BrO is only formed during photolysis and is thus undetectable in measurable quantities at night. The formation of BrO from HBr, and indeed the exsolution processes involved in HBr emission are most likely complex and dependent on the behavior of the other volatile species in the melt as well as atmospheric factors. However, OP-FTIR measurements of HCl/SO2 are practically challenging at SHV, particularly operationally, because the instrument is expensive to maintain and the measurements rely on solar occultation, which is labor-intensive. BrO abundance, like HCl, appears to be lower during eruptive pauses, and this suggests that BrO/SO2 could provide important information about the presence of magma in the shallow system – and thus be of use for volcano monitoring. Sudden high BrO emissions may herald
a renewal of eruptive activity at Soufrière Hills Volcano. Nevertheless, at the present time these results are preliminary and further work is required to consolidate them.

OClO has been detected in the plume at the SHV for the first time. It has only been detected in volcanic plumes previously at Mount Etna [Bobrowski et al., 2007] and Puyehue Cordón Caulle [Thyes et al., 2014]. Its presence is a further indication of the high rate of HCl degassing, even during pauses, and of the reactive nature of halogen chemistry in volcanic plumes [Roberts et al., 2009; Bobrowski et al., 2007; von Glasow, 2010; von Glasow et al., 2009].

Further studies involving the simultaneous measurement of dome/source temperature, aerosol content and, ideally, plume structure (e.g., using an SO2 camera) would aid interpretation of halogen species in the plume. However, experimental studies are required to constrain the solubility of HBr in magmas and the usefulness of bromine species as monitoring aids. Given the findings of this study and those of earlier studies on bromine behavior [Alletti et al., 2007; Bureau et al., 2000; Villemant et al., 2008], it is likely that bromine behaves significantly differently to chlorine in hydrous silicic melts. Experiments on natural samples of a range of compositions would aid interpretation of both models and field observations.

Additional studies to measure OClO in plumes would also be beneficial, particularly where solar occultation provides the only practical means for measuring HCl in volcanic plumes by open-path Fourier transform infra-red spectroscopy. Finally, new modeling, particularly of the influence of aerosol and meteorological conditions on the retrievals and refinement of the DOAS method would be beneficial in reducing error on the measurements of trace gases.

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