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**Enhancement of
volcanogenic
“bromine explosion”
via reactive nitrogen**

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Enhancement of the volcanogenic “bromine explosion” via reactive nitrogen chemistry (Kīlauea volcano, Hawai’i)

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Abstract

Since the first detection of bromine monoxide in volcanic plumes attention has focused on the atmospheric synthesis and impact of volcanogenic reactive halogens. We report here new measurements of BrO in the volcanic plume emitted from Kīlauea volcano – the first time reactive halogens have been observed in emissions from a hotspot volcano. Observations were carried out by ground-based Differential Optical Absorption Spectroscopy in 2007 and 2008 at Pu'u'Ō'ō crater, and at the 2008 magmatic vent that opened within Halema'uma'u crater. BrO was readily detected in the Halema'uma'u plume (average column amount of 3×10^{15} molec cm⁻²) and its abundance was strongly correlated with that of SO₂. However, anticorrelation between NO₂ and SO₂ (and BrO) abundances in the same plume strongly suggest an active role of NO_x in reactive halogen chemistry. The calculated SO₂/BrO molar ratio of ~1600 is comparable to observations at other volcanoes, although the BrO mixing ratio is roughly double that observed elsewhere. While BrO was not observed in the Pu'u'Ō'ō plume this was probably merely a result of the detection limit of our measurements and based on understanding of the Summit and East Rift magmatic system we expect reactive halogens to be formed also in the Pu'u'Ō'ō emissions. If this is correct then based on the long term SO₂ flux from Pu'u'Ō'ō we calculate that Kīlauea emits ~480 Mg yr⁻¹ of reactive bromine and may thus represent an important source to the tropical Pacific troposphere.

1 Introduction

Volcanoes release significant quantities of reactive gases and particles into the atmosphere, with fluxes and relative abundances that tend to reflect levels of volcanic activity, tectonic setting and extent of magmatic-hydrothermal interaction (e.g., Carroll and Holloway, 1994; Mather et al., 2003; Oppenheimer, 2003). Volcanism has played a crucial role in the formation of the Earth's atmosphere (e.g., Cadle, 1980; Marti and

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Ernst, 2005), and continues to play a significant role in the composition and radiative transfer of the atmosphere (e.g., Kelly et al., 1997; Grainger and Highwood, 2003). The study of volcanic emissions is thus essential not only for modelling eruptive activity and for hazard evaluation but also to evaluate fully their impacts on the Earth system. With the recent discovery of reactive halogens, notably BrO, in volcanic emissions from both passive (e.g., Bobrowski et al., 2003) and explosive (e.g., Theys et al., 2009) volcanic degassing, the role of volcanism in atmospheric ozone abundance, acidity and oxidising capacity has become the focus of interest in the wider context of the roles of halogens in the troposphere. Chlorine and fluorine species are among the most abundant volatile species in volcanic emissions following water vapour, CO₂ and SO₂ (e.g., Symonds et al., 1994). Heavy halogens, although present in lesser quantities, nevertheless are expected to partition strongly into magmatic gas phases (Bureau et al., 2003), and assume special significance on account of their important atmospheric chemistry. Typically, halogens are more abundant in gases released by convergent-plate-sited volcanoes, due to their associated water and halogen-rich magmas compared with divergent-plate-sited and hot-spot volcanoes (e.g., Hilton et al., 2002; Oppenheimer, 2003). Despite the noteworthy influence of halogens in magmatic processes (Hedenquist and Lowenstern, 1994; Aiuppa, 2008a) and atmosphere chemistry (e.g., Von Glassow et al., 2009), their role in volcano dynamics remains poorly constrained (Aiuppa et al., 2008b). Owing to the low abundance of heavy halogens in magma, more is known of their behaviour in convergent-plate magmas (e.g., Carol and Holloway, 1994; Muranatsu and Wedepohl, 1998). The inventories of bromine content in magma (e.g., Wedepohl, 1974; Wehrmann, 2005), in volcanic gas (e.g., Sugiura et al., 1963; Snyder et al., 2002), and Br-oxide emission rates (e.g. Bobrowski et al., 2007b), remain weakly constrained (Pyle and Mather, 2009).

Thanks to the proliferation of low cost ultraviolet spectrometers and associated analytical techniques such as Differential Optical Absorption Spectroscopy (DOAS) in the last decade (e.g., Platt et al., 1994; Plane and Saiz-Lopez, 2006) several volcanogenic BrO measurements have been carried out. In particular, since the first detection of BrO

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by UV DOAS (at Soufrière Hills Volcano, Montserrat; Bobrowski et al., 2003), numerous efforts have been made to advance the knowledge of the origin and contribution of this reactive halogen in volcanic plume chemistry. Several studies have argued that BrO is not a primary magmatic species, but that it forms in volcanic plumes via the so-called “bromine explosion” (Wennberg, 1999), i.e., by heterogeneous, photochemical processing originating with oxidation of a small quantity of magmatic HBr (e.g., Oppenheimer et al., 2006; Bobrowski et al., 2007a; Roberts et al., 2009). Recent observations at Masaya volcano where BrO was observed only during daylight hours provide strong evidence for the proposed chemical schemes (Kern et al., 2008).

Here we report and discuss the first observations of BrO emission from a hotspot volcano, namely Kīlauea (Hawai‘i, USA). These were obtained by ground-based UV spectroscopic observations carried out in 2007 and 2008 for plumes emitted by both the Pu‘u‘Ō‘ō crater (on the East Rift Zone) and by a new magmatic vent that opened in March 2008 within Halema‘uma‘u crater. We discuss the reactive bromine observations in light of striking results concerning the co-retrieved abundances of NO₂.

2 Observation sites and methods

During our fieldwork, Kīlauea was active along the East Rift in 2007, and at both the Summit and East Rift in 2008. Pu‘u‘Ō‘ō has been active since 1983 (Heliker et al., 2003), whereas Kīlauea summit activity began on 12 March 2008 (Orr et al., 2008; Patrick et al., 2008; Poland et al., 2008). The Summit and East Rift activity and degassing have been the subject of many studies, which demonstrate that much of the magmatic supply of CO₂ is released at the summit (e.g., Gerlach and Graeber, 1985). UV spectra were acquired within 1–1.5 km of both the Pu‘u‘Ō‘ō crater on 3 September 2007 and Halema‘uma‘u crater on 13 May 2008 (Fig. 1). Surveys were performed between 09:00 and 16:00 LT (Local Time), dictated largely by the prevailing weather conditions and wind direction. Wind data were sourced from NOAA (<http://ready.arl.noaa.gov/READYcmet.php>).

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SO₂, BrO and NO₂ Slant Column Amounts (SCA) were retrieved from successively collected passive UV skylight spectra recorded by an Ocean Optics USB2000 spectrometer with spectral range 295–375 nm and ~0.44 nm (full-width-at-half-maximum) nominal resolution. The spectrometer was housed in a thermo-stabilised enclosure (held at 15 °C) and coupled by a fibre optic bundle to a single lens telescope (full plane field of view of 8 mrad). The azimuthal viewing directions were north-west and east in 2007 and 2008, respectively; the elevation angle of the field of view was ~30°. Each spectrum was recorded with an overall time step of ~20 s by exposing the detector for ~200 ms and co-adding up to 100 successive individual spectra (so as to maximise the signal-to-noise-ratio whilst avoiding saturation in the wavelength region used in the retrieval). In each survey 3–4 datasets were recorded, each consisting of ~80 spectra collected over a ~20 min period.

The cooling and thermo-stabilisation reduced the associated dark current and avoided temperature drifts that are known to affect the performance of the detector and optical bench. For a few datasets in both surveys, the thermo-stabilised instrument was not used, in which case we collected Clear Sky Reference (CSR, out of plume), dark and offset spectra, routinely at the start and the end of each data set sampling to account for instrumental drift. The CSR spectra were recorded by pointing the telescope away from the plume with the same elevation used to observe the plume.

Each recorded spectrum was evaluated following standard DOAS methodology (e.g., Noxon, 1975; Perner et al., 1979; Platt and Stutz, 2008) using the WinDOAS V2.10 software package (Fayt and Roozendael, 2001). The Ring spectrum (e.g., Solomon 1987; Fish and Jones, 1995) was calculated from the CSR following the approach of Chance et al. (1998). Both laboratory spectra of SO₂, BrO, O₃, and NO₂ (293, 298, 293 and 223 K, respectively; Wahner et al., 1998; Bogumil et al., 2003) and the Ring spectrum were convolved to the spectrometer’s resolution. In the fitting process, a first order linear offset was also included to account for possible instrumental and/or atmospheric stray light, residual dark current and for different (time variant) Rayleigh/Mie contributions in the recorded spectra. Each spectrum was shifted and stretched until

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the best fit was achieved. The optimal fitting windows for SO₂ (305.0–316.0 nm), and BrO and NO₂ (345.0–358.0 nm) were selected to avoid interferences between gases during the retrieval, and yielded near random structures with minimal standard deviation in the residuals. Additionally, BrO and NO₂ were retrieved for a wider spectral window (330–370 nm) to check for artefacts in the retrieved column amounts. Figure 2 shows an example of the BrO and NO₂ fit over the 345.0–358.0 nm spectral range for a spectrum collected at Halema’uma’u crater on 13 May 2008.

3 Results

In Table 1, we compile the results obtained for the Pu’u’Ō’ō and Halema’uma’u crater measurements together with the prevailing environmental and plume characteristics. The Pu’u’Ō’ō spectra yield a mean SO₂ abundance around 4 times lower than those measured at the summit ($\sim 3 \times 10^{18}$ molec cm⁻²) and did not reveal BrO or NO₂. Conversely, at Halema’uma’u crater, BrO was successfully detected (mean of 3×10^{15} molec cm⁻²) as well as negative (differential) amounts of NO₂ (mean of -6×10^{16} molec cm⁻²). Note that negative abundances signify lower NO₂ relative to the background.

Figure 3 shows SO₂ versus BrO SCA measured at Halema’uma’u crater in 2008. The derived SO₂/BrO plume molar ratio is 1600 mol mol⁻¹ (R^2 :0.84) equivalent to a S/Br mass ratio of 645.

Based on weekly SO₂ flux measurements of the Halema’uma’u plume (Elias et al., 2010), this suggests a BrO emission rate of ~ 8 g s⁻¹. Note that the linear regression of the SO₂ versus BrO data does not go through the origin. We interpret this to suggest the presence of BrO in the CSR spectrum, possibly hinting at differential rates of chemical processing of SO₂ and BrO in the local atmosphere. Taking this into account as well as the likelihood that other reactive Br species are present in the plume, our

estimated BrO emission rate for the summit plume at Kīlauea underestimates the total reactive bromine flux.

Taking the mean measured BrO and SO₂ SCA and estimated optical path length through the plume of 600 m, the corresponding mean in-plume BrO and SO₂ mixing ratios were ~2.3 and 2140 ppbv, respectively.

Nitrogen oxides play significant roles in reactive halogen chemistry – for instance, high levels of NO_x increase production of BrONO₂, which accelerates the bromine explosion, (Oppenheimer et al., 2006; Roberts et al., 2009). Elevated NO_x levels (in excess of 100 ppbv) have also been associated with the active lavas at Kīlauea (Huebert et al., 1999; Witham, 2005), thus we co-retrieved NO₂ in the UV spectra with BrO to explore for possible effects. We found NO₂ strongly negatively correlated with both SO₂ ($R^2=0.87$; Fig. 4a) and BrO ($R^2=0.84$; Fig. 4b). As discussed in the next section, we believe that this striking finding reflects local depletion of NO_x as a result of reactive bromine chemistry that acts to promote BrO formation.

4 Discussion

The first question to address is why BrO was detected at the Halema'uma'u vent but not at Pu'u'Ō'ō. The most likely explanation is that the optical density of the plume gas species was around 4 times higher in the case of the observations at the summit crater, thus making it easier to detect associated levels of BrO. Given that previous studies have not revealed any evidence for significant fractionation of halogens between the summit and rift zone magmatic degassing (see data compilation in Symonds et al., 1994), we consider that BrO is very likely present in the (daytime) Pu'u'Ō'ō plume but not in sufficient abundance to detect readily with our instrumental set up (consider that the maximum SCA of SO₂ detected at Pu'u'Ō'ō was 3×10^{18} molec cm⁻² (Table 1) and consult Fig. 3, and it is readily apparent that conclusive detection of BrO at Pu'u'Ō'ō would have been challenging for our spectrometers (the detection limit of BrO is $\sim 3 \times 10^{14}$ molec cm⁻²).

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Other factors can contribute to the detection of reactive halogen species, including sensitivity and selectivity of the spectrometer and the spectroscopy, as well as diurnal, seasonal and meteorological factors (e.g., RH, temperature, actinic flux, and cloudiness, which can affect the quality of the CSR; see Bobrowski and Platt, 2007; Kern et al., 2008; Von Glasow et al., 2009). In addition, the section of the plume transected (margins versus core) and its young age (i.e., distance from source and wind speed less than 2 min) can significantly affect the observed SO₂/BrO ratio (Bobrowski et al., 2007b, 2009; Oppenheimer et al., 2006; Vogel et al., 2008), as well as the overall source flux, which affects plume-air mixing (Bani et al., 2009). Our observations pertain to plume ages of ~2–8 min during which time the Br explosion is underway; thus, observed SO₂/BrO ratios may be quite sensitive to the exact plume age (at Mt. Etna, Oppenheimer et al., 2006, observed BrO formation within 2–3 min of emission from source). Variability in air entrainment into the plume likely accounts for some of the observed scatter in the plot of SO₂ versus BrO seen in Fig. 3.

Note that the plumes at both Summit and East Rift were occasionally ashy and dense and the admixture of water droplets and aerosols resulted in high plume opacity.

If we assume that the measured SO₂/BrO ratio characterises the near source emission for eruptive vents on Kīlauea, then we can take the long-term SO₂ flux observed for the volcano (0.62 Tg yr⁻¹; Sutton et al., 2001; Elias and Sutton, 2002, 2007) and the S/Br mass ratio to calculate a nominal minimum production of ~15 g s⁻¹ of reactive Br (equivalent to ~480 Mg yr⁻¹). This is within the range of estimates of other volcanoes, including Soufrière Hills Volcano and Mt. Etna (Bobrowski et al., 2003; Oppenheimer et al., 2006).

Gerlach (2004) predicted that although non-arc basaltic magmas at 1100–1200 °C are expected to contain less HBr compared with arc gases, the Kīlauea plume should contain reactive halogens in comparable quantities to those of arc volcanoes on account of the oxidising capacity associated with its high SO₂ abundance. His predictions are thus borne out by our detection of BrO.

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A further key issue to address regarding the observations is the anticorrelation between BrO (and SO₂) and NO₂ abundance in the retrievals of the differential spectra. The pattern strongly suggests a deficit of NO₂ within the plume compared to an elevated background. The mean “missing” NO₂ in the plume is $\sim 6 \times 10^{16}$ molec cm² (Table 1). This is equivalent to a mixing ratio in the ambient atmosphere at Kīlauea summit of around 50 ppbv. This is well in excess of the typical NO_x mixing ratio in the Hawaiian free troposphere (e.g., <1 ppbv measured at the Mauna Loa Observatory; Carroll et al., 1992) but NO_x levels of 10 s to a few 100 s of ppbv have been reported in the immediate vicinity of Kīlauea associated with thermal fixation of atmospheric nitrogen at the high temperature surfaces of active lava (Hubert et al., 1999). Witham (2005) reported NO₂ mixing ratios measured along the Chain of Craters Road in the Hawaii National Park that average ~ 150 ppbv; even background sites had NO₂ levels of around 24 ppbv. If these observations are indicative then there appears to be plenty of NO_x in the local atmosphere at Kīlauea to account for our observed deficit in the young volcanic plumes. Given the parallel observations of BrO in the plume, we speculate that the differential spectra indicating NO₂ loss in the plume reflect rapid titration of NO₂ out of entrained ambient air via the following chemical schemes (Oppenheimer et al., 2006; Roberts et al., 2009):



NO₂ and BrO combine to form BrONO₂ which reacts with HBr in aerosol via a multi-stage process to form HNO₃ and Br₂. Photolysis of Br₂ (once released to the gas phase) generates Br radicals that react with ozone to form BrO, with an overall doubling of BrO in this autocatalytic cycle (see Roberts et al., 2009). In this way, the presence of

NO_x promotes the bromine explosion and may represent a relevant process enhancing reactive bromine production at Kilauea and other volcanoes where high temperature lava surfaces or high temperature gas jets generate NO_x (Huebert et al., 1999; Mather et al., 2004; Oppenheimer et al., 2005; Martin et al., 2006, 2009). Note that dissociation, or photolysis of BrONO₂ can also occur (regenerating BrO and NO₂, or Br and NO₃), but that the reaction of BrONO₂ on aerosol is sufficiently rapid under the acidic, high-aerosol loading of volcanic plumes to promote the bromine explosion. The presence of NO_x also alters the distribution of reactive bromine species between different forms, for example increasing BrONO₂ at the expense of BrO. Thus, despite promoting the overall bromine explosion, volcanogenic NO_x can reduce BrO abundance making it harder to detect by UV spectroscopy.

Because of the path-integrated nature of the DOAS measurements it is difficult to confirm this hypothesis with the data available to us but the evidence for complex chemical pathways involving halogens, NO_x, NO_y and ozone in plumes is mounting (e.g., Oppenheimer et al., 2010). Careful in situ measurements, combined with model studies, are required to resolve the details. Model simulations (Roberts et al., 2009) of volcanic plume halogen chemistry have predicted in-plume NO₂ depletion and formation of nitric acid (HNO₃) via the BrONO₂ reaction scheme, supporting our observations. The combined observations and model simulations thus provide an explanation for elevated concentrations of HNO₃ that were reported at other volcanoes, including Villarrica, Masaya, Etna Láscar and Erebus (Mather et al., 2004; Oppenheimer et al., 2010), and cannot be explained by high-temperature chemistry alone (Martin et al., 2006). These findings highlight the importance of NO_x for BrO-chemistry in volcanic plumes, and identify NO_x to HNO₃ conversion as a consequence of volcanic plume halogen chemistry, in addition to known impacts such as ozone depletion.

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5 Concluding remarks

In 2007 and 2008, we carried out UV spectroscopy measurements of the volcanic plume emitted by Pu'u'Ō'ō crater and by the new magmatic vent that opened in March 2008 within the Kīlauea Summit caldera. While BrO was not conclusively detected at Pu'u'Ō'ō, we observed BrO slant column amounts of 10^{14} to 10^{15} molec cm⁻² and BrO/SO₂ molar ratio of 1600 mol mol⁻¹ for the Summit plume. We observed apparent depletion of NO₂ ($\sim 6 \times 10^{16}$ molec cm⁻²), equivalent to ~ 50 ppbv of NO₂ loss within the plume, with amounts strongly correlated with SO₂ and BrO abundance suggesting an active role of NO_x in the plume chemistry. Specifically, the negative NO₂ amounts might result from its reaction with BrO, enhancing the “bromine explosion” and converting NO_x into nitric acid (which has also been detected close to source; Witham, 2005). Based on a mean optical path through the plume of 600 m, we estimate a characteristic BrO mixing ratio of ~ 2.3 ppbv, roughly double that observed in other tropospheric volcanic plumes. Based on the observed BrO/SO₂ ratio and the long term SO₂ emission rate from Kīlauea, we estimate that the volcano emits on the order of 480 Mg yr⁻¹ of reactive bromine, suggesting that it might play a significant role in local ozone depletion and NO_x to HNO₃ conversion. The observation of BrO in emissions from a relatively halogen-poor magma confirms predictions for Kīlauea based on thermodynamic arguments (Gerlach, 2004) and extends the database on the global volcanogenic reactive bromine source to include a hotspot volcano for the first time.

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5 References

- Aiuppa, A.: Degassing of halogens from basaltic volcanism: Insights from volcanic gas observations, *Chem. Geol.*, 263, 99–109, doi:10.1016/j.chemgeo.2008.08.022, 2008a.
- Aiuppa, A., Baker, D. R., and Webster, J. D.: Halogens in volcanic systems, *Chem. Geol.*, 263, 1–18, doi:10.1016/j.chemgeo.2008.10.005, 2008b.
- 10 Bani, P., Oppenheimer, C., Tsanev, V. I., Carn, S. A., Cronin, S. J., Crimp, R., Calkins, J. A., Charley, D., Lardy, M., and Roberts, T. R.: Surge in sulphur and halogen degassing from Ambrym volcano, Vanuatu. *Bull. Volcanol.*, 71(10), 1159–1168, doi:10.1007/s00445-009-0293-7, 2009.
- Bobrowski, N., Hönninger, G., Galle, B., and Platt, U.: Detection of bromine monoxide in a volcanic plume, *Nature*, 423, 273–276, 2003.
- 15 Bobrowski, N., von Glasow, R., Aiuppa, A., Inguaggiato, S., Louban, I., Ibrahim, O. W., and Platt, U.: Reactive halogen chemistry in volcanic plumes, *J. Geophys. Res.*, 112, D06311, doi:10.1029/2006JD007206, 2007a.
- Bobrowski, N. and Platt, U.: SO₂/BrO ratios studied in five volcanic plumes, *J. Volcanol. Geoth. Res.*, 166, 147–160, doi:10.1016/j.jvolgeores.2007.07.003, 2007b.
- Bobrowski, N. and Giuffrida, G.: Halogen/sulphur ratios in connection to volcanological observations 2006–2009 at Etna volcano, Conferenza Rittmann “La vulcanologia italiana: stato dell’arte e prospettive future”, Istituto Nazionale di Geofisica e Vulcanologia – sezione di Catania, 11–13 June 2009, Nicolosi, Italy, 2009.
- 25 Bogumil, K., Orphal, J., and Burrows, J. P.: Temperature-dependent absorption cross-sections of O₃, NO₂, and other atmospheric trace gases measured with the SCIAMACHY spectrometer, in *Proceeding of ERS-ENVISAT Symposium: Looking down to Earth in the New Millennium*, Gothenburg, Sweden, 16–20 October, 2000.

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Bureau, H., Keppler, H., and Metrich, N.: volcanic degassing of bromine and iodine: experimental fluid/melt partitioning data and applications to stratospheric chemistry, *Earth Planet. Sci. Lett.*, 183, 51–60, 2000

Cadle, R. D.: A Comparison of Volcanic With Other Fluxes of Atmospheric Trace Gas Constituents, *Rev. Geophys.*, 18(4), 746–752, 1980.

Carroll, M. A., Ridley, B. A., Montzka, D. D., Hubler, G., Walega, J. G., Norton, R. B., Huebert, B. J., and Grahek, F. E.: Measurements of Nitric Oxide and Nitrogen Dioxide During the Mauna Loa Observatory Photochemistry Experiment, *J. Geophys. Res.*, 97(D10), 10361–10374, 1992.

Carroll, M. R. and Holloway, J. R.: Volatiles in magmas, *Reviews of Mineralogy*, 30, Mineral Society of America, Washington, DC, 1994.

Chance, K.: Analysis of BrO measurements from the Global Ozone Monitoring Experiment, *Geophys. Res. Lett.*, 25, 3335–3338, 1988.

Elias, T. and Sutton, A. J.: Sulfur Dioxide emission rates of Kīlauea Volcano, Hawaii, an update: 1998–2001, US Geological Survey, Open File Rep. 02-460, 2002.

Elias, T. and Sutton, A. J.: Sulfur Dioxide emission rates of Kīlauea Volcano, Hawaii, an update: 2002–2006, US Geological Survey, Open File Rep. 2007-1114, 37, 2007.

Elias, T. and Sutton, A. J.: Sulfur Dioxide Emission Rates from Kīlauea Volcano, Hawaii 2007–2009, US Geological Survey, Open File Rep., in preparation, 2010.

Fayt, C. and Van Roozendael, M.: WinDOAS 2.1 – Software User Manual, Institut d’Aéronomie Spatiale de Belgique, Brussels, Belgium, 2001.

Fish, D. J. and Jones, R. L.: Rotational Raman scattering and the ring effect in zenith-sky spectra, *Geophys Res. Lett.*, 22, 811–814, 1995.

Gerlach, T. M. and Graeber, E. J.: Volatile budget of Kīlauea volcano, *Nature*, 313, 273–277, 1985.

Gerlach, T. M.: Volcanic sources of tropospheric ozone-depleting trace gases, *Geochem. Geophys. Geosy.*, 5(9), Q09007, doi:10.1029/2004GC000747, 2004.

Grainger, R. G. and Highwood, E. J.: Changes in stratospheric composition, chemistry, radiation and climate caused by volcanic eruptions, in: *Volcanic degassing*, edited by: Oppenheimer, C., Pyle, D. M., and Barclay, J., *Geol. Soc. Spec. Publ.*, 213, 329–347, 2003.

Hedenquist, J. W. and Lowenstern, J. B.: The role of magmas in the formation of hydrothermal ore deposits, *Nature*, 370, 519–527, 1994.

Heliker, C., Swanson, D. A., and Takahashi, T. J.: The Pu'u O'o-Kupaianaha eruption of Kīlauea Volcano, Hawai'i: The first 20 years, Professional paper; 1676, United States Geological Survey, 2003.

Hilton, D. R., Fisher, T. P., and Marty, B.: Noble gases and volatile recycling at subduction zones: Reviews in Mineralogy and geochemistry, 47, 319–370, 2002.

Huebert, B., Vitousek, P., Sutton, J., Elias, T., Heath, J., Coeppicus, S., Howell, S., and Blomquist, B.: Volcano fixes nitrogen into plant-available forms, Biogeochemistry, 47, 111–118, 1999.

Kelly, P. M.: Volcanic dust veil and North Atlantic climatic change, Nature, 268, 616–617, 1977.

Kern, C., Sihler, H., Vogel, L., Rivera, C., Herrera, M., and Platt, U.: Halogen oxide measurements at Masaya Volcano, Nicaragua using active long path differential optical absorption spectroscopy, Bull. Volcanol., 71(6), 659–670, doi:10.1007/s00445-008-0252-8, 2008.

Kern, C., Deutschmann, T., Vogel, L., Wöhrbach, M., Wagner, T., and Platt, U.: Radiative transfer corrections for accurate spectroscopic measurements of volcanic gas emissions, Bull. Volcanol., 72(2), 233–247, doi:10.1007/s00445-009-0313-7, 2009.

Marti, J. and Ernst, G. G. J.: Volcanoes and the Environment, Cambridge University Press, Cambridge, 2005.

Martin, R. S., Mather, T. A., and Pyle, D. M.: High-temperature mixtures of magmatic and atmospheric gases, Geochem. Geophys. Geosys., 7, Q04006, doi:10.1029/2005GC001186, 2006.

Martin, R. S., Roberts, T. J., Mather, T. A., and Pyle, D. M.: The implications of H₂S and H₂ kinetic stability in high-T mixtures of magmatic and atmospheric gases for the production of oxidized trace species (e.g., BrO and NO_x), Chem. Geol., 263, 143–150, 2009.

Mather, T., Pyle, D. M., and Oppenheimer, C.: Tropospheric volcanic aerosol, in: Volcanism and the Earth's Atmosphere, edited by: Robock, A. and Oppenheimer, C., American Geophysical Union Monograph, USA, 139, 189–212, 2003.

Mather, T. A., Allen, A. G., Pyle, D. M., Davison, B. M., Oppenheimer, C., and McGonigle, A. J. S.: Nitric acid from volcanoes, Earth Planet. Sci. Lett., 218, 17–30, 2004.

Muranatsu, Y. and Wedepohl, K. H.: The distribution of iodine in the Earth's crust, Chem. Geol. 147, 201–216, 1998.

Noxon, J. F.: Nitrogen dioxide in stratosphere and troposphere measured by ground-based absorption spectroscopy, Science, 189, 547–549, 1975.

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- Oppenheimer, C.: Volcanic degassing, in: The Crust Vol. 3, Treatise on Geochemistry, edited by: Rudnick, R. L., Elsevier-Pergamon, Oxford, 123–166, 2003.
- Oppenheimer, C., Kyle, P. R., Tsanev, V. I., McGonigle, A. J. S., Mather, T. A., and Sweeney, D.: Mt. Erebus, the largest point source of NO₂ in Antarctica, *Atmos. Environ.*, 39, 6000–6006, 2005.
- Oppenheimer, C., Tsanev, V. I., Braban, C. F., Cox, R. A., Adams, J. W., Aiuppa, A., Bobrowski, N., Delmelle, P., Barclay, J., and McGonigle, A. J.: BrO formation in volcanic plumes, *Geochim. Cosmochim. Acta*, 70(12), 2935–2941, 2006.
- Oppenheimer, C., Kyle, P., Eisele, F., Crawford, J., Huey, G., Tanner, D., Kim, S., Mauldin, L., Blake, D., Beyersdorf, A., Buhr, M., and Davis, D.: Atmospheric chemistry of an Antarctic volcanic plume, *J. Geophys. Res.*, 115, D04303, doi:10.1029/2009JD011910, 2010.
- Orr, T., Patrick, M., Wooten, K. M., Swanson, D. A., Elias, T., Sutton, A. J., Wilson, D. C., and Poland, M. P.: Explosions, Tephra, and Lava: A Chronology of the 2008 Summit Eruption of Kīlauea Volcano, Hawai‘i, AGU Fall Meeting, 15–19 December 2008, San Francisco, USA, V11B-2018, 2008.
- Patrick, M., Wilson, D., Fee, D., Orr, T., Swanson, D., Sutton, A., and Elias, T.: Gas-Pistoning associated with the 2008 summit eruption of Kīlauea volcano (Hawai‘i), AGU Fall Meeting, 15–19 December 2008, San Francisco, USA, V51E-2082, 2008.
- Perner, D. and Platt, U.: Detection of Nitrous Acid in the Atmosphere by Differential Optical Absorption, *Geophys. Res. Lett.*, 6, 917–920, 1979.
- Plane, J. M. C. and Saiz-Lopez, A.: UV-Visible Differential Optical Absorption Spectroscopy (DOAS), in: *Analytical Techniques for Atmospheric Measurement*, edited by: Heard, D., Blackwell Publishing, 2006.
- Platt, U.: Differential Optical absorption spectroscopy (DOAS), in: *Air monitoring by spectroscopy techniques*, Chemical analysis Series 127, edited by: Sigrist, M. W., Wiley, New York, 27–84, 1994.
- Platt, U. and Stutz, J.: *Differential Optical Absorption Spectroscopy Principles and Applications*, Series: Physics of Earth and Space Environments, Springer, 2008.
- Poland, M. P. and Sutton, A. J.: Kīlauea activity during 2007–2008: A failed eruption and an eruption should have failed, 2008, AGU Fall Meeting, 15–19 December 2008, San Francisco, USA, V51D-2073, 2008.
- Pyle, D. M. and Mather, T. A.: Halogens in igneous processes and their fluxes to the atmosphere and oceans from volcanic activity: A review, *Chem. Geol.*, 263(1–4), 110–121, 2009.

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- Roberts, T. J., Braban, C. F., Martin, R. S., Oppenheimer, C., Adams, J. W., Cox, R. A., Jones, R. L., and Griffiths, P. T.: Modelling reactive halogen formation and ozone depletion in volcanic plumes, *Chem. Geol.* 263, 151–163, 2009.
- Solomon, S., Schmeltekopf, A. L., and Sanders, R. W.: On the interpretation of zenith sky absorption measurements, *J. Geophys. Res.*, 92, 8311–8319, 1987.
- Sugiura, T., Mizutani, Y., and Oana, S.: Fluorine, chlorine, bromine and iodine in volcanic gases, Nagoya Univ., *J. Earth. Sci.*, 11, 272, 1963.
- Sutton, A. J., Elias, T., Gerlach, T. M., Stockes, J. B.: Implications for eruptive process as indicated by sulfur dioxide emissions from Kilauea Volcano, Hawaii, 1979–1997, *J. Volcanol. Geoth. Res.*, 108, 283–302, 2001.
- Symonds, R. B., Rose, W. I., Bluth, G., and Gerlach, T. M.: Volcanic gas studies: methods, results, and applications, in: *Volatiles in Magmas: Mineralogical Society of America Reviews in Mineralogy*, edited by: Carroll, M. R. and Holloway, J. R., 30, 1–66, 1994.
- Snyder, G. T. and Fehn, U.: Origin of iodine in volcanic fluids: 129I results from the Central American Volcanic arc, *Geochim. Cosmochim. Acta*, 21, 3827–3838, 2002.
- Theys, N., Van Roozendael, M., Dils, B., Hendrick, F., Hao, N., and De Mazière, M.: First satellite detection of volcanic bromine monoxide emission after the Kasatochi eruption, *Geophys. Res. Lett.*, 36, L03809, doi:10.1029/2008GL036552, 2009.
- Vogel, L., Kern, C., Fickel, M., Wöhrbach, M., and Platt, U.: Halogen oxides in volcanic plumes: Simultaneous measurements at different plume ages, AGU Fall Meeting, 15–19 December 2008, San Francisco, USA, A51C-0102, 2008.
- von Glasow, R., Bobrowski, N., and Kern, C.: The effects of volcanic eruptions on atmospheric chemistry, *Chem. Geol.*, 263, 131–142, 2009.
- Wahner, A. R., Ravishankara, A., Sander, S. P., and Friedl, R. R.: Absorption cross section of BrO; between 312 and 385 nm at 298 and 223 K, *Chem. Phys. Lett.*, 152, 507–512, 1988.
- Wedepohl, K. H.: *Handbook of Geochemistry*, II/4, 35-E-1 to 35-E-5 and 53-E-3 to 53-E-5, 1974.
- Wennberg, P.: Bromine explosion, *Nature*, 397, 299–300, 1999.
- Wehrmann, H.: Volatile degassing and plinian eruption dynamics of the mafic Fontana Tephra, Nicaragua, Ph. D, University of Kiel, Germany, 2005.
- Witham, C. S.: Volcanic plumes: impacts, chemistry and dispersion, Ph. D, University of Cambridge, 2005.

Table 1. Summary of BrO, SO₂, and NO₂ retrievals for spectra collected at Pu'u'Ō'ō and Halema'uma'u on 3 September 2007 and 13 May 2008, respectively. Geographic location, timing of data collection, and environmental and chemical parameters are given. See Fig. 1 for location map.

parameter	Pu'u'Ō'ō	Halema'uma'u
day of collection	3 Sep 2007	13 May 2008
time data collection (LT)	15:00–15:30	10:45–12:10
age of the plume (min)	~2	~8
weather	Mostly Cloudy	Partly Sunny
Coordinates (Latitude and Longitude)	19.38 N; 155.111 W	19.42 N; 155.289 W
Temp. (°C) and Relative Humidity	25; 80%	20; 72%
min SO ₂ SCA	1 × 10 ¹⁶	1 × 10 ¹⁷
max SO ₂ SCA	3 × 10 ¹⁸	7 × 10 ¹⁸
mean SO ₂ SCA	8 × 10 ¹⁷	3 × 10 ¹⁸
min BrO SCA		7 × 10 ¹⁴
max BrO SCA		5 × 10 ¹⁵
mean BrO SCA		3 × 10 ¹⁵
min NO ₂ SCA		–1 × 10 ¹⁷
max NO ₂ SCA		7 × 15 ¹⁵
mean NO ₂ SCA		–6 × 10 ¹⁶
BrO/SO ₂ (mol mol ⁻¹)		~5 × 10 ⁻⁴
SO ₂ /BrO (mol mol ⁻¹)		1600
R ²		0.84
SO ₂ /NO ₂ ratio (mol mol ⁻¹)		–49
R ²		0.87
NO ₂ /BrO ratio (mol mol ⁻¹)		–30
R ²		0.84
BrO Flux (g s ⁻¹)		8.5
BrO mixing ratio (ppb)		2.30
S/Br mass ratio		645
SO ₂ mixing ratio (ppb)	1320	2140

SCA = Slant Column Amount (molecules cm⁻²)

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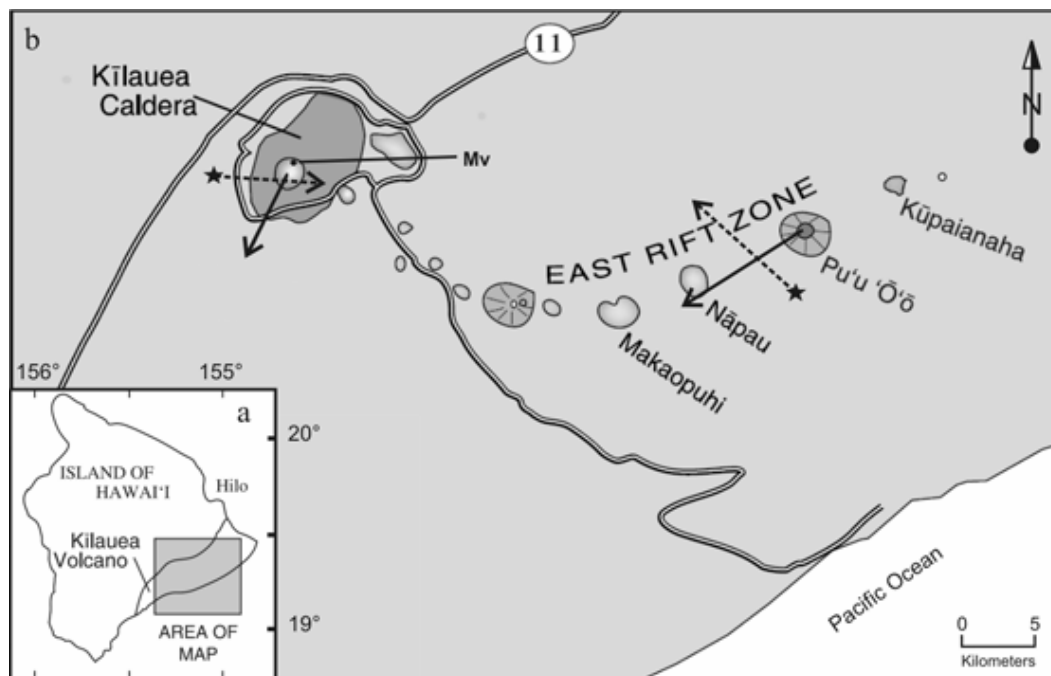


Fig. 1. (a) Map of the Island of Hawai'i showing the location of Kīlauea Volcano (b), the Halema'uma'u Summit caldera, the East Rift Zone, and the Pu'u'Ō'ō cone. Solid stars indicate the sites from which UV spectra were collected in 2007 and 2008. Dotted arrows represent the two different viewing directions; approximate direction of plume dispersion is shown by the other arrows. The label Mv denotes the location of the magmatic vent in the caldera; during the period of survey it measured about 20–30 m in diameter (modified after Thornber, 2003).

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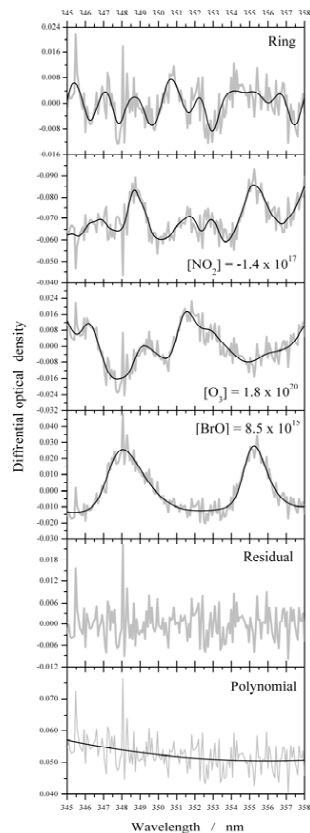


Fig. 2. Example of fitting process for a spectrum with high volcanic gas content. The spectrum was collected in the plume emitted from the new magmatic vent in Halema'uma'u crater on 13 May 2008. The measured differential optical density (grey curves) is fitted by the Ring, NO_2 , O_3 , and BrO differential laboratory spectra (black curves). The residual after fitting shows random modulation, validating the quality of the fit. Systematic structures at ~ 345.5 and ~ 348.0 nm are due to instrumental noise (hot pixels). A second order polynomial was applied to subtract low frequency contributions to the atmospheric attenuation due to Rayleigh and Mie scattering. The high differential ozone SCA results from the difference in the optical paths through the whole atmosphere of the CSR compared with the through-the-plume spectra.

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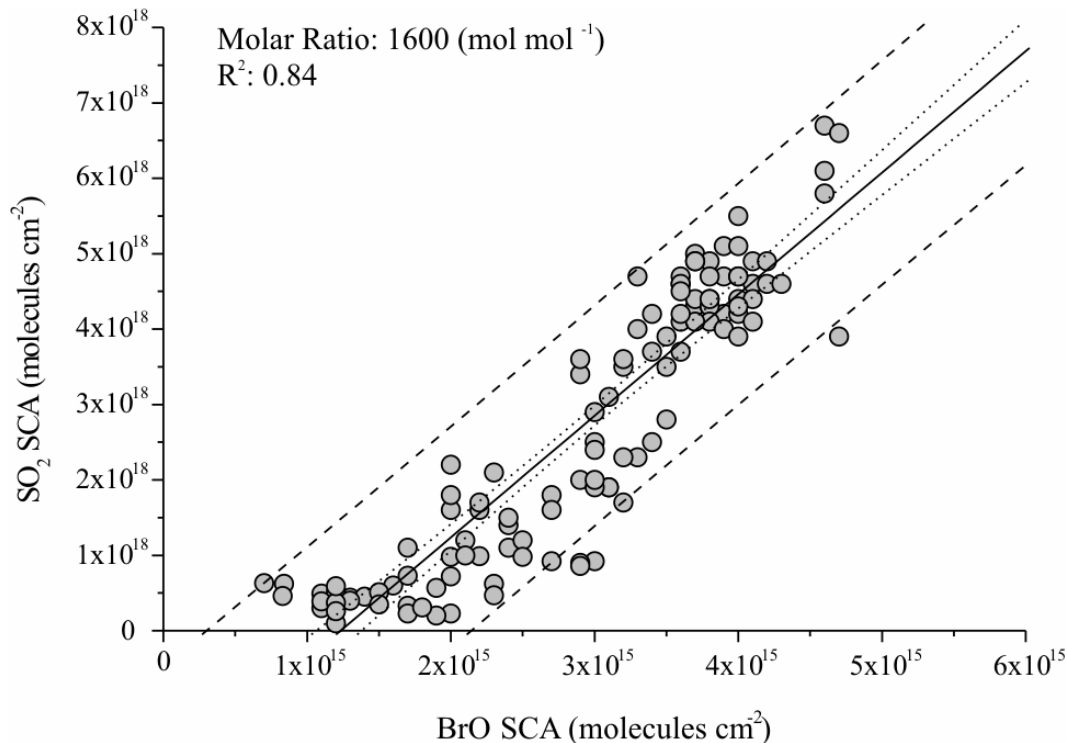


Fig. 3. Scatter plot of SO₂ versus BrO SCA for data collected on 13 May 2008 at Halema'uma'u. The species are strongly correlated ($R^2=0.84$) and are fit by linear regression (solid line) indicating $\text{SO}_2/\text{BrO}=1600 \text{ mol mol}^{-1}$. The dotted and dashed lines represent prediction and 95% confidence limits of the regression, respectively. The scatter is believed to reflect the influence of environmental and volcanological effects and associated variability of SO₂ and BrO mixing ratios within the plume. The intercept is discussed in the text.

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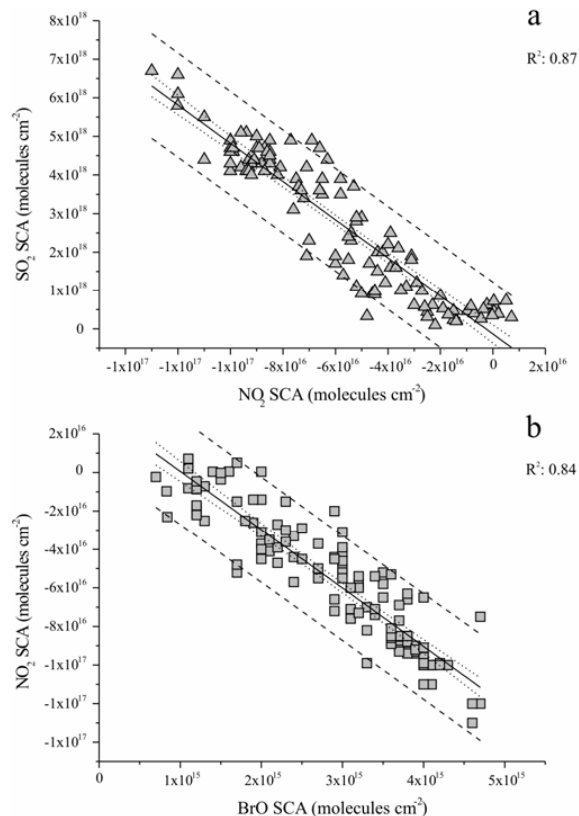


Fig. 4. Scatter plots showing SCA of **(a)** SO₂ versus NO₂, and **(b)** NO₂ versus BrO. The retrieved NO₂ SCA at Halema’uma’u, is strongly anti-correlated with both SO₂ and BrO ($R^2=0.87$ and 0.84, respectively). This close relationship between the three species, suggests active involvement of NO_x in reactive bromine formation. The solid lines indicate the linear regression fitted to the data, and the dotted and dashed lines represent prediction and 95% confidence limits of the regression, respectively.

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