Mt. Erebus, the largest point source of NO$_2$ in Antarctica

C. Oppenheimer$^{a,*}$, P.R. Kyle$^b$, V.I. Tsanev$^a$, A.J.S. McGonigle$^a$, T.A. Mather$^c$, D. Sweeney$^b$

$^a$Department of Geography, University of Cambridge, Downing Place, Cambridge CB2 3EN, UK
$^b$Department of Earth and Environmental Science, New Mexico Institute of Mining and Technology, 801 Leroy Place, Socorro, N.M. 87801-4796, USA
$^c$Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, UK

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Abstract

We report here the first observations of NO$_2$ 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 NO$_2$ flux, measured by scattered light ultraviolet spectroscopy in December 2003, was equivalent to $\sim$0.6 Gg (N) yr$^{-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 NO$_2$ 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 NO$_2$. 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.

Keywords: Troposphere; Plume; NO$_x$; DOAS

1. Introduction

Nitrogen oxides (NO$_x$ = NO + NO$_2$) as well as reactive odd nitrogen (NO$_y$ = NO, HONO$_2$, HONO, NO$_3$, N$_2$O$_5$, HNO$_4$, 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...
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 SO$_2$ and NO$_2$ 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 SO$_2$ have been measured repeatedly (Kyle et al., 1990, 1994), and supplemented by more sporadic measurements of CO$_2$ 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 $\sim$1200 m$^2$. 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 $\sim$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

SO$_2$ and NO$_2$ 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 $\mu$m 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, $\sim$2100 m from the summit crater.

NO$_2$ and SO$_2$ 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 SO$_2$ and NO$_2$ column amounts. The optimal fitting windows (309.2–334.5 nm for SO$_2$ and 330.7–349.0 nm for NO$_2$) 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
spectra for NO$_2$ (from Vandaele et al., 1998) and SO$_2$ (from Rufus et al., 2003), with the instrument line shape (FWHM 0.65 nm), and then removing the low-frequency component.

SO$_2$ 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 SO$_2$ column amounts were projected on to the plane perpendicular to the plume transport direction (each spectrum was located from a continuous GPS record). The SO$_2$ emission rate was then obtained from the product of the integrated SO$_2$ 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 SO$_2$ 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 NO$_2$ (as well as SO$_2$): Set 'A' was acquired between 22:14 and 22:19 UTC, and Set 'B' between 23:05 and 23:25 UTC. Based on retrieved SO$_2$ 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 SO$_2$ and NO$_2$) 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 SO$_2$ and NO$_2$ columns that exceeded the significance thresholds. The correlation between SO$_2$ and NO$_2$ (Figs. 4 and 5) indicates a molar SO$_2$/NO$_2$ ratio of ~7–12 in the plume. The observation that the correlation is clear but not strong is expected, since NO$_2$ is not a direct volcanic gas emission whose column amount would then scale linearly with SO$_2$. Instead, the likely origin of NO$_2$ in the plume is thermal fixation of atmospheric and/or magmatic N$_2$ at the lava lake surface to generate NO (Huebert et al., 1999; Mather et al., 2004a, b):

$$\text{O}_2 + \text{M} \rightarrow 2\text{O} + \text{M}, \quad (1)$$

$$\text{O} + \text{N}_2 \rightarrow \text{NO} + \text{N}, \quad (2a)$$

$$\text{N} + \text{O}_2 \rightarrow \text{NO} + \text{O}, \quad (2b)$$

followed by in-plume oxidation of the nitric oxide to NO$_2$ (e.g., Atkinson et al., 2004),

$$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2, \quad (3)$$

$$\text{NO} + \text{HO} \rightarrow \text{HONO}, \quad (4a)$$

$$\text{HONO} + \text{HO} \rightarrow \text{NO}_2 + \text{H}_2\text{O}, \quad (4b)$$

$$\text{NO} + \text{O} \rightarrow \text{NO}_2, \quad (5)$$

$$\text{NO} + \text{HO}_2 \rightarrow \text{HO} + \text{NO}_2. \quad (6)$$

It is also conceivable that combustion of reduced magmatic gas species (e.g., CO, H$_2$S and H$_2$) 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 SO$_2$ and NO$_2$ might prevail due to proportionality between magmatic gas and thermal fluxes from lava lakes (Kyle et al., 1994; Oppenheimer et al., 2004a).

The SO$_2$ 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 SO$_2$/NO$_2$ molar ratio as ~10 (Figs. 4 and 5) indicates an
NO$_2$ flux of $\sim 60$ g s$^{-1}$ ($\sim 2$ Gg yr$^{-1}$), which is equivalent to $\sim 20$ g (N) s$^{-1}$ ($\sim 0.6$ Gg (N) yr$^{-1}$).

From the known scanning rate ($\sim 8$ mrad s$^{-1}$) of the rotating platform used for the NO$_2$ measurements and the plume profiles (Fig. 3), we estimate that the width of the vertically rising plume was $\sim 350$–$500$ m. Assuming that the peak NO$_2$ column amounts ($\sim 0.3$–$0.5$ molec cm$^{-2}$ from Figs. 4 and 5) correspond to the full plume width, then the corresponding mean mixing ratio of NO$_2$ in the plume is $\sim 30$–$50$ 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 ($\sim 30$ 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 NO$_2$ over ozone is real (rather than due to underestimating the plume width), it could reflect formation of NO$_2$ by other mechanisms, such as reaction with volcanogenic HO$_x$ (e.g., Gerlach, 2004), or combustion at the lava lake surface.

The estimated NO$_2$ flux from the summit crater of Erebus ($60$ g s$^{-1}$, or the equivalent $0.6$ Gg (N) yr$^{-1}$) is modest compared to some sources. For example, NO$_2$ fluxes of $\sim 250$ 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 HONO$_2$ (from the Southern Hemisphere mid-latitudes; e.g., Jacobi and Schrems, 1999), which slowly release NO$_x$ by photolysis (with the rate increasing with...
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 $7.6 \times 10^{17}$ molec cm$^{-2}$ yr$^{-1}$ (Jones et al., 2001). This is an order of magnitude greater than our estimate of the point emission of N(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 $4$ km above sea level (Fig. 1b). A further contrast between the two sources is that, if we have correctly surmised its origin, the NO$_x$

\[
\text{Set A - reliable part} \\
\text{SO}_2 = 3.4 + 7.4 \text{NO}_2 \\
R = 0.81 \\
N = 163
\]

\[
\text{Set A - data exceeding threshold} \\
\text{SO}_2 = 8.6 + 6.6 \text{NO}_2 \\
R = 0.65 \\
N = 72
\]

\[
\text{Set B - reliable data} \\
\text{SO}_2 = 6.9 + 12.1 \text{NO}_2 \\
R = 0.83 \\
N = 131
\]

\[
\text{Set B - data exceeding threshold} \\
\text{SO}_2 = 1.6 + 8.6 \text{NO}_2 \\
R = 0.65 \\
N = 37
\]

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 ($0.63 \times 10^{17}$ molec cm$^{-2}$ for SO$_2$ and $0.17 \times 10^{17}$ 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 ($0.43 \times 10^{17}$ molec cm$^{-2}$ for SO$_2$ and $0.27 \times 10^{17}$ molec cm$^{-2}$ for NO$_2$). The dashed and dotted lines show 95% confidence limits and prediction bands of the regression, respectively.
Further work is required to characterise the NO\textsubscript{y} nitrogen, as well as other species, deposited to the ice. Chemistry, and represents a sustained source of volcano plays a significant role in Antarctic tropospheric expedition in 1841. We suggest, therefore, that the time of the first observations made by the Ross appears to have had an active lava lake since at least NO\textsubscript{2} to contain other reactive nitrogen species and the total oxidation. The NO\textsubscript{2} flux, estimated in December 2003, appears to contain other reactive nitrogen species and the total surface of the active lava lake that is located within the summit crater of the volcano, followed by in-plume oxidation. The NO\textsubscript{2} flux, estimated in December 2003, was equivalent to \( \sim 0.6 \text{ Gg (N)} \text{yr}^{-1} \). The plume is likely to contain other reactive nitrogen species and the total NO\textsubscript{2} emission 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\textsubscript{2} emission from Erebus, and to develop our understanding of the complex chemical environments of young volcanic plumes.

4. Conclusions

Using UV spectroscopy, we have detected and quantified NO\textsubscript{2} in the volcanic plume emitted into the free troposphere by Mount Erebus, Antarctica. The source of NO\textsubscript{2} 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 NO\textsubscript{2} flux, estimated in December 2003, was equivalent to \( \sim 0.6 \text{ Gg (N)} \text{yr}^{-1} \). The plume is likely to contain other reactive nitrogen species and the total NO\textsubscript{2} 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\textsubscript{2} emission from Erebus, and to develop our understanding of the complex chemical environments of young volcanic plumes.

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References


