

Mt. Erebus, the largest point source of NO₂ in Antarctica

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Abstract

We report here the first observations of NO₂ emission from Mt. Erebus, a volcano with an active lava lake located on Ross Island, Antarctica. Erebus generates a persistent plume, which is entrained at an altitude of about 4 km above sea level. Its NO₂ flux, measured by scattered light ultraviolet spectroscopy in December 2003, was equivalent to ~0.6 Gg(N) yr⁻¹. The total reactive nitrogen supply may be significantly higher than this since other NO_y species are likely to have been present in the plume. We believe the NO₂ is generated by thermal fixation of atmospheric nitrogen at the hot lava surface, forming NO, which then reacts rapidly with oxidants including ozone to yield NO₂. Erebus volcano has displayed lava lake activity for many decades and may, therefore, play a significant long-term role in Antarctic tropospheric chemistry, and represent an important source of nitrogen deposited to the ice surface.

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1. Introduction

Nitrogen oxides (NO_x = NO + NO₂) as well as reactive odd nitrogen (NO_y = NO_x, HONO₂, HONO, NO₃, N₂O₅, HNO₄, peroxyacetyl nitrate (PAN), etc.) play crucial roles in tropospheric chemistry, nutrient cycles, and, indirectly, the Earth's radiation budget (Bradshaw et al., 2000). In Antarctica, where there are limited contributions from the main global NO_x sources (fossil fuels, biomass burning, lightning and soils), tropospheric nitrogen chemistry appears surprisingly complex (e.g., Chen et al., 2001; Crawford et al., 2001; Davis et al., 2001) and is receiving increasing attention

(e.g., Davis, 2004) because of its significance for understanding the oxidising potential of the polar atmosphere, and for interpretation of glaciochemical records.

Molecular nitrogen is a trace constituent of volcanic emissions (e.g., Zimmer et al., 2004) but comparatively little is known about the nitrogen chemistry of volcanic plumes. Some consideration has been given to stratospheric nitrogen chemistry in the presence of volcanic sulphate aerosol (Rinsland et al., 2003), and it is increasingly apparent that nitrogen species are present in tropospheric volcanic emissions: in dilute plumes from explosive volcanism (Hobbs et al., 1991, 1982; Bandy et al., 1982; Hunton et al., 2005), above lava flows (Huebert et al., 1999), and in plumes associated with open-vent degassing (Mather et al., 2004a, b; Uematsu et al., 2004). While NO_x detected in explosively produced plumes may originate from volcanic lightning

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generated by ash charging (Sobral et al., 2004), reactive nitrogen above active lava bodies has been attributed to the reaction between atmospheric oxygen and nitrogen at the high prevailing temperatures (Huebert et al., 1999; Mather et al., 2004a, b).

Here, we report on simultaneous detection of SO₂ and NO₂ in the plume emitted by Mt. Erebus, Antarctica (summit altitude 3794 m above sea level). The measurements were obtained by ground-based ultraviolet (UV) differential optical absorption spectroscopy (DOAS) using scattered Sunlight. Erebus is renowned for its long-lived lava lake of anorthoclase phonolite composition (Fig. 1a), and is routinely monitored despite its remote location (Aster et al., 2004). During the summer field seasons, emission rates of SO₂ have been measured repeatedly (Kyle et al., 1990, 1994), and supplemented by more sporadic measurements of CO₂ and CO (Wardell et al., 2004), halogens and other species (Zreda-Gostynska et al., 1993, 1997). The motivation for these studies has been, in part, to understand the impacts of the Erebus plume (Fig. 1b), which typically drifts at an altitude of 4 km, on the atmospheric and

cryospheric environments. During our fieldwork in November–December 2003, the lava lake area was ~1200 m². Based on thermal infrared observations, much of its crusted surface was at temperatures above 850 K, hotter than the crust found on lava lakes elsewhere (e.g., Oppenheimer et al., 2004a). The hottest parts of the lake, exposed in regions of magma upwelling and fissured crust, must approach the estimated magmatic temperature of ~1270 K (Kyle et al., 1992). For detailed information on the volcano and its environment, the Mount Erebus Volcano Observatory website is worth consulting (<http://www.ees.nmt.edu/Geop/mevo/mevo.html>).

2. Methods

SO₂ and NO₂ column measurements were made using a small Ocean Optics USB2000 UV spectrometer (described in Galle et al., 2003). The spectrometer was coupled across a 50 μm entrance slit by fibre optic bundle to a simple two-lens telescope (full plane field of view 8 mrad). The spectrometer spanned the spectral interval 228–379 nm with a resolution of 0.65 nm (FWHM), and the telescope was mounted on a rotating platform so as to scan the plume as it rose vertically from the crater. Based on observed rise rates, we estimate that the age of the plume at the point of measurement was around 1 min. Individual spectra were recorded for exposure times varying between 80 and 100 ms. Up to 100 individual spectra were composited to improve the signal-to-noise ratio. Observations were made from Lower Erebus Hut, ~2100 m from the summit crater.

NO₂ and SO₂ columns were retrieved following standard DOAS procedures outlined in Platt (1994), McGonigle et al. (2004) and Oppenheimer et al. (2004b) as follows: (i) subtraction of the dark spectrum from all measured spectra, including the background (out-of-plume) spectrum; (ii) normalisation of all spectra, including those recorded within the plume, by the background spectrum; (iii) removal of the low-frequency component of the spectrum by either a binomial high-pass filter or ninth-order polynomial; (iv) calculation of the logarithm of each ratio, yielding the differential absorption spectrum of the plume, which was then smoothed by a binomial low-pass filter; (v) fitting the resulting spectrum, i.e. the differential optical density (Fig. 2), by scaling the differential reference spectrum using both linear and non-linear least-squares algorithms, and thereby evaluating the SO₂ and NO₂ column amounts. The optimal fitting windows (309.2–334.5 nm for SO₂ and 330.7–349.0 nm for NO₂) were found by obtaining a near random fit residual structure with minimal standard deviation. The reference spectra for both gases were obtained by convolving high-resolution



Fig. 1. Photographs of (a) the lava lake (dimensions ~45 × 35 m) taken from summit crater rim on 7 December 2003, and (b) the plume (altitude typically ~4 km above sea level) on 11 December 2003.

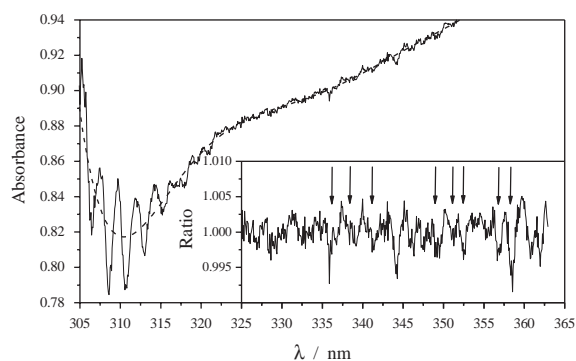


Fig. 2. Removal of the low-frequency component of the absorbance spectrum (solid line) by a ninth-order polynomial (dashed line). The strong oscillations below 320 nm result from absorption by SO₂, whereas the weaker structure at longer wavelengths is due to NO₂. The inset shows the ratio of the measured absorbance and the polynomial fit within the range of NO₂ absorption. Arrows indicate the positions of strongest NO₂ absorption bands.

spectra for NO₂ (from Vandaele et al., 1998) and SO₂ (from Rufus et al., 2003), with the instrument line shape (FWHM 0.65 nm), and then removing the low-frequency component.

SO₂ fluxes were estimated on several days during the field campaign by traversing beneath the plume (by helicopter or snowmobile), with the spectrometer viewing the zenith sky. The observed SO₂ column amounts were projected on to the plane perpendicular to the plume transport direction (each spectrum was located from a continuous GPS record). The SO₂ emission rate was then obtained from the product of the integrated SO₂ column amounts across this plane and the plume speed. We measured plume speed using two spectrometers collecting scattered light from the zenith sky, and spaced about 100 m apart, beneath and parallel to the plume axis (i.e., the wind direction). By determining the correlation function between the two high-temporal-resolution records of SO₂ column amount obtained, and knowing the horizontal separation of the instruments (determined using laser ranging binoculars), the apparent plume speed was calculated. This apparent speed provides an upper limit for the true drift speed of the plume allowing for some discrepancy between the vector between the two instruments and the wind vector. We focus on measurements from 11 December 2003 when meteorological conditions were particularly favourable.

Two sets of spectra were analysed for NO₂ (as well as SO₂): Set 'A' was acquired between 22:14 and 22:19 UTC, and Set 'B' between 23:05 and 23:25 UTC. Based on retrieved SO₂ column amounts, the spectra in each set were separated into two groups: one represents measurements within the plume; the other represents 'background' observations outside the plume. A linear

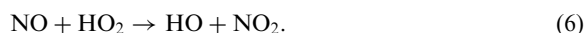
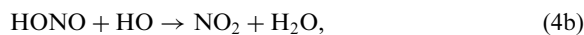
fit was then applied to the time-series of background spectra (both SO₂ and NO₂) so as to characterise any baseline drift, and to determine significance thresholds (based on twice the standard deviation of the retrieved column amounts).

3. Results and discussion

The full time-series of data, corrected for baseline trend, are shown in Fig. 3. For each set of spectra (A and B), two scatter plots were then derived, one (Figs. 4a and 5a) for all the reliable data, the other (Figs. 4b and 5b) a subset of retrieved SO₂ and NO₂ columns that exceeded the significance thresholds. The correlation between SO₂ and NO₂ (Figs. 4 and 5) indicates a molar SO₂/NO₂ ratio of ~7–12 in the plume. The observation that the correlation is clear but not strong is expected, since NO₂ is not a direct volcanic gas emission whose column amount would then scale linearly with SO₂. Instead, the likely origin of NO₂ in the plume is thermal fixation of atmospheric and/or magmatic N₂ at the lava lake surface to generate NO (Huebert et al., 1999; Mather et al., 2004a, b):



followed by in-plume oxidation of the nitric oxide to NO₂ (e.g., Atkinson et al., 2004),



It is also conceivable that combustion of reduced magmatic gas species (e.g., CO, H₂S and H₂) results in additional nitrogen fixation, though temperatures would need to be around 2000 K for this to be significant. Over timescales of weeks or longer, a loose correspondence between SO₂ and NO₂ might prevail due to proportionality between magmatic gas and thermal fluxes from lava lakes (Kyle et al., 1994; Oppenheimer et al., 2004a).

The SO₂ emission rate on 11 December, determined from 13 airborne UV spectrometer traverses and the apparent plume speed (5.1 m s⁻¹), was 0.86 ± 0.20 kg s⁻¹ (≡ 74 ± 17 Mg per day; dispersion indicates the standard deviation of the 13 measurements). Taking the SO₂/NO₂ molar ratio as ~10 (Figs. 4 and 5) indicates an

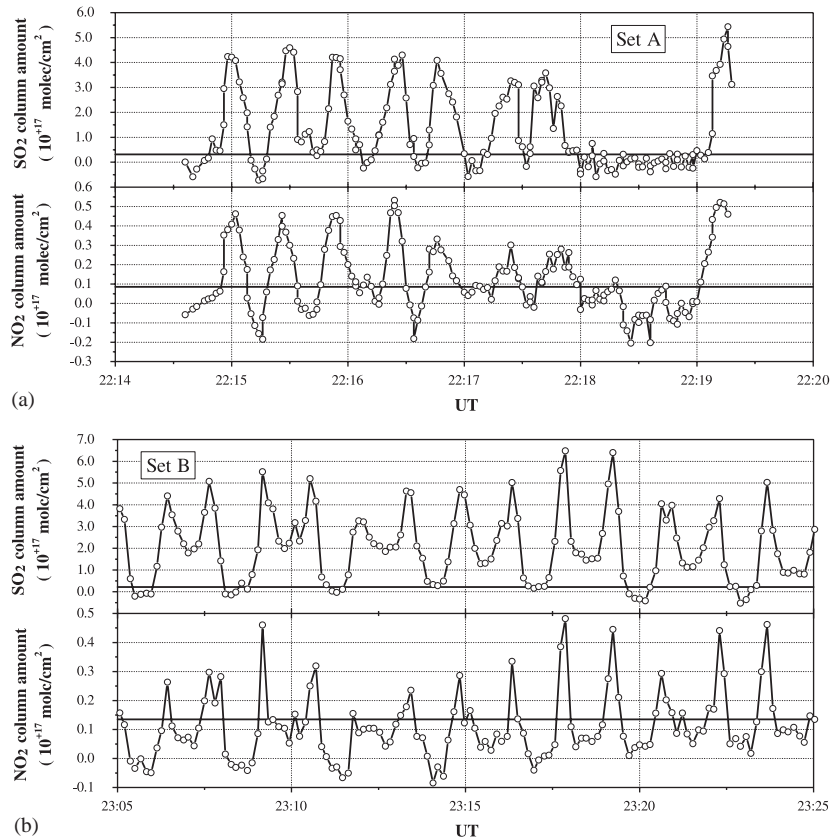


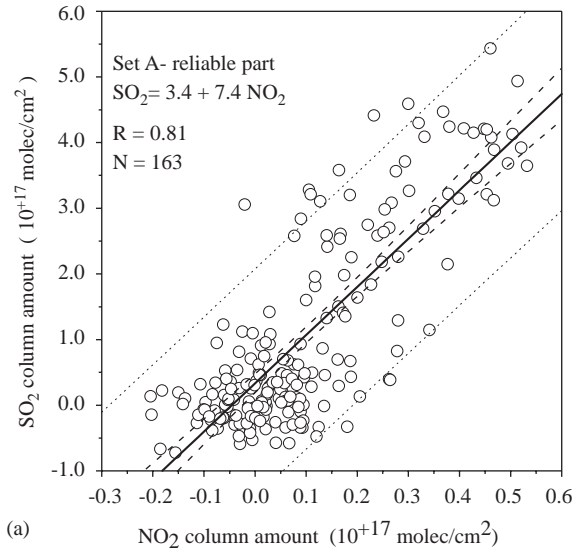
Fig. 3. Time-series of SO₂ and NO₂ column amount measurements made on 11 December 2003 for (a) Set A (100 ms exposure time and four consecutive co-added spectra), and (b) Set B (80 ms exposure time and 100 consecutive co-added spectra). Each cycle represents alternating scans back-and-forth across the vertically rising plume (clearest in the SO₂ record). The plume width was estimated as 350–500 m. The horizontal lines indicate the significance levels for each dataset. Note that for Set B the measured column amounts do not return to zero (in the SO₂ record) as the scanner has not rotated far enough for the field of view to exit the plume.

NO₂ flux of $\sim 60 \text{ g s}^{-1}$ ($\sim 2 \text{ Gg yr}^{-1}$), which is equivalent to $\sim 20 \text{ g (N) s}^{-1}$ ($\sim 0.6 \text{ Gg (N) yr}^{-1}$).

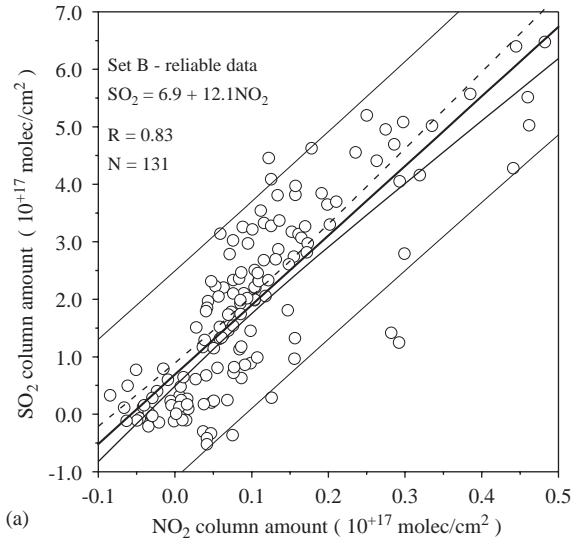
From the known scanning rate ($\sim 8 \text{ mrad s}^{-1}$) of the rotating platform used for the NO₂ measurements and the plume profiles (Fig. 3), we estimate that the width of the vertically rising plume was $\sim 350\text{--}500 \text{ m}$. Assuming that the peak NO₂ column amounts ($\sim 0.3\text{--}0.5 \text{ molec cm}^{-2}$ from Figs. 4 and 5) correspond to the full plume width, then the corresponding mean mixing ratio of NO₂ in the plume is $\sim 30\text{--}50 \text{ ppbv}$. This range is several orders of magnitude higher than background values for the Antarctic troposphere (e.g., Jones et al., 1999, 2000; Weller et al., 2002). It is comparable, however, to the expected mixing ratio of ozone ($\sim 30 \text{ ppbv}$; e.g., Crawford et al., 2001). It is possible, therefore, that we have effectively measured the titrated amount of ozone (Eq. (3)) in which case, there was likely to be remaining NO in the plume. If the apparent modest excess of NO₂ over ozone is real (rather than due to underestimating the plume width), it could reflect

formation of NO₂ by other mechanisms, such as reaction with volcanogenic HO_x (e.g., Gerlach, 2004), or combustion at the lava lake surface.

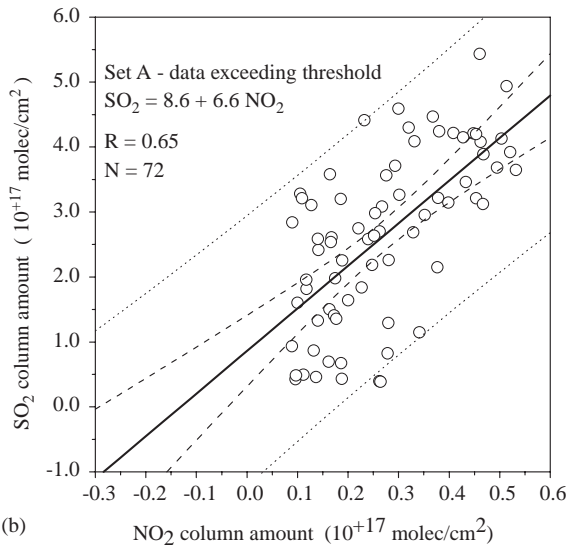
The estimated NO₂ flux from the summit crater of Erebus (60 g s^{-1} , or the equivalent $0.6 \text{ Gg (N) yr}^{-1}$) is modest compared to some sources. For example, NO₂ fluxes of $\sim 250 \text{ g s}^{-1}$ from a power station (McGonigle et al., 2004), and of up to 240 g s^{-1} from agricultural burns (Oppenheimer et al., 2004b) have been measured using similar techniques. However, in the context of the Antarctic free troposphere, it appears significant, especially since it is likely that Erebus emits other reactive nitrogen species that we have not measured. Several sources contribute to the Antarctic tropospheric NO_x budget: (i) minor in situ anthropogenic emissions from Antarctic bases and aircraft operations (Lyons et al., 2000); (ii) long-range transport of PAN and HONO₂ (from the Southern Hemisphere mid-latitudes; e.g., Jacobi and Schrems, 1999), which slowly release NO_x by photolysis (with the rate increasing with



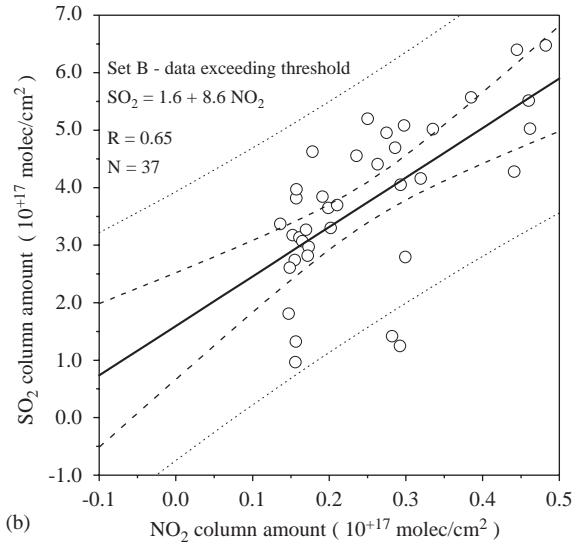
(a)



(a)



(b)



(b)

Fig. 4. Scatter plots for SO_2 vs. NO_2 for Set A spectra showing (a) all reliable data, and (b) retrievals exceeding significance thresholds ($0.63 \times 10^{17} \text{ molec cm}^{-2}$ for SO_2 and $0.17 \times 10^{17} \text{ molec cm}^{-2}$ for NO_2). The dashed and dotted lines show 95% confidence limits and prediction bands of the regression, respectively.

Fig. 5. Scatter plots for SO_2 vs. NO_2 for Set B spectra showing (a) all reliable data, and (b) retrievals exceeding significance thresholds ($0.43 \times 10^{17} \text{ molec cm}^{-2}$ for SO_2 and $0.27 \times 10^{17} \text{ molec cm}^{-2}$ for NO_2). The dashed and dotted lines show 95% confidence limits and prediction bands of the regression, respectively.

altitude); (iii) stratospheric HONO_2 , whose flux is related to that of the ozone flux from the stratosphere (e.g., Olsen et al., 2001); and (iv) photolysis of nitrate (e.g., Chu and Anastasio, 2003; Cotter et al., 2003) and pernitric acid (Slusher et al., 2002) in snow pack. The NO_x flux from nitrate photolysis for the whole of Antarctica has been estimated as $\sim 7.6 \text{ Gg(N) yr}^{-1}$ (Jones et al., 2001). This is an order of magnitude greater than our estimate of the point emission of $\text{N}(\text{NO}_2)$ from Mt. Erebus. However, since NO , HONO_2

and other species may be present in the plume (e.g., Mather et al., 2004b; Hunton et al., 2005), the total reactive nitrogen flux may significantly exceed our estimated NO_2 emission rate. It is also worth noting that the amount of reactive nitrogen reaching the free troposphere from the snow pack source appears limited (Huey et al., 2004) whereas the Erebus plume emerges at $\sim 4 \text{ km}$ above sea level (Fig. 1b). A further contrast between the two sources is that, if we have correctly surmised its origin, the NO_x

emission from Erebus is sustained throughout the year.

4. Conclusions

Using UV spectroscopy, we have detected and quantified NO₂ in the volcanic plume emitted into the free troposphere by Mount Erebus, Antarctica. The source of NO₂ is thought to be thermal fixation of atmospheric and/or magmatic nitrogen close to the surface of the active lava lake that is located within the summit crater of the volcano, followed by in-plume oxidation. The NO₂ flux, estimated in December 2003, was equivalent to ~0.6 Gg(N) yr⁻¹. The plume is likely to contain other reactive nitrogen species and the total NO_y emission rate may be significantly greater. Erebus appears to have had an active lava lake since at least the time of the first observations made by the Ross expedition in 1841. We suggest, therefore, that the volcano plays a significant role in Antarctic tropospheric chemistry, and represents a sustained source of nitrogen, as well as other species, deposited to the ice. Further work is required to characterise the NO_y emission from Erebus, and to develop our understanding of the complex chemical environments of young volcanic plumes.

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