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Ozone Depletion in Tropospheric Volcanic Plumes: From Halogen-Poor to Halogen-Rich Emissions

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Abstract: Volcanic halogen emissions to the troposphere undergo a rapid plume chemistry that destroys ozone. Quantifying the impact of volcanic halogens on tropospheric ozone is challenging, only a few observations exist. This study presents measurements of ozone in volcanic plumes from Kilauea (HI, USA), a low halogen emitter. The results are combined with published data from high halogen emitters (Mt Etna, Italy; Mt Redoubt, AK, USA) to identify controls on plume processes. Ozone was measured during periods of relatively sustained Kilauea plume exposure, using an Aeroqual instrument deployed alongside Multi-Gas SO₂ and H₂S sensors. Interferences were accounted for in data post-processing. The volcanic H₂S/SO₂ molar ratio was quantified as 0.03. At Halema'uma'u crater-rim, ozone was close to ambient in the emission plume (at 10 ppmv SO₂). Measurements in grounding plume (at 5 ppmv SO₂) about 10 km downwind of Pu'u 'Ō'ō showed just slight ozone depletion. These Kilauea observations contrast with substantial ozone depletion reported at Mt Etna and Mt Redoubt. Analysis of the combined data from these three volcanoes identifies the emitted Br/S as a strong but non-linear control on the rate of ozone depletion. Model simulations of the volcanic plume chemistry highlight that the proportion of HBr converted into reactive bromine is a key control on the efficiency of ozone depletion. This underlines the importance of chemistry in the very near-source plume on the fate and atmospheric impacts of volcanic emissions to the troposphere.

Keywords: BrO; reactive halogen; O₃; atmospheric chemistry; plume

1. Introduction

Volcanoes release large quantities of gases and aerosols to the atmosphere. Very large explosive eruptions inject gases directly to the stratosphere, but a significant number of smaller eruptions and continuously passive degassing volcanoes release their emissions to the troposphere; the total global SO₂ flux from passive degassing over 2004–2016 was recently estimated as 23 Tg/yr on average, exceeding volcanic eruptive emissions by about one order of magnitude [1]. To date, studies of the atmospheric chemistry and climate impacts of volcanic emissions have mostly focused on SO₂ and its oxidation to sulfate particles in both the stratosphere (e.g., [2]) and troposphere (e.g., [3]). Volcanic sulfates also catalyse gas-aerosol reactions leading to reductions in stratospheric ozone levels, e.g., [4,5]. However, the volcanic release contains a number of other gases and particles, including notably the emission of volcanic halogens such as HBr and HCl (e.g., [6]). These were initially assumed to be simply washed out of the plume in the troposphere and deposited. Volcanic halogens can occasionally be injected into the stratosphere as evidenced by recent observations of HCl, OCIO, BrO, and IO by satellite [7–10] and of HCl and HF by an instrumented aircraft that transected a high-altitude volcanic cloud [11]. Volcanic halogens that reach high altitudes may cause reductions in stratospheric ozone levels. This has been both observed [11] and simulated by numerical models (e.g., [12,13]) using atmospheric chemistry schemes that were originally developed to study impacts from anthropogenic sources of halogens (chlorofluorocarbons, CFCs) on stratospheric ozone.

The discovery of BrO in a volcanic plume in the troposphere through ground-based remote sensing by Borowski et al. [14] showed that volcanic HBr emissions can become transformed into reactive bromine over very short time-scales (minutes). Volcanic BrO has subsequently been observed in many tropospheric volcano plumes globally, e.g., [15,16] and references therein. A global analysis of satellite observations of volcanic BrO is provided by Hörmann et al. [17]. Volcanic OClO has also been reported in some tropospheric plumes [18–21]. The mechanism for reactive halogen formation in the troposphere at such very fast rates was not well understood. It was proposed that the formation of BrO in volcanic plumes could occur via a volcanic version of the autocatalytic “bromine explosion” (similar to that first identified in the polar boundary layer) [14,22]. This mechanism would lead to depletion of tropospheric ozone immediately downwind from the volcano, as has been confirmed by observations [23,24]. To better understand the fate of volcanic halogen emissions in the troposphere and their atmospheric chemistry impacts, two 1D or box models of the volcanic plume halogen chemistry were developed, [18,25,26], and the plume halogen chemistry was recently incorporated into a regional model [27]. The tropospheric chemistry model mechanisms are briefly outlined below.

Bromine is the main halogen species responsible for ozone depletion in volcanic plumes in the troposphere. Volcanic HBr emissions are converted into reactive bromine via an autocatalytic “bromine explosion” mechanism, involving gas-phase, photolytic, and heterogeneous (gas-aerosol) reactions; for a review, see Von Glasow et al. [28]. Cycles involving the formation and reactive uptake of HOBr and BrONO₂ act to convert volcanic HBr into the reactive form Br₂ that photolyses and can then deplete ozone via the reaction of Br with O₃. A rapid interconversion cycle between BrO (self-reaction) and Br (that reacts with ozone to reform BrO) is suggested to be a major cause of ozone loss at high halogen concentrations (e.g., in the near-source plume). Upon depletion of plume HBr the reactive uptake of HOBr can form BrCl, promoting the formation of reactive chlorine through a non-autocatalytic cycle that can also contribute to ozone loss. Key controls on the plume chemistry are described by Roberts et al. [29] and include the following: the halogen emission flux, the primary volcanic aerosol emission that catalyses key heterogeneous (gas-aerosol) reactions of reactive halogens, and the rate of plume-air mixing that entrains oxidants including ozone into the plume. A high-temperature near-vent chemistry generates radicals that act to “kick-start” the downwind plume chemistry, thereby accelerating the (low-temperature) formation of BrO.

Comparison of the box/1D model simulations to plume observations enables testing of the underlying model mechanisms and is an important first step towards assessing regional-to-global-scale tropospheric impacts from volcanic halogen emissions. In such comparisons, the data is typically scaled to SO₂ that acts as a quasi-plume-tracer over short time-scales. This enables to distinguish between plume chemistry and dilution effects. The model simulations were able to reproduce the observed magnitude and trends in volcanic BrO/SO₂ downwind from Mt Etna [25,26,29], and to broadly capture the magnitude of reported OClO/SO₂ [30]. Recent studies have also demonstrated a modelling capability to reproduce ozone depletion observed in the Mt Redoubt (AK, USA) plume [23] and at Mt Etna (Italy) [24]. Other model-predicted impacts of volcanic plume reactive halogen chemistry in the troposphere include depletion of HO_x and NO_x (the latter converted into nitric acid) [25] and conversion of inert mercury to a more reactive and easily deposited form [26]. A regional modelling study by Jourdain et al. [27] also highlighted the potential for volcanic plume reactive halogens to undergo secondary transport to the stratosphere (e.g., via convective events) for further impacts. However, uncertainties remain in our understanding of the very complex volcanic plume chemistry given the model parameter-space is vast and is constrained by rather few observations, particularly regarding the impacts of volcanic plume halogens on tropospheric ozone. This study presents field-measurements of ozone in the Halema’uma’u and Pu’u ‘Ō’ō plumes of Kīlauea (HI, USA) on 3 September 2007 and 19 July 2008, respectively, and compares them to reported observations at Mt Etna and Mt Redoubt. As a low halogen emitter, Kīlauea provides a useful “end-member” to complement the existing case-studies of the higher halogen emitters Mt Etna and Mt Redoubt, [23,24].

The goals of this study are: (i) to quantify the H₂S emission alongside SO₂ (i.e., H₂S/SO₂ ratio) enabling the prediction of cross-sensitivity on the Aeroqual ozone measurement; (ii) to measure ozone in the crater-rim plume; (iii) to measure ozone in the chemically more evolved downwind plume; and (iv) to interpret the ozone observations in the context of volcanic plume halogen chemistry and tropospheric ozone depletion reported in volcanic plumes globally.

Section 2 below outlines the challenges to measuring ozone in volcanic plumes; Section 3 describes the instruments and field-deployment; Section 4 presents the ozone measurements made at Kīlauea; and Section 5 discusses these observations in a wider volcanic plume chemistry context.

2. Challenges to In-Situ Measurement of Ozone in the Near-Source Volcano Plume

2.1. Interferences of Volcanic Gases on the Ozone Measurement

Ozone is present in the background troposphere at mixing ratios of tens of nmol/mol (or ppbv). Two main in-situ approaches to measuring atmospheric ozone are ultra-violet (UV) spectroscopy on ground-based or aircraft platforms (with instruments often operating at 254 nm, within the Hartley ozone absorption band) and the ozone (electrochemical) balloon sonde. A challenge to measuring ozone in volcanic plumes is the presence of other interfering gases at much higher abundances (e.g., $\mu\text{mol/mol}$ or ppmv) than typically occur in the background atmosphere. These can induce positive or negative interferences to yield an erroneously high or low ozone measurement, respectively.

Specifically, volcanic SO₂ induces a negative interference on electrochemical cell measurements of ozone. For example, ozone-sondes launched into the Eyjafjallajökull 2010 eruption plume over Europe detected severely disturbed profiles [31], but the low ozone signal could not be quantifiably attributed to volcanic plume chemistry due to the interference from SO₂. Volcanic SO₂ induces a positive interference on UV spectroscopic measurements of ozone due to its absorption at 254 nm. This interference can be automatically corrected in dual channel instruments that contain a second (ozone scrubbed) channel, or may be subtracted in data post-processing using co-measured SO₂, provided that the plume is sufficiently dilute [23]. Several airborne measurements of ozone in volcanic plumes have been reported; ozone concentrations were observed below ambient levels in a study of volcanic plumes predominantly from Alaska [32]. Ozone was depleted by at least a third compared to background, reaching up to 90% depletion in the 1980 Mount St. Helens eruption plume, during both ash-rich and ash-poor (passive degassing following the eruption) conditions [33,34]. Oppenheimer et al. [35] reports ozone depletion up to 35% with respect to background in the Mt Erebus (Antarctica) plume, alongside measurements of volcanic sulfur and nitrogen species, but also with some evidence for a very rapid (and unexplained) near-source reduction in SO₂. Instrumented aircraft campaigns by Vance et al. [36] and Schumann et al. [37] measured ozone depletion alongside volcanic SO₂ and other gases and particles in the 2010 Eyjafjallajökull eruption plume dispersed over Europe. Volcanic BrO was also observed in the downwind plume. However, the total volcanic bromine emission from Eyjafjallajökull was not well monitored. Finally, an instrumented aircraft campaign spatially mapped ozone depletion alongside SO₂ in the 2010 Mt Redoubt eruption plume over 2–20 km downwind [27]. In this study, Kelly et al. also quantified the volcanic bromine emission by filterpack ($\text{HBr}/\text{SO}_2 = 4.1 \times 10^{-3} \text{ mol/mol}$), enabling interpretation of the observations and a comparison to an atmospheric box model. Their study captured a rapid decrease in ozone in the near-downwind plume reaching up to tens of ppbv O₃ loss, followed by a slow (partial) recovery in the dispersing plume. This demonstrated the need to characterise plume ozone-depleting chemistry over short spatial-timescales very near to the source. To do so, diffusion tubes were installed on Mt Etna flanks by Vance et al. [36], who reported an ozone depletion signature that was anti-correlated with SO₂. However, corrosion problems prevented a measurement very close to the crater-rim. Some initial measurements were also made using a UV ozone instrument with CrO₃ scrubber [36]. This approach was significantly furthered by Surl et al. [24], whose novel observations quantified the rate of ozone depletion through measurements on Mt Etna's flanks. Their approach involved

a portable single-channel UV spectroscopic instrument combined in series with CrO₃ scrubbers to remove SO₂ from the air inlet, with the ozone losses on the scrubber quantified and treated in the data post-processing. This enabled—for the first time—quantification of ozone depletion in very near-to-source plumes containing tens of ppmv of volcanic SO₂ that was co-measured by small electrochemical sensor (Multi-Gas instrument). The volcanic bromine emission was also characterised during the field-campaign (HBr/SO₂ = 6.13×10^{-4} mol/mol). Through observations made at up to several hundred meters distance from the summit emission source (equivalent to up to a few minutes travel time), Surl et al. [24] derived a linear equation for ozone loss in Mt Etna's near-source plume as a function of travel time downwind from the summit craters, finding a gradient of $\Delta\text{O}_3/\Delta\text{SO}_2 = (-1.02 \pm 0.07) \times 10^{-5} \text{ s}^{-1}$ and intercept of $(-6.2 \pm 0.05) \times 10^{-4} \text{ mol/mol}$. The non-zero intercept suggests that some depletion of ozone had already occurred before the gases reached the crater-rim. The ozone depletion rate (gradient) has been compared to atmospheric 1D and box model simulations by Surl et al. [24] and Roberts et al. [30].

Here, we used an Aeroqual instrument (WO₃ sensor; Aeroqual Limited, Auckland, New Zealand) to measure ozone in the Kīlauea volcanic plumes (Halema'uma'u and Pu'u 'Ō'ō, HI, USA). The instrument is much less sensitive to interference from volcanic SO₂ than other methods, see Table 1. However, the sensor exhibits other cross-sensitivities as listed in Table 1. The most important cross-sensitivity for volcanic plumes is that of H₂S at −2.5% that needs to be considered in data post-processing. The importance of this interference depends on the magmatic conditions specific to each volcano. Fumarolic emissions are H₂S-rich (e.g., Vulcano, with H₂S/SO₂ molar ratios of ~1 [38]). Oxidized magma emissions are H₂S-poor and dominated by SO₂ (e.g., Masaya, Mt Etna, Kīlauea with H₂S/SO₂ molar ratios of just a few percent [39]). The H₂S-poor nature of the Kīlauea volcanic emission is further verified by our in-situ real-time sensing of H₂S and SO₂ alongside ozone (see Results). Alongside our field-measurements of ozone, the bromine content of Kīlauea emissions was characterized by Mather et al. [40], finding HBr/SO₂ = 2.9×10^{-5} mol/mol.

Table 1. Cross-sensitivities of Aeroqual ozone instrument (tungsten oxide sensor). Source: www.Aeroqual.com [41].

Test Gas	Mixing Ratio (ppmv)	Sensor Reading (ppmv)	Sensitivity (%)
Ammonia (NH ₃)	25	−0.02	−0.08
Butane	1000	0	0
Carbon monoxide (CO)	100	0	0
Carbon dioxide (CO ₂)	1000	0	0
Chlorine (Cl ₂)	0.5	0.2	−40
Ethanol	20	−0.02	−0.1
Ethyl acetate	100	−0.02	−0.02
Heptane	100	0	0
Hydrogen sulfide (H ₂ S)	4	−0.1	−2.5
Isopropanol	20	0	0
Methane (CH ₄)	5000	0	0
Nitrogen dioxide (NO ₂)	0.5	0.1	20
Ozone (O ₃)	0.3	0.3	100
Perchloroethylene	50	0	0
Propane	5000	0	0
Sulfur dioxide (SO ₂)	10	0	0
Toluene	50	0	0

2.2. Intermittent Plume Exposure and Sensor Response Times

In-situ measurements of SO₂ at the volcano crater-rim typically exhibit a high temporal variability. Rapid variations in local gas concentrations are often observed near to the volcanic source due to the complex local wind fields that advect the volcanic gases towards and away from the sensors. To characterize the emissions, the correlation in the time-series from two sensors (e.g., SO₂ and H₂S) is

analyzed to derive a gas ratio, e.g., $\text{H}_2\text{S}/\text{SO}_2$. However, the response times of Multi-Gas and other sensors are not all identical, which can introduce uncertainty in the volcanic gas measurement [42]. Rapid variations in gas concentrations are also a challenge to the Aeroqual instrument that makes measurements of ozone at one-minute resolution. As mentioned in Section 2.1 above, the instrument sensor is sensitive to other gases, including (volcanic) H_2S . These cross-sensitivities have been individually quantified by Aeroqual in laboratory experiments at constant gas abundance, Table 1. However, field-deployment of the Aeroqual instrument at volcanoes can expose it to time-varying abundances of volcanic gases. Very large and rapid temporal variations in interfering gas abundances may lead to anomalous values in the ozone measurement that are difficult to correct in data post-processing (see Section 3, Materials and Methods). A potential solution is to attempt to perform measurements under conditions of more sustained exposure to the volcanic plume. Such conditions are rather uncommon due to the local wind-field conditions near-to-source and because buoyant volcanic plumes tend to become elevated above ground. Here, we present in-situ observations of SO_2 , H_2S , and ozone in the near-source and near-downwind Kīlauea (Halema'uma'u and Pu'u 'Ō'ō, HI, USA) plumes obtained during two rare periods of relatively sustained plume exposure (>10 min at "plume strengths" of 5–10 ppmv SO_2) on 3 September 2007 and 19 July 2008.

3. Materials and Methods

The Aeroqual portable ozone monitor is a hand-held instrument for measuring ozone at low mixing ratios at one-minute resolution using a tungsten oxide (WO_3) sensor. The range is 0 to 150 ppbv and a reported resolution of 1 ppbv, accuracy $<\pm 5$ ppbv (datasheets: www.Aeroqual.com [41]). The WO_3 sensor is highly sensitive to ozone, but a major challenge to its use for atmospheric ozone measurements is sensitivity drift. The Aeroqual instrument uses propriety software to correct for WO_3 sensitivity drift that involves different phases of sensor operation during the one-minute measurement period. Cross-sensitivities to the ozone measurement are reported by Aeroqual for fixed gas concentrations (such as for H_2S , Table 1), however, the interferences caused by time-varying gas exposure under time-varying sensor operation are more complex to characterize or quantitatively account for in data post-processing. Therefore, this study focuses on Aeroqual measurements during some (rare) periods of relatively sustained plume exposure, and relies on co-measurements of SO_2 and H_2S to aid interpretation of the Aeroqual ozone observations.

Volcanic gases were measured at 1 Hz resolution using the pumped Multi-Gas system described by Roberts et al. [43] that includes Alphasense Ltd (Essex, UK) electrochemical sensors SO_2 -AF and H_2S -A1 to measure SO_2 and H_2S respectively. Reported resolution of the sensors is <0.1 ppmv (SO_2), <0.05 ppmv (H_2S), and response time is <35 s (www.Alphasense.com [44]). The sensor current output was converted into ppmv mixing ratio time-series using sensitivities and cross-sensitivities determined from laboratory calibrations prior to the fieldwork. The H_2S -A1 sensor exhibits a positive interference to SO_2 that was subtracted in the data post-processing (using SO_2 simultaneously measured by the SO_2 -AF sensor and calibration (cross)-sensitivities). Further details on the instrument and data analysis are provided by Roberts et al. [43].

Kīlauea volcano was emitting three plumes during the fieldwork: an emission from the Halema'uma'u summit crater (measured prior to the 2008 appearance of a lava-lake), the emission from Pu'u 'Ō'ō (east rift zone vents), and an emission resulting from lava contact with sea-water (not sampled). Field-measurements were made at relatively sustained plume exposure on 3 September 2007 to sample Halema'uma'u crater-rim emissions and on 19 July 2008 sampling grounding plume downwind from Pu'u 'Ō'ō, on chain of craters road. This latter site is about 10 km distance from the Pu'u 'Ō'ō vent emission source. Linear regressions were performed to determine $\text{H}_2\text{S}/\text{SO}_2$ and $\Delta\text{O}_3/\Delta\text{SO}_2$ using robust-fit algorithms that yield similar results to least-squares but are less affected by outliers. The reported linear model trends exhibit p -values < 0.05 that indicate significant explanatory power. The R^2 coefficient of determination (ratio of the explained variation to the total variation) was calculated using coefficients of correlation and is also provided in the Results.

4. Results

4.1. Volcanic SO₂, H₂S, and Ozone Measured in the Halema'uma'u Crater Rim Emission Plume

Time-series of volcanic SO₂ and H₂S gas abundances measured at Halema'uma'u crater-rim are well-correlated (p -value < 0.05 and R -squared = 0.52), and linear-regression finds a H₂S/SO₂ molar ratio of 0.030, see Figure 1. This result confirms the low H₂S content of the Kilauea plume, although the H₂S/SO₂ molar ratio is somewhat higher than has been reported previously [39]. This might reflect changing magmatic conditions over time. The scatter in the data is most likely due to instrument response times [41]. Nevertheless, a H₂S measurement is still possible, due to the relatively sustained exposure (e.g., around 10 ppmv SO₂ for tens of minutes). The statistical uncertainty in the gas ratio is very low ($<10^{-3}$) due to the very large number of data points. The actual measurement uncertainty is probably somewhat higher as discussed in Section 4.2.

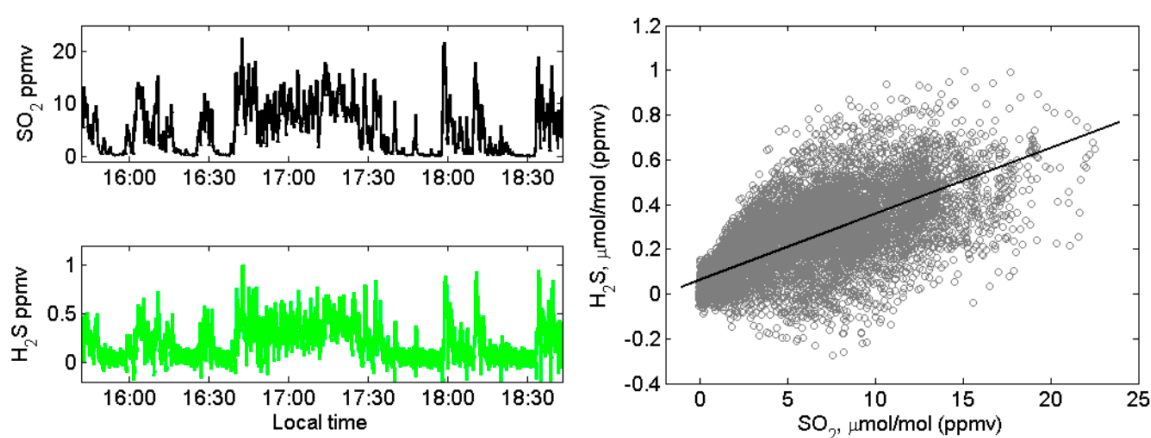


Figure 1. Volcanic plume SO₂ and H₂S abundances measured at 1 Hz resolution in the crater-rim emissions from Halema'uma'u on 3 September 2007. These two volcanic gas time-series are well-correlated; a scatter plot with linear regression yields the H₂S/SO₂ molar ratio of 0.030 mol/mol. p -value < 0.05 and R -squared = 0.52.

The volcanic SO₂ time-series was filtered to make one-minute averaged data and these are compared to the ozone time-series (1 min resolution) in Figure 2. The measured ozone abundance fluctuates around 20 to 40 ppbv with a few (anomalous) zero data points. No clear trend is visible in the time-series although a scatter plot of the SO₂, and ozone data show a weak anti-correlation (p -value < 0.05 and R -squared = 0.13). The gradient of the linear regression is $-0.72 (\pm 0.13) \times 10^{-3}$ mol/mol. This measured $\Delta O_3/\Delta SO_2$ closely matches the predicted Aeroqual instrument response to a 2.5% H₂S interference for volcanic plume with H₂S/SO₂ = 0.03 mol/mol ($-2.5/100 \times 0.03 = -0.75 \times 10^{-3}$ mol/mol). Accounting for the H₂S interference leads to the deduction in that actual in-plume ozone concentrations were very close to ambient levels in the emission plume at Halema'uma'u crater rim.

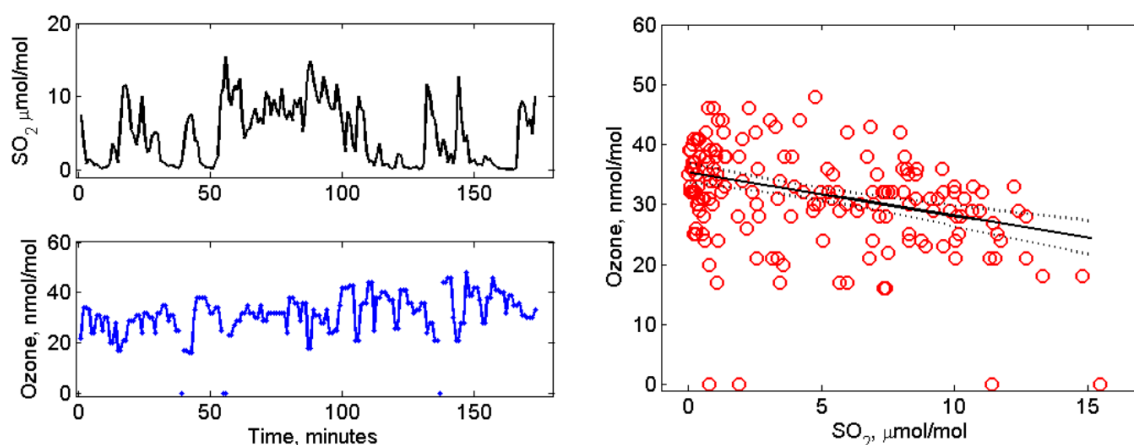


Figure 2. Volcanic plume SO_2 and ozone abundances measured at 1 min resolution in the crater-rim emissions from Halema'uma'u on 3 September 2007. The data show a degree of scatter (with some zero ozone observations that are likely instrument anomalies) and weak anti-correlation between measured ozone and SO_2 . The linear regression has gradient $\Delta\text{O}_3/\Delta\text{SO}_2 = -0.72 (\pm 0.13) \times 10^{-3} \text{ mol/mol}$ with intercept corresponding to 35 nmol/mol ambient ozone. p -value < 0.05 and R -squared = 0.13. Dashed lines denote regression trend with coefficients $\pm 2 \times$ standard error (95% CI).

4.2. Volcanic SO_2 , H_2S , and Ozone Measured in the Near-Downwind Plume from Pu'u 'Ō'ō

Time-series of volcanic SO_2 and H_2S gas abundances measured in the plume ~10 km downwind from Pu'u 'Ō'ō are also well-correlated (p -value < 0.05 and R -squared = 0.50), and linear-regression finds a $\text{H}_2\text{S}/\text{SO}_2$ molar ratio of 0.034, Figure 3. Visually, the data appear less scattered compared to those in Figure 1, reflecting improved instrument performance when exposed to more slowly fluctuating gas concentrations. However, instrument noise becomes important at these low H_2S abundances in relatively dilute plume, leading to similar R^2 as for Figure 1. The gas ratio is slightly higher than found for the crater-rim emissions from the Halema'uma'u ($\text{H}_2\text{S}/\text{SO}_2 = 0.030 \text{ mol/mol}$) which could be due to (i) slight differences in the $\text{H}_2\text{S}/\text{SO}_2$ emitted from Pu'u 'Ō'ō and Halema'uma'u despite their common magma source; (ii) partial atmospheric oxidation of SO_2 in the Pu'u 'Ō'ō plume by up to 14% (this would indicate a relatively fast in-plume SO_2 oxidation); or (iii) uncertainty in the Multi-Gas measurement.

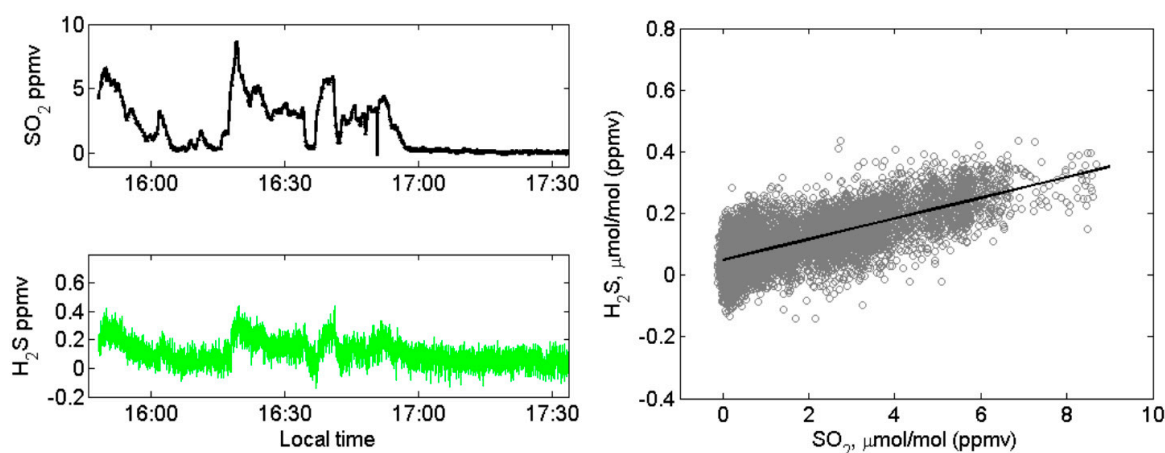


Figure 3. Volcanic plume SO_2 and H_2S abundances measured at 1 Hz resolution in the grounding plume ~10 km from the Pu'u 'Ō'ō emission source on 19 July 2008. These two volcanic gas time-series are well-correlated; a scatter plot with linear regression yields an $\text{H}_2\text{S}/\text{SO}_2$ molar ratio of 0.0335 mol/mol. p -value < 0.05 and R -squared = 0.50.

The one-minute averaged SO_2 time-series is compared to the ozone measurement (at 1 min resolution) in Figure 4. The measured ozone abundance fluctuates between 30 and 50 ppbv. The last 20 min of the time-series appear mostly plume-free (low SO_2) so show the natural variability in ozone abundance. There were no (anomalous) zero data points. A clear tendency (seen particularly in the first 50 min) is that ozone decreases in conjunction with maximum peaks in SO_2 . A scatter plot of the SO_2 and ozone data confirms this anti-correlation (p -value < 0.05 and R -squared = 0.30). The R^2 is higher than found at the crater-rim (Figure 2), i.e., the anti-correlation of ozone to SO_2 explains a greater ratio of the variation in ozone compared to total variation for the Pu'u 'Ō'ō downwind plume measurements than for that of the Halema'uma'u crater-rim measurements. The gradient of the linear regression is $-1.15 (\pm 0.18) \times 10^{-3}$ mol/mol. This measured $\Delta\text{O}_3/\Delta\text{SO}_2$ exceeds the Aeroqual instrument response to volcanic H_2S calculated as -0.84×10^{-3} mol/mol for a plume with $\text{H}_2\text{S}/\text{SO}_2$ molar ratio of 0.034. Accounting for the negative H_2S interference on measured ozone at $\text{H}_2\text{S}/\text{SO}_2 = 0.034$ suggests an actual in-plume $\Delta\text{O}_3/\Delta\text{SO}_2$ of $-0.31 (\pm 0.18) \times 10^{-3}$ mol/mol.

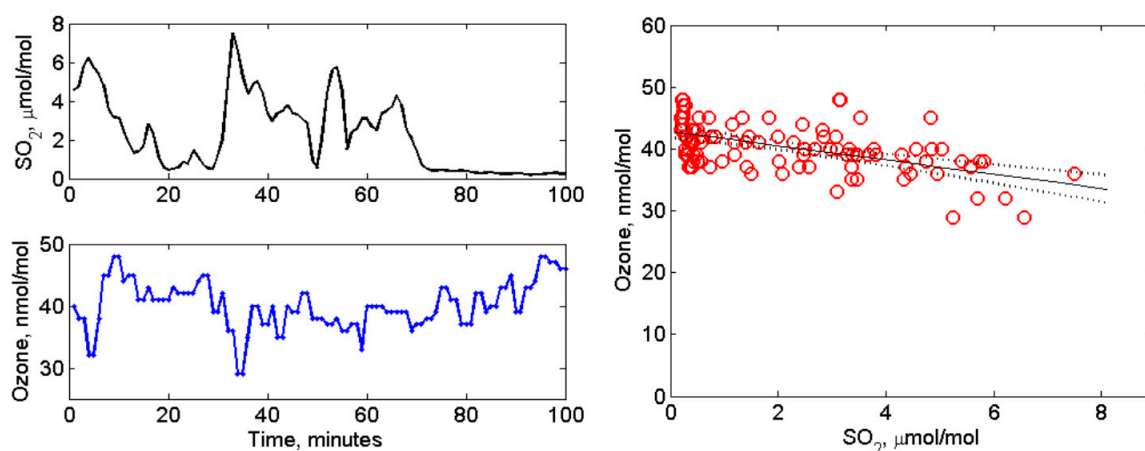


Figure 4. Volcanic plume SO_2 and ozone abundances measured at 1 min resolution in grounding plume on a chain of craters road on 19 July 2008. This location is approximately 10 km downwind of the Pu'u 'Ō'ō volcanic emission source. Peak maxima in the volcanic SO_2 time-series correspond to clearly defined minima in the ozone time-series. The anti-correlation between ozone and SO_2 is confirmed by scatter-plot; the linear regression has gradient $\Delta\text{O}_3/\Delta\text{SO}_2 = -1.15 (\pm 0.18) \times 10^{-3}$ mol/mol with intercept corresponding to 43 nmol/mol ambient ozone. Dashed lines denote regression trend with coefficients $\pm 2 \times$ standard error (95% CI). p -value < 0.05 and R -squared = 0.30. This measured $\Delta\text{O}_3/\Delta\text{SO}_2$ exceeds the Aeroqual instrument response to volcanic H_2S , therefore, it indicates an ozone depletion. See text for further details and quantification.

A source of uncertainty in the ozone depletion measurement is variation in background ozone, which appears to descend then ascend during the time-period, and also exhibits short-term variability. Additional uncertainties can arise from uncertainty in the interference from H_2S , for example, an error of ± 0.005 in the measured $\text{H}_2\text{S}/\text{SO}_2$ molar ratio would induce an uncertainty in the detected $\Delta\text{O}_3/\Delta\text{SO}_2$ of $\pm 0.125 \times 10^{-3}$ mol/mol, whilst an error of ± 0.01 would induce an uncertainty in $\Delta\text{O}_3/\Delta\text{SO}_2$ of $\pm 0.25 \times 10^{-3}$ mol/mol. Nevertheless, results from the crater-rim observations suggested that $\text{H}_2\text{S}/\text{SO}_2$ measured by the Multi-Gas sensors is fully consistent with the expected interference. In summary, the data show that ozone in the downwind Pu'u 'Ō'ō plume was likely slightly depleted below ambient levels but only by a small magnitude.

5. Discussion and Conclusion: Ozone Depletion from Halogen-Poor to Halogen-Rich Volcanic Plumes

Measurements of ozone in volcanic plumes are challenging. This study demonstrates the need to consider the interference of H_2S on Aeroqual measurements of ozone, the need for sustained plume

exposure (as 1 min measurements can be affected by rapid changes in gas concentration), and also illustrates natural variability in background ozone that can act to mask an observable ozone depletion signature. Nevertheless, the Aeroqual measurements provide a useful constraint on the magnitude of ozone depletion in the Kīlauea volcanic plumes at short distances from the source. In particular, the observations provide a valuable end-member example that quantifies ozone in the plume of a low halogen emitter. This contrasts to studies to date that mostly focused on volcanic plumes with higher halogen contents. To interpret the field-data, ozone depletion is scaled relative to co-measured SO₂ in order to distinguish between chemistry and plume dilution effects, and it is interpreted in terms of distance or travel time downwind and the bromine emission.

For the Kīlauea plumes, ozone was shown to be close to ambient levels during plume exposures of up to 10 ppmv SO₂ at the Halema'uma'u crater-rim, and they were only slightly depleted in the grounding plume at around 10 km downwind from Pu'u 'Ō'ō (e.g., by up to 2 ppbv measured at 5–8 ppmv SO₂). The measurements indicate that the volcano emission has only a limited impact on tropospheric ozone, as might be expected for a low halogen emitter. This contrasts with findings for higher halogen emitters. A study of Mt Etna plume ozone by Surl et al. [24], for example, found 11 ppbv ozone depletion measured in plume exposure of 9 ppmv SO₂ at just 300 m downwind. Surl et al. [24] also suggest that ozone in the Mt Etna crater-rim plume was depleted below background, finding from their near-source field-campaign that $\Delta O_3/\Delta SO_2 = (-1.02 \pm 0.07) \times 10^{-5} \text{ s}^{-1}$ with an intercept of $(-6.2 \pm 0.05) \times 10^{-4} \text{ mol/mol}$. A much greater depletion of tropospheric ozone (tens of ppbv ozone loss in plume of 1 ppmv SO₂) was observed by Kelly et al. [23] through spatial mapping of the Mt Redoubt 2009 eruption plume. The $\Delta O_3/\Delta SO_2$ data from Kelly et al. [23] is shown in Figure 5 as a function of distance downwind for two flight campaigns. A smaller ozone depletion was observed in August compared to June 2009. We focus our comparison on the June 2009 data for which the volcanic halogen emission was also quantified (just one day prior to the aircraft campaign) that yields a linear regression in $\Delta O_3/\Delta SO_2$ of $(-7.2 \pm 1.3) \times 10^{-3} \text{ mol/mol km}^{-1}$, with intercept close to zero (within statistical uncertainty). Table 2 summarizes these field measurements and interconverts $\Delta O_3/\Delta SO_2$ per unit travel time or per distance downwind using available or estimated wind-speeds. Not shown in Table 2 are aircraft studies of the 2010 Eyjafjallajökull eruption plume over Europe [36,37] that found large ozone depletions in the far-field dispersed plume but which are difficult to interpret because the halogen emission was poorly constrained and the assumption of SO₂ as a quasi-plume-tracer (in $\Delta O_3/\Delta SO_2$) may not be valid.

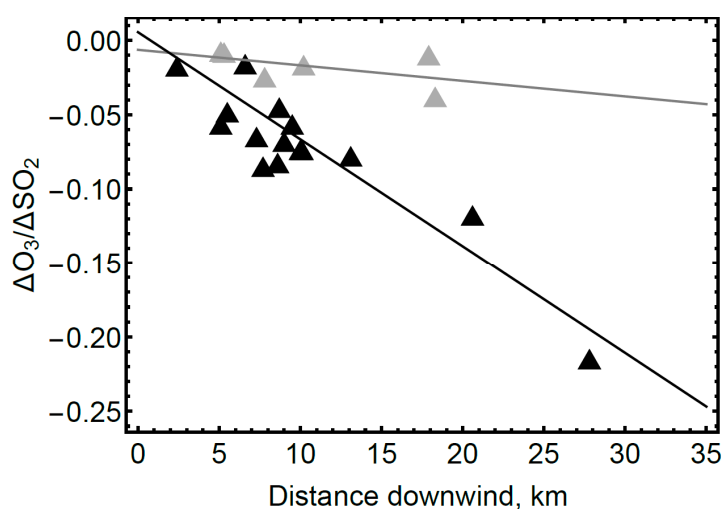


Figure 5. Ozone depletion (scaled to co-measured SO₂) in the Mt Redoubt 2009 eruption plume as a function of distance downwind during the aircraft campaigns on 21 June (black triangles) and 19 August (grey triangles) 2009. Data from Kelly et al. [23]. The gradient of the linear regression for 21 June is $(-7.2 \pm 1.3) \times 10^{-3} \text{ mol/mol km}^{-1}$.

Table 2. Studies of ozone depletion in volcanic plumes where the halogen emission was also reported: Br/S in the emission and $\Delta\text{O}_3/\Delta\text{SO}_2$ per km downwind or per second of travel time.

Volcano	Br/S (mmol/mol)	Distance (km)	Wind Speed * m/s	Time (min)	$\Delta\text{O}_3/\Delta\text{SO}_2$ Per km (km^{-1}) $\times 10^{-3}$	$\Delta\text{O}_3/\Delta\text{SO}_2$ Per Second (s^{-1}) $\times 10^{-5}$	Reference
Mt Redoubt 2009 eruption	4.1	2.4–27.8	4.4	9–105	-7.2 ± 1.3	-3.2 ± 0.6	[23] (Figure 5 this study)
Mt Etna passive degassing 2012	0.613	0.15–0.40	~2.2	1–4	(-4.4 ± 0.3)	-1.02 ± 0.07	[24]
Kīlauea plumes 2007–2008	0.029 ± 0.025	~10	~5	~30	Up to -0.03	(Up to 0.02)	This study ($\Delta\text{O}_3/\Delta\text{SO}_2$) [40] (2012) (Br/S)

* Wind-speed reported directly by Kelly et al. [23] for the study of Mt Redoubt, calculated from the reported 380 m distance downwind equivalent to about 175 s travel time in the study of Mt Etna by Surl et al. [24], and estimated from Hilo radiosonde data for the study of Kīlauea. Values of ozone depletion rate in brackets were obtained by interconverting time and distance data using the wind-speeds of Table 2.

Figure 6 presents the $\Delta\text{O}_3/\Delta\text{SO}_2$ scaled to distance or travel time downwind (i.e., rate of ozone depletion) as a function of Br/S in the volcano emission for the three case studies of Table 2 (Kīlauea, Mt Etna, and Mt Redoubt). The data show that ozone depletion is a non-linear function of the bromine emission; greater ozone loss occurs for a higher Br/S emission, as expected. However, the rate of ozone depletion for the volcano with the highest Br/S emission (Mt Redoubt) is disproportionately slow, i.e., the Mt Redoubt plume is found to be less efficient at destroying tropospheric ozone than would be expected. This non-linearity is initially a surprising result given the role of volcanic bromine in the depletion of tropospheric ozone through a “bromine explosion” that is autocatalytic (i.e., self-enhancing). A potential reason could be the complete titration of plume ozone (thereby preventing any further ozone depletion), but this is ruled out based on the measurements of Kelly et al. [23]; ozone in the Mt Redoubt plume was reduced to less than ambient levels but was not fully depleted. Instead, an explanation is provided by atmospheric box modelling of the near-source plume chemistry. Model studies point to non-linearities in the conversion of emitted HBr into reactive bromine species, depending on the bromine content of the emissions [24,29]. For high Br/S emissions, not all of the emitted HBr may become converted into reactive bromine. This was shown in a model sensitivity study by Roberts et al. [29] for Mt Etna that predicts HBr is rapidly and fully converted into reactive forms over tens of minutes for an emission with HBr/SO₂ molar ratio of 7.4×10^{-4} , but HBr is more slowly and only partially (~50% after one hour) converted into reactive bromine for an emission with a higher HBr/SO₂ molar ratio of 2.4×10^{-3} . Furthermore, the model simulation of the Mt Redoubt 2009 eruption plume by Kelly et al. [23] predicts that only 30% of emitted HBr was converted into reactive forms, for an emission with even higher HBr/SO₂ molar ratio of 4.1×10^{-3} . However, another difference between the plumes is the emission flux, with 4.3 kg/s SO₂ flux for Mt Redoubt and ~20 kg/s SO₂ flux for the Mt Etna simulation. The net conversion of emitted volcanic HBr into reactive bromine reflects the balance of plume chemistry processes (that form reactive halogens from HBr and that can re-form HBr from reactive halogens) as a function of plume properties such as gas flux, aerosol, plume-air mixing, etc., and is also a function of time. For plumes younger than one minute, recent observations by Rüdiger et al. [45] suggest reactive bromine accounts for less than 44% of total bromine, consistent with the models. The modeled plume Br-speciation predicted by Roberts et al. [23] and [29] are shown in Figure 7, illustrating the proportion of emitted HBr converted into reactive bromine during the first hours of plume chemical evolution. These model outputs are used to re-evaluate the non-linear trend in Figure 6. When the Br/S content of the emissions is adjusted to reflect the modeled plume “reactive bromine”/S (e.g., reduced to 30% of the total emitted Br/S for Mt Redoubt: open triangle, Figure 6), there is more linearity (broadly proportional trend) between the volcanic (reactive) bromine/S and the rate of plume ozone depletion. It is nevertheless expected

that other variables, e.g., aerosol and plume-air mixing rate, may affect $\Delta O_3/\Delta SO_2$ depending on the volcanic-meteorological setting.

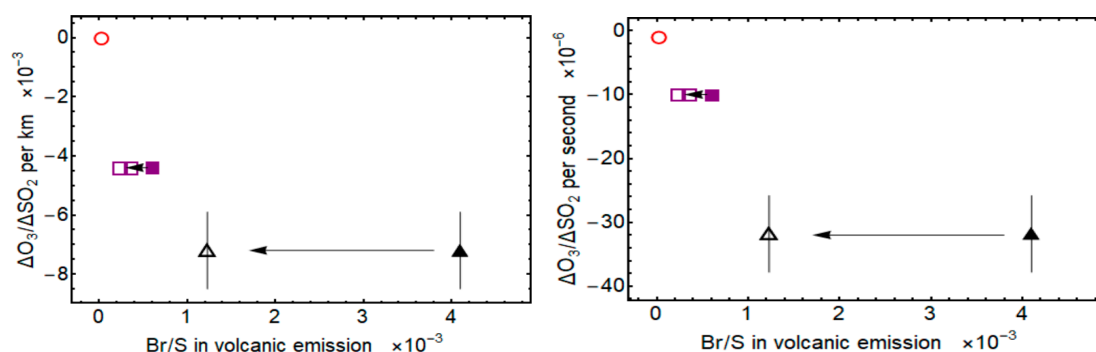


Figure 6. Depletion in ozone scaled to volcanic SO_2 (as a quasi-plume-tracer) and scaled with (i) km distance downwind or (ii) seconds travel time downwind, plotted as a function of the bromine/ SO_2 molar ratio in the emission. Data are available for three volcanic systems: Kīlauea (red circle, this study), Mt Etna (purple square, [24]), and Mt Redoubt (black triangle, [23]), in ascending order of Br/S in their emissions. Arrow and open triangle denote adjustments in the Br/S content that accounts for partial rather than full conversion of emitted HBr into reactive bromine. See text for details.

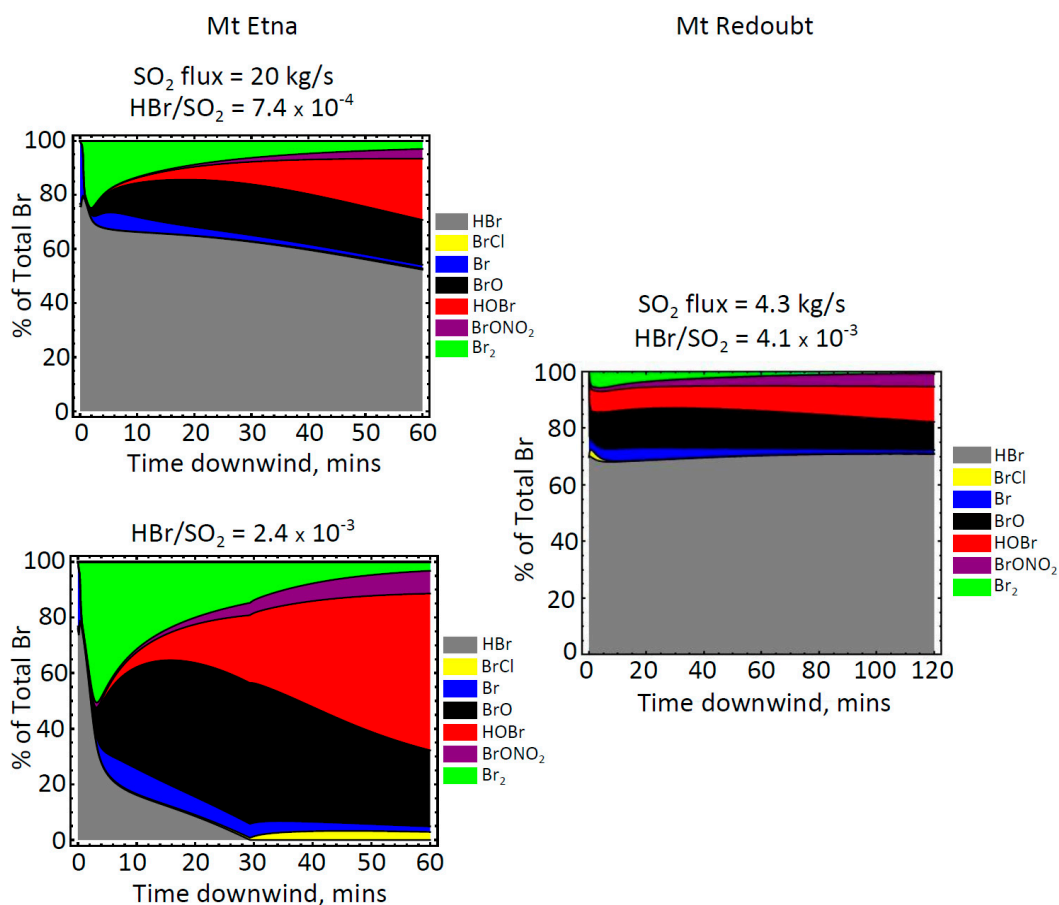


Figure 7. Model simulated reactive bromine speciation in the plumes of Mt Etna and Mt Redoubt, from Roberts et al. [29], and Kelly et al. [23] illustrating varying degrees (complete, partial) of conversion of HBr into reactive bromine. Reproduced with permission from Kelly et al. [23], JVGR; published by Elsevier.

In conclusion, chemistry in the near-source volcanic plume exerts an important influence on the fate of volcanic halogens entering the troposphere. Plume chemistry converts the volcanic HBr emission into reactive bromine, causing the depletion of tropospheric ozone. Measurements of ozone in the near-source volcanic plume are challenging to make but they can provide useful observational constraints on the volcanic plume halogen chemistry. This study presents observations of ozone in the volcanic plumes from Kīlauea, a low-halogen emitter. Ozone was close to ambient levels in crater-rim Halema'uma'u emissions and only slightly depleted in the plume 10 km downwind from Pu'u 'Ō'ō. This contrasts with observations of much larger ozone depletion (tens of ppbv) in the near-source and near-downwind plumes of two higher halogen emitters: Mt Etna and Mt Redoubt [23,24]. The available observations combined with numerical modelling of the plume chemistry suggest that the volcanic Br/S emission and its (partial or complete) conversion into reactive bromine are key controls in the depletion of tropospheric ozone downwind from the volcano. Characterizing the near-source volcanic plume chemistry is thus an essential step to quantifying the fate and downwind impacts of volcanic emissions to the atmosphere.

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