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On bromine, nitrogen oxides and ozone depletion in the tropospheric plume of Erebus volcano (Antarctica)

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Abstract

Since the discovery of bromine oxide (BrO) in volcanic emissions, there has been speculation concerning its role in chemical evolution and notably ozone depletion in volcanic plumes. We report the first measurements using Differential Optical Absorption Spectroscopy (DOAS) of BrO in the tropospheric plume of the persistently degassing Erebus volcano (Antarctica). These are the first observations pertaining to emissions from an alkaline phonolitic magma. The observed BrO/SO₂ ratio of 2.5×10^{-4} is similar to that measured at andesitic arc volcanoes. The high abundance of BrO is consistent with high abundances of F and Cl relative to sulfur in the Erebus plume.

Our estimations of HBr flux and BrO production rate suggest that reactive bromine chemistry can explain a 35% loss of tropospheric O₃ observed in the Erebus plume at approximately 30 km from source (Oppenheimer et al., 2010).

Erebus also has a permanent lava lake, which could result in generation of NO_x by thermal fixation of atmospheric N₂ at the hot lava surface. Any NO_x emission could play a potent role in reactive bromine chemistry. However, the presence of NO₂ could not be detected in the plume, about 400 m above the lake, in our DOAS observations of 2005. Nor could we reproduce spectroscopic retrievals that reportedly identified NO₂ in DOAS observations from 2003 made of the Erebus plume (Oppenheimer et al., 2005). Based on the NO₂ detection limit of our analysis, we can state an upper limit of the NO₂/SO₂ ratio of ≤ 0.012 , an order of magnitude lower than previously reported. Our new result supports a rapid oxidation of NO_x in the young plume and is more consistent with measurements of NO_y species measured using an instrumented aircraft flying in the plume. Model simulations, tuned for Erebus, were performed to reproduce the BrO/SO₂ observed in the young plume and to investigate the impact of NO_x emissions at source on the subsequent formation of BrO in the plume. They support our hypothesis of rapid conversion of NO_x to NO_y in the vicinity of the lava lake. This study thus places new constraints on the interaction between reactive nitrogen and bromine species in volcanic plumes, and its effects on ozone.

Highlights

► 1st observation of BrO simultaneously to O₃ depletion in a volcanic plume. ► 1st detection of BrO in the plume of Erebus which impacts the Antarctic troposphere. ► 1st detection of BrO for a phonolitic volcano. ► Reactive Br chemistry can cause the ozone depletion observed in the plume of Erebus. ► Observations and model simulations support a rapid conversion of NO_x to NO_y species.

Keywords: Volcanic plume; Antarctic troposphere; Reactive bromine chemistry; Reactive nitrogen chemistry; Ozone depletion; Phonolitic magma

1. Introduction

Both the sustained ‘quiescent’ degassing of volcanoes (Halmer et al., 2002) and sporadic explosive eruptions contribute significant quantities of reactive gases and aerosols to the atmosphere ([Robock and Oppenheimer, 2003] , [Oppenheimer et al., 2003] , [Mather, 2008] and [von Glasow et al., 2009]). Much attention has been paid to major gases including CO₂, an important greenhouse gas, SO₂ a precursor for sulfate aerosols which impact radiative forcing, and HCl and HF responsible for acid deposition with potentially significant environmental and agronomic impacts. The reactive trace halogen species, BrO, was first reported in volcanic plumes by Bobrowski et al. (2003) (see Table 1 for a review of all available observations to date). Also, reactive trace nitrogen species have been identified ([Hobbs et al., 1982] , [Hobbs et al., 1991] , [Huebert et al., 1999] , [Mather et al., 2004b] and [Oppenheimer et al., 2005]). Reactive nitrogen oxides (NO_x) are thought to be generated initially via thermal fixation of atmospheric N₂ near the surface of a hot lava body and/or in a high-temperature mixture of magmatic and atmospheric gases, followed by in-plume oxidation ([Huebert et al., 1999] , [Mather et al., 2004b] , [Oppenheimer et al., 2005] and [Martin et al., 2006]). Reactive halogens are not emitted directly from magma, but are formed from hydrogen halides (e.g., HCl and HBr) (Gerlach, 2004) as a result of heterogeneous chemical reactions during plume transport and mixing with background air ([Oppenheimer et al., 2006] and [Bobrowski et al., 2007]). The autocatalytic formation of BrO (also called the ‘BrO explosion’) is the result of a complex sequence of reactions taking place in the plume. It first involves gas phase reactions generating HOBr and BrONO₂ and/or BrNO₂ which then heterogeneously interact with acid aerosols to form Br₂ or BrCl species. Further photolysis and reaction with O₃ sourced by entrainment of ambient air, generates BrO. Readers are referred to the review of von Glasow and Crutzen (2003) and papers of [Oppenheimer et al., 2006] , [Bobrowski et al., 2007] and [Roberts et al., 2009] and von Glasow (2010) for a more complete and detailed description of these sequences of chemical reactions. Despite their low abundances, reactive halogens can play a key role in a volcanic plume as they have the potential to consume ambient O₃ ([Bobrowski et al., 2003] and [Roberts et al., 2009]), which is fundamental in the troposphere, as the primary source of hydroxyl radicals and as a strong oxidizing agent. NO_x species also deserve attention since they can strongly perturb reactive halogen chemistry. Whereas observations of ozone depletion have been made in volcanic plumes from Mt. St. Helens (Hobbs et al., 1982), Hekla (Rose et al., 2006) and Eyjafjallajökull (Schumann et al., 2010), the simultaneous presence of reactive halogens in a tropospheric plume has not been reported previously.

Erebus volcano provides an exceptional opportunity to understand the chemical evolution of volcanic plumes and their impact on the troposphere. Because of its southerly location on Ross Island in Antarctica ($77^{\circ} 32' \text{ S}$, $167^{\circ} 10' \text{ E}$), this volcano affects the near pristine polar atmosphere (Graf et al., 2010). It also presents a sustained activity, as it degasses persistently from a permanent lava lake, first observed in the 1970s ([Giggenbach et al., 1973] and [Kyle et al., 1982]), but possibly already present in 1841 (Ross, 1847). The summit crater of the volcano reaches up to 3794 m in altitude typically entraining the plume at a height of close to 4000 m above sea level. This promotes a long atmospheric lifetime of gas and aerosol species and a consequently wide dispersion (Graf et al., 2010). The influence of Erebus' degassing has been identified more than 1000 km away above the polar plateau thanks to numerous observations: particle, trace metals and chlorine deposits ([Chuan et al., 1986], [Chuan, 1994], [Zoller et al., 1974], [Meeker et al., 1991] and [Zreda-Gostynska et al., 1997]), as well as airborne sulfate aerosols, SO_2 and gas phase NO_y species (Slusher et al., 2010). Ice cores from East Antarctica contain also evidence of volcanic (Erebus) input (Vallelonga et al., 2002). Determining the exact influence of Erebus' emissions, including reactive trace species, is thus important for understanding the state of the Antarctic troposphere and even for interpretation of glaciochemical records extracted from the polar ice.

The data already gathered at this volcano are extensive. They include near-source rim observations of gas flux and composition ([Zreda-Gostynska et al., 1993], [Zreda-Gostynska et al., 1997], [Kyle et al., 1994], [Wardell et al., 2004], [Sweeney et al., 2008], [Oppenheimer and Kyle, 2008] and [Boichu et al., 2010]), and of particle emissions ([Meeker et al., 1991], [Zreda-Gostynska et al., 1997], [Wardell et al., 2008] and [Ilyinskaya et al., 2010]), but also airborne in-situ measurements of aerosols ([Radke, 1982], [Chuan et al., 1986], [Chuan, 1994] and [Oppenheimer et al., 2010]) and various gas species in the aged plume ([Rose et al., 1985] and [Oppenheimer et al., 2010]). Oppenheimer et al. (2010) recently showed evidence for ozone depletion in the plume, ~ 30 km downwind from source. This result importantly demonstrates ozone depletion in plumes within the free troposphere, in contrast to boundary-layer ozone depletion events (ODE's) that occur during springtime in Antarctica as solar radiation becomes available (see Simpson et al., 2007, for a review). As a consequence, the impact of in-plume reactive bromine chemistry on this destruction of O_3 begs investigation.

Here we report the first differential optical absorption spectroscopy (DOAS) observations of BrO in the Erebus plume in December 2005. These are the first observations pertaining to phonolitic magma (see Table 1). Together with calculations of HBr source emissions, this enables evaluation of the dynamics of the 'BrO explosion' at this volcano.

Oppenheimer et al. (2005) reported the presence of NO_2 in the Erebus plume based on evaluation of ultraviolet spectra collected in December 2003. However, NO_2 was not detected in DOAS measurements and observations from instrumented aircraft flying in the plume (Oppenheimer et al., 2010) collected in December 2005. To investigate this puzzling observation, we also carry out here a reassessment of the DOAS observations reported by Oppenheimer et al. (2005) and find a weaker abundance of NO_2 than previously reported. Our observations and model simulations of reactive plume chemistry clarify aspects of the conversion of NO_x produced at the lava lake, to NO_y species, and the impact on reactive Br-chemistry. In the light of our new estimations of BrO, HBr and NO_x abundances, and application of recently developed models of the chemical evolution of volcanic plumes, we offer a qualitative evaluation of the impact of Erebus on polar tropospheric ozone.

2. Methodology

2.1. Experiment description

UV DOAS measurements were collected in December 2005, from Lower Erebus Hut at ~2 km from the crater rim. Spectra were collected with two thermo-stabilized (~15°C) Ocean Optics USB2000 spectrometers spanning a wavelength range of about 288–434 nm with a resolution of ~0.45 nm and 0.60 nm (FWHM). The spectrometers were coupled to a simple quartz-lens telescope (field of view of 8 mrad) held in a fixed position above the crater (elevation of 15°). A young plume of ~3–7 min after emission from the lava lake was sampled, assuming a typical rise rate for the plume of 1–2.5 m s⁻¹ (Boichu et al., 2010) and a lava lake at 3515 m above sea level (Csatho et al., 2008). Spectra were recorded with a total integration time ranging between 5 and 10 s (details are given in Table 2 and Table 3). DOAS observations on 11 December 2003, reported by Oppenheimer et al. (2005), were re-examined. These spectra were collected from the same location under similar conditions (total integration time of 8 s), except the telescope was mounted on a platform rotating so as to scan the vertically rising plume. The spectrometer, with an elevation of 14°, was viewing a ~2.5–6 min old plume.

2.2. Spectroscopic retrieval

SO₂, BrO and NO₂ column amounts were retrieved following DOAS procedures (Platt and Stutz, 2008). For December 2005 data, a moving average of 5 consecutive spectra was used to increase the signal-to-noise ratio before the DOAS analysis. The reference spectra included in the non-linear fit were obtained by convolving high-resolution absorption cross-sections of SO₂ (243 K, air) (Bogumil et al., 2003), BrO (243 K, air) (Fleischmann et al., 2004), O₃ (223 K, air) (Voigt et al., 2001) and O₄ (296 K, 335–666 nm, from Hermans, 2002), with the instrumental line shape. For testing the presence of nitrogen species in the plume, NO₂ (246 K, air) (Voigt et al., 2002) and HONO (298 K, air) (Stutz et al., 2000) high-resolution absorption cross-sections were also used. The temperatures chosen for these laboratory cross-sections correspond to tropospheric and stratospheric temperatures at Erebus (except for O₄ and HONO cross-sections only available for 296–298 K). Temperatures at Erebus summit in December were typically around 243–253 K. Stratospheric temperatures at 20 km altitude averaged over 50 years during the months of December to February, are approximately 230–240 K, with a maximum variation of -15 K about the mean (David et al., 2010).

DOAS analysis is usually performed in the optical density space. However, small differences in the calibration of collected and background spectra (e.g. due to thermal effects) may generate high-frequency artifacts in the optical density, resulting in an increase of the noise level. To tackle this issue, the DOAS analysis was made in the intensity space and the logarithm of the background spectrum was included as a cross-section in the fitting routine. The coefficient of this ‘artificial’ cross-section must be very close to 1 to validate the method, and this was verified afterward. A Ring spectrum (Fish and Jones, 1995), calculated from the background spectrum using DOASIS software (Kraus, 2006), was also included in the fit, as well as a third order polynomial to remove broad band structures from the logarithm of the measured intensity spectra. In the non-linear fit, shift and squeeze permitted for the reference spectra were constrained by the values of shift and squeeze evaluated for the logarithm of the background spectrum, which ranged in 0.97–1.03 and [-0.3; 0.3] nm, respectively.

The instrumental line shape was determined using WinDOAS (IASB/BIRA software developed by C. Fayt and M. Van Roozendaal) by fitting a measured Fraunhofer spectrum to the Kurucz high-resolution spectrum convolved with the instrument line shape chosen to be a wavelength dependent gaussian function (taking the Ring effect and the absorption of O₃ into account). Background spectra were identified from the collected spectra as those with the lowest retrieved SO₂ column amount for each group of data. A fitting window covering both SO₂ and BrO absorption ranges (310.9–377.8 nm) was selected to yield a fit residual with minimal standard deviation, but also to include a sufficient number of absorption bands to constrain well the fit of both absorbers (~10 bands for BrO and 4 for SO₂). The fit residual still contained some structure associated to SO₂ absorption at shorter wavelengths but we were unable to improve the fit.

Analysis of the December 2003 spectral data was identical to that used by Oppenheimer et al. (2005) so as to enable a rigorous comparison. Two fit windows were used, with the first covering the range of strongest SO₂ absorption (309.2–334.5 nm), and the second tuned to detect NO₂ (330.7–349.0 nm).

3. Results

3.1. First estimation of BrO

We report the first observation of BrO in the gas plume emitted from Erebus volcano on 3 December 2005. The prevailing conditions were light wind and a cloud-free sky. An example of the DOAS fit for various species is shown in Fig. 1. Time-series of retrieved SO₂ and BrO slant column amounts (SCA) show a strong correlation (Fig. 2). The linear regression gives a BrO/SO₂ molecular ratio of 2.5×10^{-4} (correlation coefficient $R^2 = 0.71$). Mean errors on column amounts displayed in Fig. 2 only include those associated to the non-linear fit performed in the DOAS retrieval ([Stutz and Platt, 1996] and [Hausmann et al., 1999]). Additional errors in column amounts are linked to scattering of light by air molecules and particles in and around volcanic plumes ([Millan, 1980], [Platt et al., 1997], [Mori et al., 2006] and [Kern et al., 2010]). However, using the same fit window for both absorbers, the radiative transfer related errors similarly affect BrO and SO₂ SCA and thus tend to cancel in their ratio. Some scatter in the BrO vs. SO₂ SCA plot can result from variations in the plume chemistry related to the dynamics of magma degassing at Erebus (Oppenheimer et al., 2009).

BrO was not detected on 4 other days of observations. As detailed in Table 3, assuming a molecular BrO/SO₂ ratio of 2.5×10^{-4} , the maximum BrO column amounts expected during these days are well below the detection limit of our DOAS analysis. The main challenge in detecting BrO at Erebus results from a comparatively low overall flux of sulfur and halogens. The SO₂ gas flux is typically below 1.0 kg s^{-1} (Sweeney et al., 2008) while HCl and HF fluxes are both in the region of 0.24 kg s^{-1} (Oppenheimer and Kyle, 2008). Given that SO₂ SCA above $10^{18} \text{ molec cm}^{-2}$, as observed on 3 December 2005, are rarely observed, and indeed are typically below $5 \times 10^{17} \text{ molec cm}^{-2}$, the expected BrO column amount should typically be below $1.3 \times 10^{14} \text{ molec cm}^{-2}$, corresponding to a hardly detectable amount (see Table 1).

The BrO/SO₂ ratio at Erebus is substantial but not the highest recorded (Table 1), ranking below those observed at the arc volcanoes of Soufrière Hills (Montserrat), Sakurajima (Japan) and Ambrym (Vanuatu). However, BrO/SO₂ ratios at Erebus could be up to an order of magnitude higher at greater distances from the source, as shown by modeling studies of plume

atmospheric chemistry ([Bobrowski et al., 2007] and [Roberts et al., 2009]). The plume BrO abundance is expected initially to increase with distance from source (see Fig. 5) reflecting its photochemical production and mixing with background air and consequent reaction with tropospheric ozone ([Oppenheimer et al., 2006] , [Bobrowski et al., 2007] and [Roberts et al., 2009]). Indeed, the experiment presented in this study samples a young plume (~3–7 min after emission from the lava lake).

The high BrO/SO₂ ratio of the Erebus plume probably corresponds to the magma composition, but it is hard to be sure as it is also strongly controlled by atmospheric processing. The phonolitic magma at Erebus is enriched in F and Cl compared to S, which is removed by crystal fractionation during the evolution of the magma (Kyle et al., 1992). As a result, the gas emitted by Erebus has high HCl/SO₂ and HF/SO₂ mass ratios of 0.28–0.92 and 0.18–0.53 respectively ([Zreda-Gostynska et al., 1997] , [Wardell et al., 2008] and [Oppenheimer and Kyle, 2008]). These are amongst the highest in the world (Pyle and Mather, 2009).

3.2. Nitrogen dioxide

We did not detect NO₂ in any DOAS observations in 2005 (Fig. 1). The presence of NO₂ in ultraviolet spectra collected at Erebus on 11 December 2003 (Oppenheimer et al., 2005) is re-examined. At the time of this publication, the correction of the Ring effect was not commonly included in DOAS analysis. However, Vountas et al. (1998) showed that this correction is required for the DOAS retrieval of trace gas species when using scattered solar radiation as a light source for the measurements. The Ring effect is caused by rotational Raman light scattering and leads to a reduction or “filling-in” of the observed optical densities of solar Fraunhofer lines (Grainger and Ring, 1962). This effect strongly depends on the atmospheric light path (Fish and Jones, 1995). We show here that including the Ring spectrum in the DOAS retrieval decreases significantly the estimated NO₂ abundances.

We re-examined the 11 December 2003 data (set B) using the same fit window 330.7–349.0 nm as Oppenheimer et al. (2005), with identical retrieval parameters but including the Ring spectrum in the fit scenario. As illustrated by the fit of a spectrum with a high SO₂ SCA (Fig. 3), taking into account the Ring effect in the modeling decreases the standard deviation of the fit residual by a factor two (1.3×10^{-3} versus 2.6×10^{-3}). Furthermore, the NO₂ fit spectrum shows no evidence of the presence of NO₂, with an amplitude significantly smaller than the one of the fit residual. As illustrated in Figure S-1, NO₂ slant column amounts are always below the NO₂ detection limit of 4×10^{16} molec cm⁻². In addition, the correlation between NO₂ and SO₂ time-series disappears. Consequently, the presence of large amounts of NO₂ on 11 December 2003 is an artifact of the DOAS analysis of Oppenheimer et al. (2005).

The NO₂ cross-section presents great similarities with the Ring spectrum, as underlined by Vountas et al. (1998), and the Ring effect can be confused with NO₂ absorption if not corrected. Results of DOAS analysis performed by Oppenheimer et al. (2005) were particularly sensitive to this, as the version of the DOASIS software used at that time was not properly removing low frequency components of spectra. In addition, the Ring effect is strongly modulated by the presence of the volcanic cloud. Indeed, the existence of an aerosol-rich plume leads to a decrease of the light received by the spectrometer, as illustrated in the upper plot of Fig. S-1 by the anti-correlation between SO₂ and light intensity. Simultaneously, the light path length is increased by multiple light scattering in the plume, implying a larger Raman scattering due to a greater number of collisions of light photons with air molecules.

These processes, affecting both light intensity and Raman scattering magnitude, explain a significant increase of the Ring effect due to the plume (de Beek et al., 2001). As a consequence, the Ring is highly correlated to the SO₂ abundance, as shown in Fig. S-1 (upper and lower plots). This explains the spurious correlation of NO₂ and SO₂ time-series found by Oppenheimer et al. (2005) when not correcting for the Ring effect.

According to our analysis, the amount of NO₂ in the plume has to be lower than 2×10^{16} molec cm⁻² on 3 December 2005. This value corresponds to the limit of detection of our analysis, estimated from a fit residual with a standard deviation of 1.0×10^{-3} (see Fig. 1) and a peak-to-peak amplitude of the differential NO₂ cross-section at its strongest peaks of absorption in the 310.9–377.8 nm fit window of 1.0×10^{-19} cm² molec⁻¹. Assuming a correlation between SO₂ and NO₂ variations, we expect to record the highest NO₂ abundance when the highest SO₂ abundance is observed. This would yield a molecular NO₂/SO₂ ratio lower than 0.012, based on the highest SO₂ column amount of 1.7×10^{18} molec cm⁻². This ratio, representing already an upper bound, is smaller by one order of magnitude than reported by Oppenheimer et al. (2005).

Note that HONO was not detected in any of the ultraviolet spectra.

4. Discussion

4.1. Dynamics of the BrO explosion

Combined gas and particulate analyses from filter pack measurements performed in December–January of 1986/87, 1988/89, 1989/90, 1991/92 at the crater rim indicated a Br/S mass concentration ratio of $2\text{--}4 \times 10^{-3}$ (Zreda-Gostynska et al., 1997). If we assume the same Br content in the plume at the crater rim in December 2005, and no loss of SO₂ in the plume, we can estimate from the Br/S mass ratio of 6×10^{-4} (deduced from molecular BrO/SO₂) that 15–30% of the total available Br at the crater rim (i.e. the sum of HBr gas phase and particulate Br, both sampled with filter packs) is converted in BrO in about 1–3 min, i.e. the time for plume to travel from crater rim, at a distance of ~225 m from the lava lake (Csatho et al., 2008), to the 400 m high DOAS field of view assuming a vertical plume speed in $1\text{--}2.5$ m s⁻¹ (Boichu et al., 2010). The plume is only ~3–7 min old at the altitude of the DOAS field of view where BrO is measured. Note that we consider in this estimation HBr to be the most abundant gas phase Br species, neglecting the presence of BrNO₂ (and/or BrONO₂), BrO, Br_{2(g)} and Br_(g) at the crater rim given the very young plume age, which is consistent with the Br speciation modeled by von Glasow (2010). So, despite low atmospheric temperature and a plume absolute humidity which may be low, the autocatalytic heterogeneous oxidation of source HBr_(g) is very rapid on 3 December 2005, similarly to estimates at Etna with 40% of HBr_(g) transformed into BrO in a 3–4 min plume age (Oppenheimer et al., 2006). The high abundance of HCl may help the partitioning of HBr from the gas to the aerosol phase (Oppenheimer et al., 2006), as demonstrated by the relatively high aerosol Br⁻ content with a Br⁻/SO₄²⁻ molar ratio in 0.022–0.028 for December 2006 and 2007 (Ilyinskaya et al., 2010).

The formation of HNO₃ and HO₂NO₂ observed in the downwind plume cannot result from the incorporation of background NO_x into the plume during its dispersion, given the very low levels of pollution or other NO_x sources in the Antarctic troposphere. Thus, this finding suggests conversion of volcanogenic NO_x very early in the plume's history, i.e. probably at the lava lake. As shown by Roberts et al. (2009), HNO₃ may be formed in a dispersing plume

via the BrO-mechanism ($\text{BrO} + \text{NO}_2 \rightarrow \text{BrONO}_2$ then $\text{BrONO}_2 + \text{HBr}_{aq} \rightarrow \text{Br}_2 + \text{HNO}_3$; actually a parameterization of a multi-stage aerosol-phase processes involving $\text{BrONO}_2 + \text{H}_2\text{O} \rightarrow \text{HOBr} + \text{HNO}_3$ and $\text{HOBr}_{(aq)} + \text{HBr} \rightarrow \text{Br}_2 + \text{H}_2\text{O}$), at a rate much faster than via the OH radical mechanism (see Fig. 5). Alternatively, HNO_3 could be produced via the OH mechanism and/or from HO_2NO_2 , which is itself generated from $\text{NO}_2 + \text{HO}_2 \rightarrow \text{HO}_2\text{NO}_2$. The presence of elevated in-plume HO_2NO_2 reported by Oppenheimer et al., (2010) supports the high-temperature formation of NO_x and HO_x , indicating that these reactions most likely occur near the lava lake.

4.3. In-plume reactive bromine chemistry and ozone depletion

Oppenheimer et al. (2010) reported on airborne intercepts of the Erebus plume on 9 and 10 December 2005 (i.e. the same period as the observations of BrO reported here). Analyses of major and trace volcanic gases, collected with an integration time of 1 min (corresponding to ~ 4 km of flight line), at distances ranging from 1 to 56 km from the crater were reported. O_3 depletion, up to 35% relatively to background level, was observed for a plume age in 4–6 h (Figure S-2).

DOAS spectrometers also measure the ozone abundance but, contrary to aircraft measurements, it is integrated over a long light path crossing a large part of atmosphere from the sun to the instrument. The negative values of the O_3 column amounts estimated by DOAS (Fig. 1 and Fig. 3) do not indicate ozone depletion in the plume relatively to the background, but are an artifact of the DOAS method. Indeed, we observe an apparent depletion of $\sim 10^{+18}$ molec cm^{-2} of ozone in the plume. Given a background O_3 concentration of ~ 0.025 ppmv (Oppenheimer et al., 2010), this would correspond to a complete ingestion of background O_3 by the plume over a distance of 16 km, which is irrelevant. Consequently, the negative column amounts of O_3 , but also O_4 , result from a shorter light path, crossing less atmospheric O_3 and O_4 , when the plume is in the DOAS field of view.

Based upon modeling studies of Bobrowski et al. (2007) and Roberts et al. (2009), the amounts of $\text{HBr}_{(g)}$ (with a HBr/SO_2 molar ratio ranging in $6 \pm 2 \times 10^{-4}$ calculated from Zreda-Gostynska (1995)) and BrO [This study] measured at Erebus may be sufficient to cause the episode of ozone depletion up to 35% of the background level observed in the plume (see Table 4 for a summary of all observations of volatile species, in gas and particle phases, available at Erebus). Fig. 5 illustrates the impact of plume reactive halogen chemistry on ambient ozone. Observation of O_3 depletion at great distance at Erebus (26–39 km or 4–6 h) highlights the dynamics of this phenomenon with plume age/distance. Both chemical reactions and plume dispersion play a role in plume reactive halogen chemistry. Consequently, models describing plume evolution require various input parameters including the chemical composition and strength of gas emissions at source, the aerosol load and dispersion parameters of the plume. According to a sensitivity study of these parameters developed by Roberts (2009), the magnitude of the depletion of O_3 at ~ 30 km observed by Oppenheimer et al. (2010) can be predicted for high gas flux and/or atmospheric conditions leading to inefficient plume mixing with ambient air. The high gas flux hypothesis can be readily discarded, as the flux of volcanic gases measured at Erebus (SO_2 flux ≤ 1 kg s^{-1}) is low compared to most actively degassing volcanoes. On the other hand, the noticeably low wind speed of 1.8 m s^{-1} , with nevertheless little plume dispersion shown by pictures taken the same day (Oppenheimer et al., 2010), may provide conditions favorable to a sustained depletion on long distances, assuming sufficient bromine is available at source. Less mixing with background air leads to a highly concentrated plume and a slower replacement of

destroyed ozone. Eventually, this observation suggests that aerosol load, needed to allow heterogeneous reactions fundamentally involved in the reactive bromine chemical cycle, is not a limiting factor at Erebus. The noteworthy small size of Erebus aerosols, in the range of the Greenfield gap 0.01–1 μm , (Radke, 1982), likely inherited from low atmospheric temperature and humidity, assures them an exceptionally long life which may be a crucial ingredient for this long-range impact of the plume.

4.2. Dynamics of NO_x conversion and impact on reactive bromine chemistry

4.2.1. Observations

In-situ measurements in the distal plume (1–56 km) detected the presence of NO_y species (HNO_3 and HO_2NO_2), with a noticeably stable $[\text{HNO}_3 + \text{HO}_2\text{NO}_2]/\text{SO}_2$ molar ratio of ~ 0.03 (Oppenheimer et al., 2010). As illustrated in Fig. 5, these nitrogen species originate from reactions of NO_x with either OH or HO_2 radicals (Martin et al., 2006), or via the involvement of reactive halogen species ([Oppenheimer et al., 2006] and [Roberts et al., 2009]). NO_x species are assumed to form by thermal fixation of atmospheric background N_2 at the hot lava lake surface ([Huebert et al., 1999] and [Mather et al., 2004a]) and/or through mixing of hot magmatic gases and ambient air (Martin et al., 2006). Previous estimations of NO_2/SO_2 of ~ 0.1 a few hundreds meters above the crater by Oppenheimer et al. (2005) were not consistent with the levels of NO_y observed in the downwind plume. This suggested the storage of some nitrogen “in excess”, as aerosol nitrate NO_3^- and/or in the form of gas phase halo-nitrates (Oppenheimer et al., 2010). From our re-evaluation of NO_2 abundance near the crater presented in this study, i.e. $\text{NO}_2/\text{SO}_2 \leq 0.012$, and assuming that NO and NO_2 abundances would be comparable (Mather et al., 2004b), it is no longer necessary to invoke “excess” nitrogen species to explain the observations. This conclusion is also consistent with the insignificant quantities of nitrate that have been observed in near vent aerosols collected using a cascade impactor at the crater rim of Erebus (Ilyinskaya et al., 2010). Moreover, because our DOAS detection limit provides an upper bound of the NO_2 abundance, this tends to support the rapid conversion of NO_x into HNO_3 and HO_2NO_2 by oxidation in the cooling plume. This result is in agreement with the absence of any NO_x in the downwind plume (Oppenheimer et al., 2010), and in-situ observations by Mather et al. (2004b) in the plume of Masaya volcano. In contrast with the typical tropospheric lifetime of NO_x of a few days, a volcanic plume may provide significant quantities of HO_x radicals to promote much faster oxidation (Gerlach, 2004).

The size and continuous overturning of the lava lake at Erebus, whose temperature has been estimated at around 1000°C and which has an area of order 1000 m^2 (Kelly et al., 2008), may make it a significant NO_x source compared to volcanoes with comparatively small vents (such as Masaya). It has been speculated that a high abundance of NO_x in a young plume could promote the cycles that form reactive bromine from HBr, but also titrate away the BrO, by converting it (once formed) to BrNO_2 (von Glasow, 2010) or BrONO_2 (Roberts, 2009). However, at Erebus, we have identified appreciable quantities of BrO just a few hundred meters above the lava lake (plume age of 3–7 min), with 15–30% of total Br available at the crater rim already consumed to form BrO (Fig. 5). Rapid oxidation of NO_x species may again be the key to explain why the BrO explosion does not seem evidently to be perturbed. As developed in the next section, model simulations add weight to this hypothesis but also

suggest that this conversion of NO_x is even more rapid than could be gauged from DOAS observations.

4.2.2. Model simulations

Numerical simulations, based on the PlumeChem model described by Roberts et al. (2009), were performed to investigate the impact of volcanic NO_x emissions at source on the subsequent formation of BrO in the plume of Erebus. As shown in Fig. 4, simulations with an initial $\text{NO}_2/\text{SO}_2 = 1$ (corresponding approximately to the ratio reported by Oppenheimer et al., 2005) result in extremely low BrO/ SO_2 in contradiction with our observations. Whenever BrO is formed, among other reactions, it can rapidly react with NO_2 to form BrONO₂ according to the reaction ($\text{BrO} + \text{NO}_2 \rightarrow \text{BrONO}_2$), thereby titrating BrO at high NO_2 concentrations. This is entirely consistent with our reinterpretation of the abundance of NO_2 in the young plume of Erebus. The simulations also show that BrO/ SO_2 only matches the observed ratio of 2.4×10^{-4} at Erebus, for a 3–7 min old plume, if NO_x species are essentially absent (or at least $\text{NO}_2/\text{SO}_2 < 0.012$).

5. Conclusions

Since the first observation of BrO in a volcanic plume, the potential for ozone depletion has been discussed (Bobrowski et al., 2003). The plausibility of the hypothesis has then been reinforced by modeling studies of atmospheric plume chemistry involving reactive halogen and nitrogen species ([Oppenheimer et al., 2006], [Bobrowski et al., 2007] and [Roberts et al., 2009]). Ozone depletion has been reported in association with elevated levels of HCl in the stratospheric plume erupted from Hekla volcano during polar winter of 2000 ([Rose et al., 2006] and [Millard et al., 2006]). Our study, in combination with that of Oppenheimer et al. (2010), provides the first evidence of BrO formation during a period of quiescent degassing of Erebus in the polar summer, coincident with ozone destruction in the distal tropospheric plume.

This is also the first estimation of BrO abundance at a phonolitic volcano (Erebus being the only one currently active on Earth). A BrO/ SO_2 ratio of 2.5×10^{-4} is evaluated for a young plume age (3–7 min). This highlights a high proportion of bromine relative to sulfur, which is consistent with the high halogen abundance observed at Erebus and particularly high HCl/ SO_2 and HF/ SO_2 ratios in the atmospheric plume.

NO_x generation at volcanoes hosting large, hot lava lakes should be substantial according to conceptual models for its formation. In an earlier study, Oppenheimer et al. (2005) had reported high abundances of NO_2 in the young plume of Erebus based on DOAS evaluations. We have re-examined the same dataset, which was collected on 11 December 2003, and been unable to reproduce the original finding. However, the detection limit of our new analysis fixes an upper bound for NO_2 abundance which suggests a ratio of $\text{NO}_2/\text{SO}_2 \leq 0.012$, an order of magnitude less than previously estimated. This reassessment shows that the amount of NO_y (HNO_3 and HO_2NO_2 here), detected in the distal plume by Oppenheimer et al. (2010), can be explained by conversion of early-formed volcanic NO_x . It no longer points to the presence of nitrate in aerosol or in the form of gas phase halo-nitrates as had been speculated. This re-evaluation of NO_2 abundance is also consistent with a rapid conversion of NO_x to NO_y . Model simulations support the idea that the BrO/ SO_2 ratio observed in the young plume of Erebus cannot be explained without early oxidation of NO_x emissions very close to the lava lake.

Finally, we estimated a molar HBr/SO₂ ratio of $6 \pm 2 \times 10^{-4}$ at the crater rim and a BrO/SO₂ ratio of 2.5×10^{-4} at ~400 m above the lake, which corresponds to a plume age of 3–7 min. Given a typical SO₂ flux of $0.7 \pm 0.3 \text{ kg s}^{-1}$ (Sweeney et al., 2008), recent modeling studies of reactive plume halogen and nitrogen chemistry ([Bobrowski et al., 2007] and [Roberts et al., 2009]) suggest that these values can account for the observed magnitude of O₃ depletion in the Erebus plume. The fact that O₃ depletion was observed in a plume about 30 km from the source supports limited further entrainment of background air to replace the consumed ozone. The particularly low wind speed during the period in which the aircraft measurements were made was probably conducive to this stability of the plume. The continental scale range of the Erebus plume has already been demonstrated and implicated by a range of observations and models (see Section 1). In future, further simulations of plume chemistry that account for the presence of reactive halogen and nitrogen species, should help to evaluate the actual overall impact of Erebus on the Antarctic troposphere. As illustrated in our study, atmospheric conditions likely play an important role, as of course will the seasonality of photochemical processes.

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Figures and Tables

Table 1. Table of reported worldwide volcanogenic BrO observations (sorted according to decreasing BrO/SO₂ molar ratio).

Date	Volcano	BrO/SO ₂ (molec) ×10 ⁻⁴	Max (or avg) BrO CA (×10 ¹⁴ molec/cm ²)	SO ₂ flux (kg/s)	Distance from source where plume is crossed (km)	Reference
May 02	Soufrière Hills	10	8.4		4	Bob03
May 04	Sakurajima	10	10	—	A few km	Lee05
Aug 07	Ambrym	4.5–7.0	6.6–8.3×10 ³ (avg)	39–59	13–14	Ban09
Jan 07		2.3–4.1	1.7×10 ⁴ (avg)	179–268	15–40	Ban09
Mar 07		0.1	1.0 ×10 ⁴ (avg)	382	11	Ban09
Jul 07		0.5	7.5 ×10 ³ (avg)	25	4	Ban09
Sep 03	Etna	4.8	1.1	—	7	Bob07
Aug 04/		0–4.5	5	—	0–19	Bob07
May 05						
Aug 04		2.1	4.8	—	2.5	Bob07
Aug 04		1.9	3	11	2–3	Opp06
Dec 05	Erebus	2.5	5.1	0.7±0.3	~ 0.4	Boi11a
Sep 04	Stromboli	2.1	6.9	—	2	Bob07
Nov 04	Villarica	1.3	1,3	—	4	Bob07
Mar 03	Masaya	0.8	1.9	—	0.6	Bob07
Apr 07		0.3	2.7		Above crater	Ker09
Nov 08	Popocatepetl	0.3	3	16–31	~ 0.4	Boi11b

Ban09: Bani et al. (2009), Bob03: Bobrowski et al. (2003), Bob07: Bobrowski and Platt (2007), Boi11a: [*This study*], Boi11b: (Boichu in preparation), Ker09: Kern et al. (2009), Lee05: Lee et al. (2005), Opp06: Oppenheimer et al (2006).

Table 2. Details of the DOAS experiment performed on 3 December 2005 in which BrO was detected.

Date, dataset	Integration time (ms), co-added spectra	Elevation, azimuth (°)	Local time
3 Dec 05, static1	100, 50	15, 160	09:29–11:47
3 Dec 05, static2	100, 50	15, 160	11:49–12:34
3 Dec 05, static3	100, 50	15, 160	12:35–13:35
3 Dec 05, static3b	100, 100	15, 160	13:59–15:33

Table 3. BrO detection limits for DOAS experiments performed in December 2005 in which BrO could not be detected. For comparison, details of the 3 December 2005 dataset from which BrO was identified are provided at the bottom of the table. All data were analyzed following the same retrieval method as described in Section 2.

Date, dataset	Integration time (ms), co-added spectra	Local time	Elevation, azimuth (°)	USB200 ID	Fit window, nm	$\Delta\sigma'_{\text{BrO}^a}$ in $10^{-17} \text{ cm}^2 \text{ mole}^{-1}$	Fit residual std in 10^{-3}	BrO detection limit ^b in $10^{14} \text{ molec cm}^{-2}$	Max SO ₂ CA in $10^{17} \text{ molec cm}^{-2}$	Expected max BrO CA ^c in $10^{14} \text{ molec cm}^{-2}$
4 Dec, static 1	200, 25	17:23–17:39	15, 160	11108	310.9–377.8	1.4	1.5	2.1	2.2	0.5
4 Dec, static 2	125, 50	17:46–18:21	12, 250	11108	310.9–377.8	1.4	0.8	1.1	1.2	0.3
4 Dec, static 3	150, 40	18:32–18:58	15, 210	11108	310.9–377.8	1.4	0.9	1.3	1.5	0.4
4 Dec, static 4	250, 20	18:32–18:58	15, 160	11108	310.9–377.8	1.4	2.9	4.1	4.9	1.2
5 Dec, static 1	125, 40	14:42–20:24	15, 160	11108	310.9–377.8	1.4	3.4	4.8	4.4	1.1
9 Dec, static 1	80, 100	07:32–08:55	15, 195	11107	310.9–377.8	1.55	2.6	3.3	2.5	0.6
9 Dec, static 2	75, 100	14:10–18:09	15, 195	11107	310.9–377.8	1.55	2.3	3.0	2.2	0.5
21 Dec, scan3	50, 100	10:22–10:39	variable	11107	320.6–377.6	1.4	3.9	5.6	7.0	1.7
21 Dec, scan4	90, 50	10:45–12:06	15, 160	11107	315.3–367.7	1.55	1.4	1.8	4.2	1.0
21 Dec, scan5	60, 100	12:08–18:48	15, 160	11107	310.9–377.8	1.55	2.7	3.5	6.1	1.5
3 Dec, static 3b	100, 100	13:59–15:33	15, 160	11108	310.9–377.8	1.4	1.0	1.4	10.2	2.5

^a $\Delta\sigma'_{BrO}$ represents the peak-to-peak amplitude of the differential BrO cross-section at the strongest peak of absorption (338.5 nm).

^b The BrO detection limit is defined as the ratio of twice the standard deviation of the fit residual to $\Delta\sigma'_{BrO}$.

^c Assuming a BrO/SO₂ molecular ratio of 2.5×10^{-4} , as measured on 3 Dec 05 in this study (see Section 3.1), we estimate the maximum BrO column which is expected from the maximum SO₂ CA recorded.

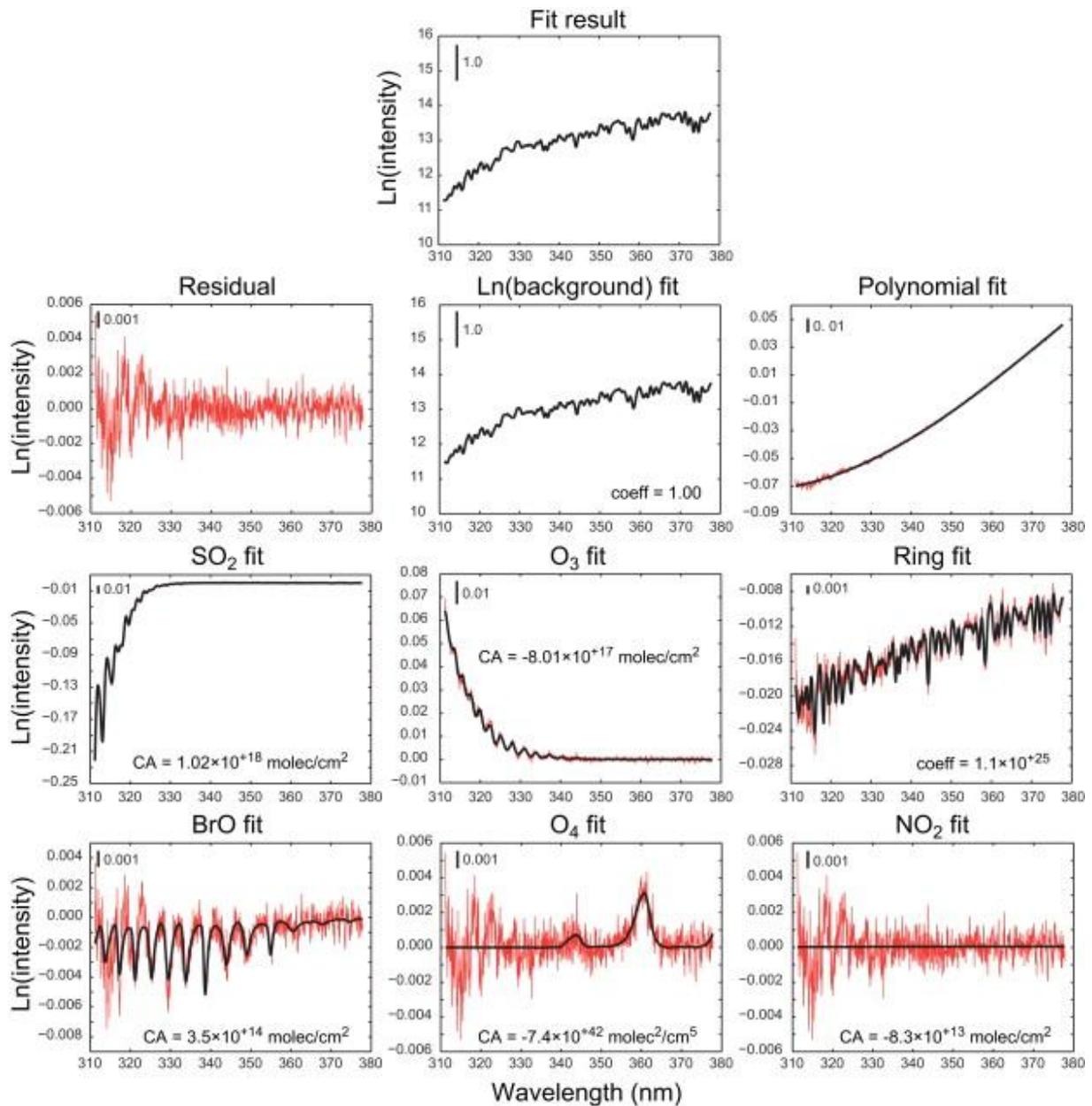


Fig. 1. : Example of BrO fitting process for a spectrum with high volcanic gas content ('static3b data set', 15:01 LT). Thick black lines represent the results of the DOAS fit (note the different scaling of the vertical axis according to the species). Note the failure to detect NO₂. Negative column amounts of O₃ and O₄ suggest a shorter atmospheric light path when the plume is in the DOAS field of view (refer to Section 4.3 for more details).

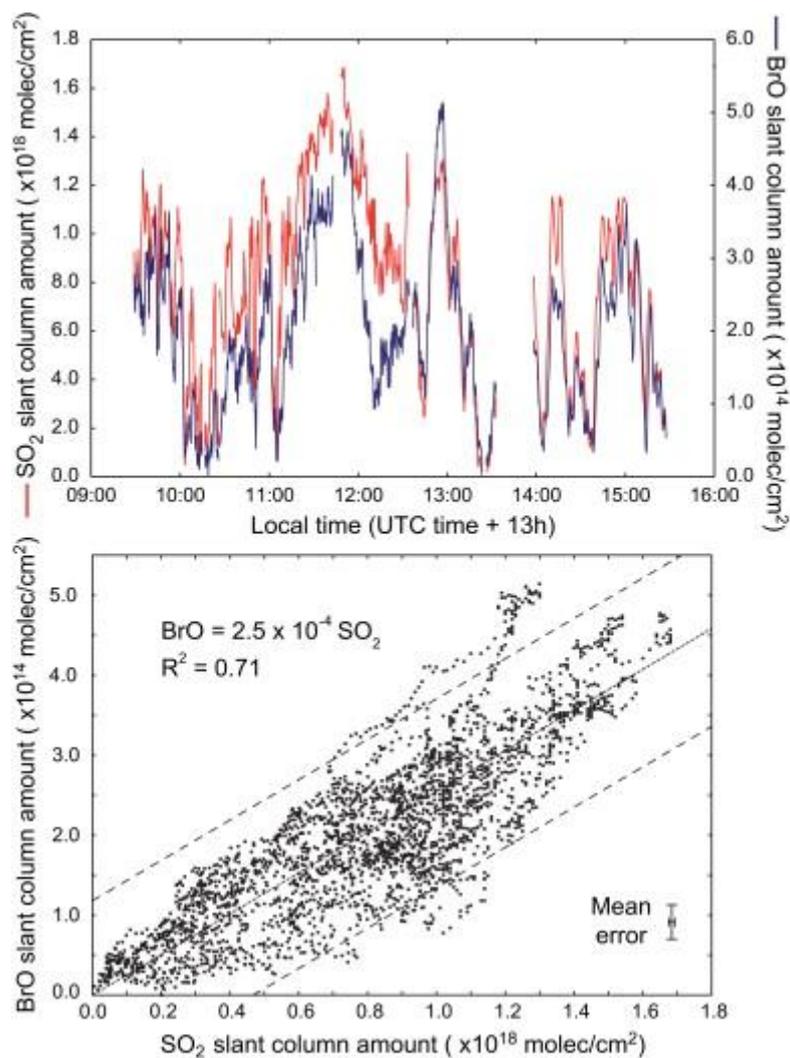


Fig. 2. : (Upper panel) Time-series of SO₂ (red) and BrO (blue) column amounts (molec cm⁻²) retrieved from spectra collected on 3 December 2005 between 9:29 and 15:30 LT. Note the different scales for each species. (Lower panel) Scatter plot for BrO vs. SO₂ column amounts. Mean error bars on column amounts are obtained from the DOAS retrieval. Dotted and dashed lines show, respectively, 95% confidence and prediction limit of the linear fit. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

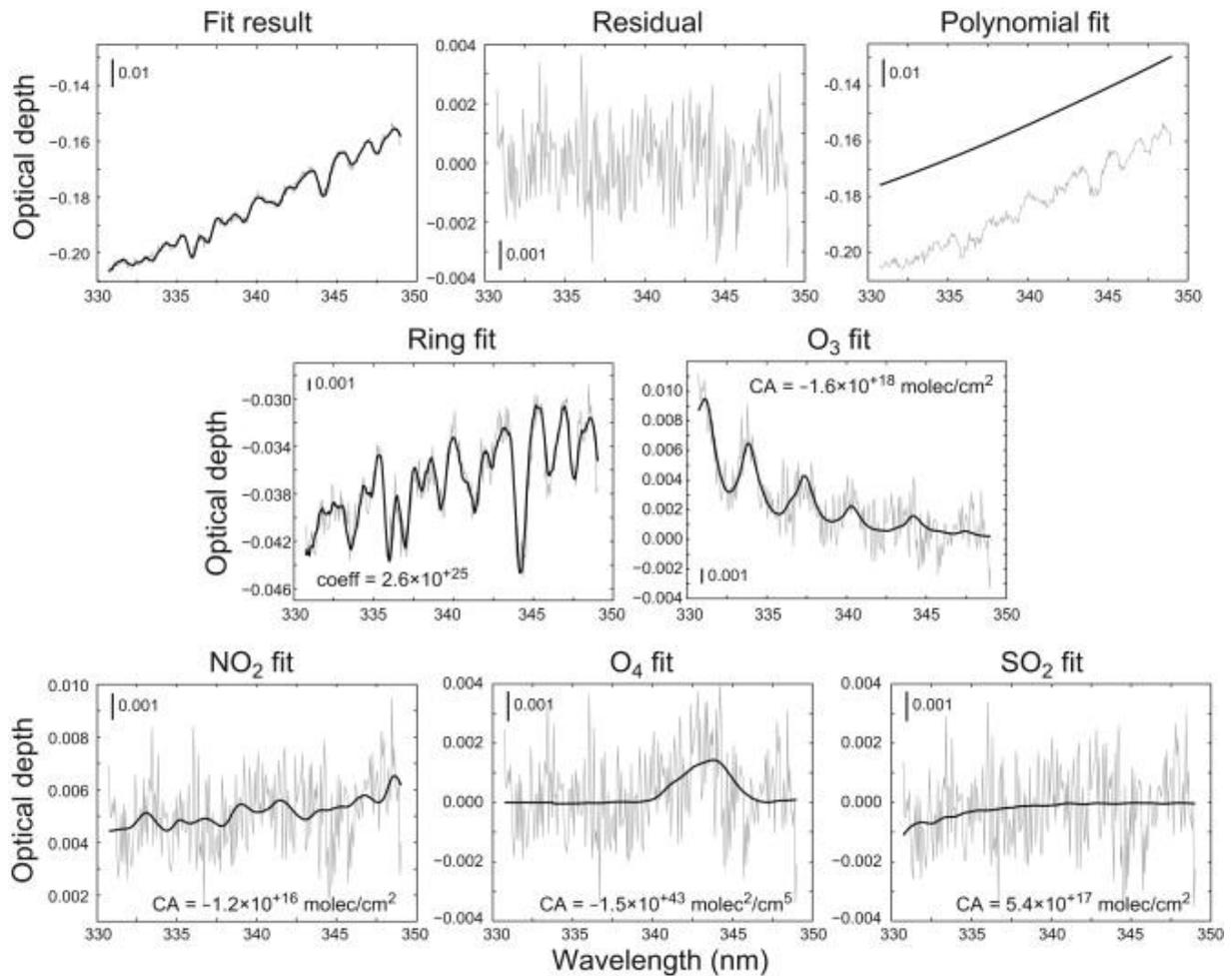


Fig. 3. : Re-evaluation of NO_2 in spectra collected on 11 December 2003 and reported by Oppenheimer et al. (2005). Example of NO_2 fitting process for spectrum with high volcanic gas content (Set B, 23:09:18 LT). Thick black lines represent the results of the DOAS fit including a third degree polynomial, a Ring spectrum calculated from the background spectrum using DOASIS, and convolved cross-sections of NO_2 (Voigt et al., 2002), SO_2 (Bogumil et al., 2003), O_3 (Voigt et al., 2001) and O_4 (Hermans, 2002). To enable direct comparison, the chosen fit window (330.7–349.0 nm) is identical to the one used by Oppenheimer et al. (2005). Note that the SO_2 SCA is fixed in that fit to $5.4 \times 10^{17} \text{ molec cm}^{-2}$ after retrieval in the range of strongest SO_2 absorption in 309.2–334.5 nm. The BrO cross-section was not included in the final fit since it was not detectable.

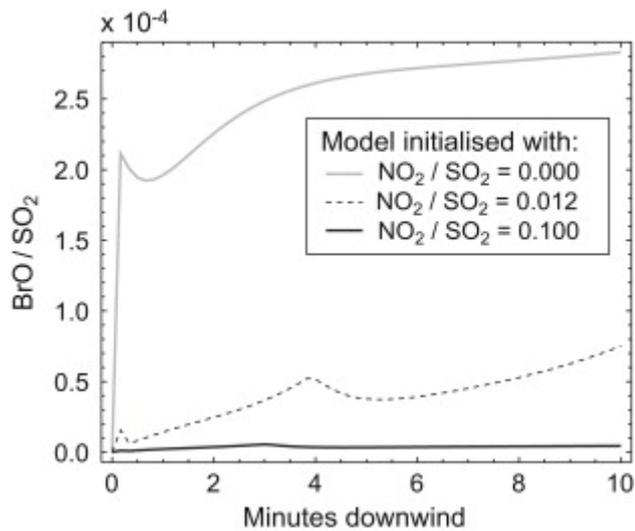


Fig. 4. : Model simulation, based on Roberts et al. (2009), of BrO/SO₂ as a function of plume age, parameterized for three potential volcanic NO_x emission ratios: NO₂/SO₂ = 0.10 (corresponding approximately to the ratio reported by Oppenheimer et al. (2005), NO₂/SO₂ = 0.012 (upper limit of [This study]) and NO₂/SO₂ = 0.00 (lower limit). Simulations were performed for constant SO₂ flux of 0.7 kg s⁻¹, wind speed of 2 m s⁻¹, and a total (aerosol + gas-phase) emitted Br/SO₂ of 0.0015. As Erebus is a weak emitter, resulting in a dilute plume, the initial plume dilution was set so that SO₂ = 2 ppmv, with further dispersion over the 10 min simulation resulting in SO₂ = 1.3 ppmv.

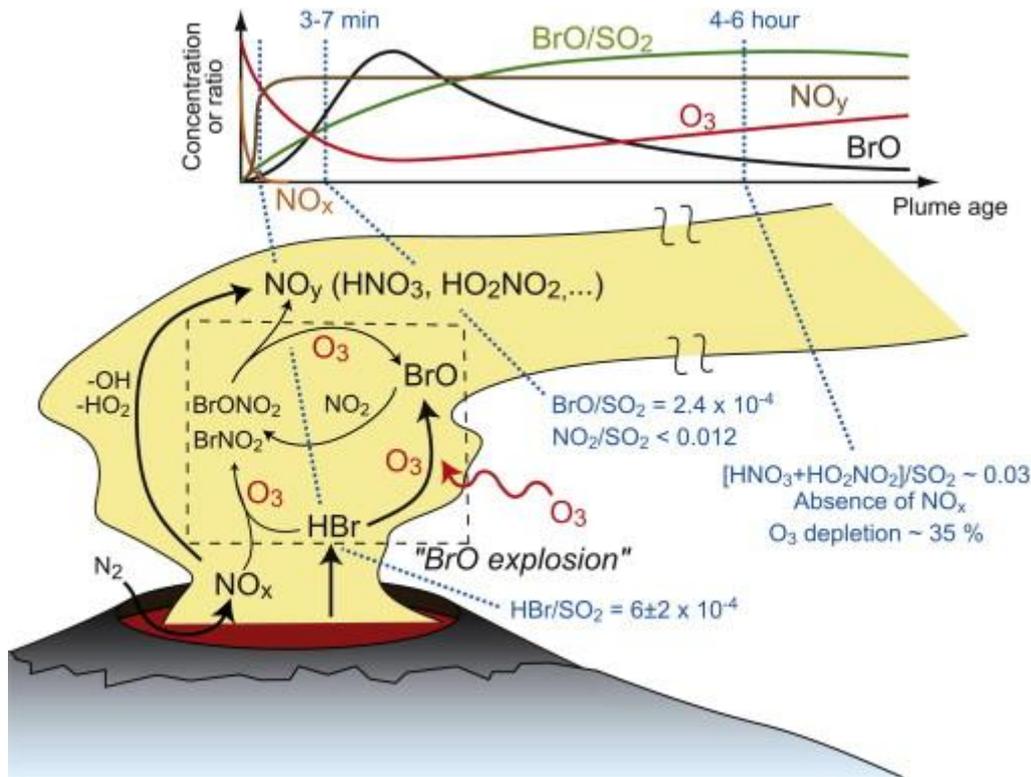


Fig. 5. : Diagram of reactive bromine and nitrogen chemistry in the tropospheric plume emitted by Erebus. (Lower panel) Simplified illustration of the autocatalytic formation of BrO (also known as the ‘BrO explosion’) from HBr, which consumes O₃. The list of reactions is not exhaustive but the interaction between reactive NO_x and Br species, which can store Br molecules in the form of BrONO₂ or BrNO₂ species and postpone the BrO explosion, as discussed in Section 4.2, is highlighted. The conversion of NO_x to NO_y, involving either reactive Br-chemistry or reactions with OH and HO₂ radicals (see Section 4.2 for more details), is also illustrated. (Upper panel) Qualitative picture of the evolution of BrO, O₃, and BrO/SO₂ as a function of plume age, deduced from models of reactive chemistry and dispersion of a volcanic plume but neglecting SO₂ depletion (Roberts et al., 2009). The rapid conversion of NO_x to NO_y, discussed in Section 4.2, is also shown. Text in blue summarizes observations (mol) available for the Erebus plume. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 4. Summary of observations pertaining to gas and aerosol phases involved in reactive halogen and nitrogen chemistry, and ozone depletion in the tropospheric plume of Erebus volcano.

Species	Crater rim, ~200 m above lake	Above crater, ~400 m above lake	Distant plume (distance from crater)	Date	Method
SO ₂ flux	–	0.7 ± 0.3 kg s ⁻¹ (avg)	–	Dec 92–06	COSPEC ^{b,c} , DOAS ^{c,d}
HBr/SO ₂	[4–8] × 10 ⁻⁴ (mol) ^a	–	–	Dec 88–89–91	Filter packs ^e
Br ⁻ /SO ₄ ²⁻	0.022–0.028 (mol)	–	–	Dec 06–07	Cascade impactor ^f
Br/S (particles)	0.019–0.032 (mass)	–	–	Dec 88–89–91	Filter packs ^e
BrO/SO ₂	–	2.5 × 10 ⁻⁴ (mol)	–	3 Dec 05	DOAS ^g
NO ₂ /SO ₂	–	≤0.012 (mol)	–	3 Dec 05	DOAS ^g
NO/SO ₂	–	–	Not found	9–10 Dec 05	Chemiluminescence ^h
HCl/SO ₂	–	0.28–0.92 (mass)	–	Dec 86–88–89–91/97–99–00/04	FP ⁱ /Chemical traps ^j /FTIR ^k
HNO ₃ /SO ₂	–	–	[17.8–18.5] × 10 ⁻³ (mol)	9–10 Dec 05	Mass spectrometry ^h
			(1–56 km)		
HO ₂ NO ₂ /SO ₂	–	–	[10.5–10.9] × 10 ⁻³ (mol)	9–10 Dec 05	Mass spectrometry ^h
			(1–56 km)		
O ₃	–	–	Depletion up to 35%	10 Dec 05	In-situ UV absorption
			(mol) (26–39 km)		

^a Calculated from a Br/S mass ratio in the acid gas phase trapped by filter packs ranging in 0.0010–0.0021 over the years 1988, 1989 and 1991, and assuming the absence of H₂S in the plume (Oppenheimer and Kyle, 2008). This value is likely an under-estimation given the use of LiOH treated filters by Zreda-Gostynska (1995), which are more than two times less efficient in trapping Br than other treated filters (Mikelich, 2006).

^b (Kyle et al., 1994).

^c (Sweeney et al., 2008).

^d (Boichu et al., 2010).

^e Calculated from Zreda-Gostynska (1995).

^f (Ilyinskaya et al., 2010).

^g [This study].

^h (Oppenheimer et al., 2010).

ⁱ (Zreda-Gostynska et al., 1997).

^j (Wardell et al., 2008).

^k (Oppenheimer and Kyle, 2008).