Atmospheric chemistry of an Antarctic volcanic plume

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[1] We report measurements of the atmospheric plume emitted by Erebus volcano, Antarctica, renowned for its persistent lava lake. The observations were made in December 2005 both at source, with an infrared spectrometer sited on the crater rim, and up to 56 km downwind, using a Twin Otter aircraft; with the two different measurement platforms, plume ages were sampled ranging from <1 min to as long as 9 h. Three species (CO, carbonyl sulfide (OCS), and SO2) were measured from both air and ground. While CO and OCS were conserved in the plume, consistent with their long atmospheric lifetimes, the downwind measurements indicate a SO2/CO ratio about 20% of that observed at the crater rim, suggesting rapid chemical conversion of SO2. The aircraft measurements also identify volcanicogenic H2SO4, HNO3 and, recognized for the first time in a volcanic plume, HO2NO2. We did not find NO in the downwind plume despite previous detection of NO2 above the crater. This suggests that near-source NOx was quickly oxidized to HNO3 and HO2NO2, and probably NO3(aq), possibly in tandem with the conversion of SO2 to sulfate. These fast processes may have been facilitated by “cloud processing” in the dense plume immediately downwind from the crater. A further striking observation was O3 depletion of up to ~35% in parts of the downwind plume. This is likely to be due to the presence of reactive halogens (BrO and ClO) formed through heterogeneous processes in the young plume. Our analysis adds to the growing evidence for the tropospheric reactivity of volcanic plumes and shows that Erebus volcano has a significant impact on Antarctic atmospheric chemistry, at least locally in the Southern Ross Sea area.


1. Introduction

[2] An important finding concerning the impact of global volcanism is the disproportionately high contribution of sulfate loading in the atmosphere due to sulfur emissions from nonexplosive, degassing volcanoes compared with other sulfur sources, including anthropogenic and oceanic emissions [e.g., Chin and Jacob, 1996; Graf et al., 1997; Stevenson et al., 2003]. This partly reflects the elevation of volcanic sources, which leads to enhanced atmospheric residence times for volcanic sulfur gases and aerosols compared with many oceanic or anthropogenic sources. Thus, the temporal and spatial variability in this “background” volcanic source may represent an important climate forcing factor that has yet to be fully characterized. In addition to the impacts from sulfur compounds, there is further evidence of enhanced atmospheric chemical reactivity induced by volcanic plumes due to the presence of reactive halogens [e.g., Bobrowski et al., 2003, 2007; Bobrowski and Platt, 2007; Oppenheimer et al., 2006; Theys et al., 2009; Roberts et al., 2009] and nitrogen species [e.g., Huebert et al., 1999; Mather et al., 2004a, 2004b; Martin et al., 2006]. In light of these findings, it is likely that, at least on a local scale, volcanic plumes strongly perturb tropospheric acidity and oxidizing capacity.

[3] Here we report airborne and ground-based measurements of Antarctica’s most persistently active volcano, Mount Erebus (77° 32'S, 167° 10’E, 3794 m above sea level). The observations were made under the auspices of the Antarctic Tropospheric Chemical Investigation (ANTCI) 2005 project (http://acd.ucar.edu/~mauldin/ANTCI_web/ANTCI_Home.htm) and the research program of the Mount Erebus Volcano Observatory (http://erebus.nmt.edu/). The primary motivation for our focus on Erebus was to investigate peculiarities in volcanic plume chemistry that might be associated with the characteristics of the Antarctic atmosphere, and, more specifically, to improve our understanding...
of NO\textsubscript{x} chemistry in volcanic plumes following previous observations of NO\textsubscript{2} emissions above the Erebus crater [Oppenheimer et al., 2005]. This NO\textsubscript{2} was thought to have been formed from oxidation of atmospheric N\textsubscript{2} at the hot surface of the volcano’s active lava lake. It was also suggested that Erebus represents the largest point source of NO\textsubscript{2} in Antarctica, and that the emission might be relevant to understanding highly elevated levels of NO (>0.6 ppbv) observed occasionally in near surface air at South Pole [Davis et al., 2001, 2004, 2008].

Prior studies of the Erebus plume using instrumented aircraft include those of Radke [1982], Rose et al. [1985], Chuan et al. [1986], and Chuan [1994]. Radke [1982] reported the results of several research flights carried out in mid-November 1980. He found that most of the plume aerosol mass was narrowly confined to particles with diameter of \(\sim\)100 nm, suggesting a single mechanism involved in aerosol production operating close to the crater. He pointed out that particles of such a size (corresponding to the so-called “Greenfield gap”) should be exceptionally long-lived due to minimum scavenging efficiency, and suggested that up to 32% of the Antarctic total sulfate budget could be sourced by Erebus alone. Based on plume sampling at the crater, Zreda-Gostynska et al. [1997] confirmed the volcano’s strong emission of many species including halogens and trace metals leading them to suggest Erebus might contribute up to 80% of the Cl deposited at South Pole.

[5] Shaw [1983] tentatively identified Erebus aerosol at South Pole on the basis of Cl and Si content, while Arimoto et al. [2004a, 2004b] suggested the volcanic contribution to sulfate and trace metals in South Pole aerosol. Chuan [1994] also argued for long-range transport of Erebus aerosol across the Polar Plateau, at least as far south as latitude 88.7°S, based on airborne collection of particles containing diagnostic Au and KCl. Vallelonga et al. [2003] also considered Erebus as the origin of trace metal peaks in the glaciochemistry of ice cores drilled at Law Dome, Wilkes Land (\(\sim\)2000 km from Erebus). More recently, Shirsat and Graf [2009] demonstrated the preeminence of Erebus’ contribution to the Antarctic atmospheric SO\textsubscript{2} budget, based on an inventory of natural and anthropogenic sources. Graf et al. [2009] used this inventory (which excludes DMS) in a limited area climate model to suggest that Erebus contributes around 10 ppbv to the tropospheric SO\textsubscript{2} burden in the Ross Sea region and is a significant source of sulfate deposition on the Royal Society mountain range.

[6] The new measurements reported here were made both by tracking the plume downwind using an instrumented aircraft, and at the summit crater using a Fourier transform infrared (FTIR) spectrometer sited on the crater rim. We were thus able to characterize several aspects of the chemical evolution of the Erebus plume as it drifted for an estimated 9 h in the troposphere (at a height of \(\sim\)3800 m above sea level). Specific aims included an assessment of the nitrogen and sulfur chemistry of the plume, with an emphasis on contrasting the gas phase composition of the very young plume (in the crater) with the aged plume drifting downwind.

2. Methods
2.1. Airborne Measurements

[7] Measurements were made on two flights (8 and 9, introduced in section 2.2) of an instrumented DHC-6 Twin Otter aircraft for the following chemical species: NO, HNO\textsubscript{3}, HO\textsubscript{2}NO\textsubscript{2}, SO\textsubscript{2}, COS, CO, O\textsubscript{3} and H\textsubscript{2}O. More limited observations were also available during flight 9 for H\textsubscript{2}SO\textsubscript{4} and OH. In all cases, air intakes for the sampling lines were located forward of the aircraft engines, and outside of the fuselage boundary layer. Controlled tests in which NO from an on-board tank was released next to the aircraft skin at different positions excluded the possibility of contamination from the cabin. In addition, flight tests were carried out in which NO was monitored while the aircraft was put through different flight maneuvers. These established that, while flying horizontally, no exhaust from the aircraft engines reached the sampling system. This was also the case for tests involving vertical spirals in which descent rates of 150 m min\(^{-1}\) were maintained. The only flight mode in which engine exhausts were occasionally detected was when the aircraft flight track involved tight 180° or 360° turns. The worst case scenario was when the aircraft made a 180° turn, followed by repositioning itself downwind of its point of passage through the plume. As indicated later in the text, this flight pattern did occasionally result in sampling of engine generated NO.

[8] The detection limit, 2\(\sigma\) random error, and the calibration uncertainty for each of the critical species measured from the aircraft are given in Table 1. The detection limit reported is typically based on a 1 min integration time. (Note that during ground-based studies the integration time can be increased by factors of 5 to 20, thus further enhancing the stated detection limit for a species.) The cited calibration uncertainty represents the maximum potential systematic error in the airborne measurements based on calibration standards. In most cases \(\text{H}_2\text{SO}_4\) being the exception) the potential systematic error was \(<20\%\) of the measured value.

[9] Measurements of NO were made using a chemiluminescence technique. This methodology has been well-established through instrument intercomparison studies involving both airborne and ground-based sampling platforms [e.g., Hoell et al., 1987; Gregory et al., 1990]. The NO system was calibrated using a standard addition methodology, which was performed at least twice per flight (for additional details, see also Davis et al. [2001, 2004, 2008]). Measurements of O\textsubscript{3} were made using a commercial UV absorption instrument, which again has undergone numerous field tests, and is a well-proven instrument [Gregory et al., 1983]. Both the random and potential systematic errors in the measurements are given in Table 1.

[10] Measurements of SO\textsubscript{2}, HNO\textsubscript{3}, HO\textsubscript{2}NO\textsubscript{2} and H\textsubscript{2}SO\textsubscript{4} involved two versions of the select ion chemical ionization mass spectrometry technique. For SO\textsubscript{2}, HNO\textsubscript{3} and HO\textsubscript{2}NO\textsubscript{2}, sampling was achieved through a heated inlet that extended \(\sim\)0.5 m from the aircraft skin. The sampling line itself was made of 1/2 inch OD Teflon tubing, approximately 2.6 m in total length. The reagent ion used to detect SO\textsubscript{2}, HNO\textsubscript{3} and HO\textsubscript{2}NO\textsubscript{2} was SF\textsubscript{6}\textsuperscript{−}, which was generated in an ion source chamber by associative electron capture. A typical measurement sequence consisted of integrating the signal at 148 amu (\(\text{SF}_6\textsuperscript{−}\)) for 25 ms, 82 amu (NO\textsubscript{3}− · HF) for 2 s, 98 amu (NO\textsubscript{2}− · HF) for 2 s, and 102 amu (F\textsubscript{2}SO\textsubscript{2}) for 0.5 s. Background measurements were collected every few minutes by diverting ambient flow through a filter containing nylon wool and activated charcoal. Typical
sensitivities obtained for HNO3 and SO2 during the field study were 7 and 4 counts per second (parts per trillion by volume) \(^{-1}\), respectively [see Huey et al., 1995, 2004; Slusher et al., 2001]. Note, for the latter instrument, we also considered a further potential systematic error not cited in Table 1 arising from the specific configuration employed during the ANTCI 2005 study. This is the slight possibility that an interference ion of nearly the same mass as that produced from HNO3 could have been generated when SO2 levels were very high (>10 ppbv). However, that this potential error was small (≤0.5% of the measured value of SO2) is strongly suggested from an examination of a subset of the HNO3 and SO2 data corresponding to lower plume abundances (up to SO2 mixing ratios of 2 ppbv). Figure 1 displays these screened data and indicates a number of data pairs where SO2 abundance ranges from background values (≤0.01 ppbv) up to ~2 ppbv but for which HNO3 is as low as 0.005 ppbv. These data clearly suggest a significant degree of heterogeneity in the plume, but more importantly, they show that there is no increasing trend evident in HNO3 levels with increasing SO2 up to ~2 ppbv. Further evidence for very limited interference is that between 2 and 10 ppbv of SO2, the trend in data pairs in Figure 1 is consistent with the trend for the entire data set, which extends to SO2 abundances in excess of 30 ppbv. Notwithstanding these comments, all plume HNO3 measurements still should be viewed as upper limit values.

[11] A final point regarding the sampling of both SO2 and HNO3 involves the small but persistent “tailing effect” seen on the larger peaks, especially those for SO2. Although some of this tailing effect may have been the result of the

<table>
<thead>
<tr>
<th>Chemical Species</th>
<th>Detection Limit</th>
<th>Random Error (2σ) (%)</th>
<th>Calibration Uncertainty (%)</th>
</tr>
</thead>
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<tr>
<td>CO</td>
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<td>5</td>
<td>10</td>
</tr>
<tr>
<td>OCS</td>
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<td>5 pptv</td>
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<td>20</td>
</tr>
<tr>
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<td>20</td>
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<td>5 pptv</td>
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<td>20</td>
</tr>
<tr>
<td>H2SO4</td>
<td>5 × 10^6 molecule cm^-3</td>
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<td>40</td>
</tr>
<tr>
<td>O3</td>
<td>2 ppbv</td>
<td>3</td>
<td>5</td>
</tr>
</tbody>
</table>

aDetection limit (DL) for S/N = 2.0.  
bTwo-sigma error when signal ≥ 5 × DL.  
cPercent of measured value.

Figure 1. SO2 and HNO3 observations from research flights carried out on 9 and 11 December 2005 in vicinity of Erebus volcano, showing only data pairs for which SO2 levels were below 10 ppbv. The lack of any trend in HNO3 versus SO2 for SO2 < 2 ppbv, the few high values of SO2 that are not matched by comparably high HNO3 levels, and the clear trend in SO2 versus HNO3 between 2 and 10 ppbv of SO2 (which is related to the visible volcanic plume) all point to negligible interference of SO2 on the HNO3 measurements. The line indicates the linear regression through all the SO2 and HNO3 observations for both flights (including the data points for concentrated plume not shown in this graph). See also Figure 6.
2.2. Airborne Plume Intercept Details

Measurements from a later ANTCI flight could only be evaluated semiquantitatively, based on mass spectrometric via the detection of the HSO4

Unfortunately, due to instrument difficulties, OH abundance could only be evaluated semiquantitatively, based on measurements from a later ANTCI flight.

2.3. Ground-Based Measurements

[13] The Erebus plume was intercepted between 4 and 20 km from the crater at ~0450–0600 UTC on 9 December 2005 (flight 8), and between 1 and 56 km from the crater at ~2230–2310 UTC on 10 December 2005 (flight 9). These distances correspond to an estimated plume age that ranges from 30 min to 2 h for flight 8, and from 10 min to nearly 9 h for flight 9. These age estimates are based on wind speed estimates from two rawinsonde launches at McMurdo Station (~35 km away) for the altitude of the plume. For flights 8 and 9 these were 3.1 and 1.8 m s⁻¹, respectively. However, it should be borne in mind that the time of the rawinsonde launches at McMurdo was several hours removed from the actual flight times. Thus, changes in wind speed and direction both before the rawinsonde launch as well as during the course of each plume study cannot be ruled out. Postanalyses of the meteorological wind fields in the immediate vicinity of Erebus volcano in the form of forward air trajectories (based on Polar MM5 modeling results) suggest that, in the very early morning hours, winds were very light and highly variable in direction. In addition, when using these wind speed data as a ‘clock’ for estimating the advection of the plume core, and hence, for estimating the chemical reaction time in the plume, it must be recognized that these data cannot provide a good guide to time scales of cross-wind plume mixing. In the latter case, different degrees of chemical processing can be encountered at different locations within the plume (different points along a radial axis reflecting the extent of dilution) even though the distance from the crater rim is the same for all points along the axis. (Note that a sampling integration time of 1 min corresponds to about 4 km of flight at the mean ground speed of ~250 km h⁻¹, which means that considerable spatial averaging of the abundances of species occurs each time the aircraft crosses the plume.)

[14] Antarctic local time was the same as New Zealand Daylight Time (UTC+13 h); thus the encounters occurred at 1750–1910 (9 December) and 1130–1210 (11 December) local time. Table 2 lists the relevant environmental and geographical data pertaining to the plume encounters. The photograph in Figure 2 illustrates the high degree of plume visibility on 11 December (as seen from ~25 km away) and thus reflects the stable atmospheric conditions prevailing around the time of takeoff for flight 9. Plume visibility was significantly lower during flight 8.

2.3. Ground-Based Measurements

[15] Measurements at the crater rim of Erebus were made using a portable FTIR spectrometer (MIDAC M-4402-1) fitted with ZnSe beam splitter and a liquid nitrogen-cooled...
the airborne in-plume data obtained in the preceding days. Little over time scales of a few weeks. Thus we are very field season demonstrate that the plume composition varies measurements throughout the 2005/2006 austral summer 2005, 24 h after flight 9 and it is the retrievals of this first gases, then results for NO and O₃. Measurements were also made for a number of organic species but none showed significant perturbations in their concentrations in the plume, and we do not therefore discuss them further.

3. Results

3.1. SO₂, CO, OCS, and H₂SO₄

The SO₂ observations, because of their highly elevated levels, provided one of more reliable indicators of the plume core. Thus, these data suggest that the emissions from Erebus were sampled in excess of 50 km downwind of the crater (Figure 3). The highest SO₂ mixing ratios, up to 30 ppbv, were measured on flight 9. However, as much as 0.238 ppbv of SO₂ was detected at ~56 km from the crater, an abundance that was ~25–50 times background values (~0.005–0.010 ppbv). Of great interest, ANTCI flight 10 also encountered evidence of the Erebus plume while sampling above the Polar Plateau on 12 December 2005, a distance of ~600 km from the volcanic source [Slusher et al., 2010]. During this mission, the aircraft flew from McMurdo to the automatic weather station at Mid-Point (75°S, 145°E). The plume was recognized by increases in both HNO₃ and SO₂. The former species reached levels that were ~0.06 ppbv above background; whereas SO₂ was 0.005–0.01 ppbv above stable background levels. Confirming the SO₂ results, there were corresponding elevations in H₂SO₄ levels. Further analyses of these data based on forward trajectory modeling confirmed Erebus as the most likely source and that the plume had been airborne for around 3–4 days by the time it was sampled.

The resulting interferograms were inverse Fourier transformed with a Mertz phase correction and triangular apodization, and the resulting single-beam spectra were analyzed by simulating the atmospheric transmittance in several discrete ‘microwindow’ wave bands [e.g., Oppenheimer et al., 1998; Burton et al., 2000; Horrocks et al., 2001] using the Reference Forward Model [Edwards and Dudhia, 1996] and line parameters from the HITRAN database [Rothman et al., 2005] for required gas species. The model considers a one-layer atmosphere with pressure, temperature and initial column amounts specified for both atmospheric and volcanic gas species. A second-order polynomial was also computed to detrend the local slope of the spectrum. The simulated spectra were adjusted to fit each observed spectrum using an optimal estimation method [Rodgers, 1976]. Relative errors were computed for each of the fitted components in the retrieval procedure based on the standard deviation of the residual (equal to the forward model minus the measurement), and, for our measurements, lie mostly in the range of 5–10% (see also Horrocks et al. [2001] for discussion of error budgets for the method). Molar abundance ratios were computed for pairs of gas species by simple, unweighted regression of the set of retrieved column amounts. Further details of the application of open-path FTIR spectroscopy on Erebus are given by Oppenheimer and Kyle [2008] and Oppenheimer et al. [2009].

The FTIR measurements began on 12 December 2005, 24 h after flight 9 and it is the retrievals of this first data set that we present here. We note that our FTIR measurements throughout the 2005/2006 austral summer field season demonstrate that the plume composition varies little over time scales of a few weeks. Thus we are very confident that the intracrater plume composition recorded by FTIR spectroscopy provides a suitable comparison for the airborne in-plume data obtained in the preceding days.

3. Results

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In clear association with SO₂, we find elevated gas phase H₂SO₄ in the plume encounters for flight 9 (Figure 4). The molar ratio of SO₂/H₂SO₄ is ~4.1 × 10⁻³. However, there is also variability in the proportions of the two species, notably several samples with much higher H₂SO₄ relative to SO₂. These results reflect our earlier discussion pointing to the fact that the Erebus plume during this field study cannot be viewed as homogeneously mixed, and that radial mixing can lead to a rather complex chemical picture.

Two other volcanic species, CO and OCS, which have been previously observed in the summit plume [Oppenheimer and Kyle, 2008] were also detected during the airborne measurements (Figure 5). The molar ratio of CO to OCS of ~300 is strikingly similar for both the airborne measurements and the summit FTIR observations. On the other hand, the SO₂/CO proportions for gas within the crater and distal plume differ markedly: the SO₂/CO molar ratio was ~0.42 at the source compared with ~0.082 downwind. Accepting comparability of the two techniques, this suggests significant depletion of SO₂ in the plume during advection. Also of note in the aircraft data, the observations for CO versus OCS are more strongly correlated than those for CO versus SO₂ (r² = 0.99 versus r² = 0.78, respectively).

The molar abundance of CO in the magmatic gas is ~2% [Oppenheimer and Kyle, 2008] so the CO maxima observed in the downwind plume (~200–350 ppbv) correspond to a dilution of the plume by ambient air on the order of 1:10⁴ to 1:10⁵. For comparison, the mixing ratio of CO at the rim of the summit crater is already as low as ~1–10 ppmv (i.e., diluted by ambient air within the crater in proportions of around 1:10³ to 1:10⁴), so the maximum CO abundance detected downwind corresponds to a further dilution of the plume (as sampled) by a factor of 10 to 100 after leaving the crater area. However, it must be borne in mind that the sampling time in flight corresponded to a cross-wind distance of ~4 km, thus there was the potential for sampling in and out of the plume during an individual measurement.
Figure 3
3.2. Volcanogenic NO$_y$

[23] The first notable finding for plume NO$_y$ chemistry was the detection of HNO$_3$. Figure 6a shows the corresponding SO$_2$ and HNO$_3$ mixing ratios measured during flight 9: the SO$_2$/HNO$_3$ molar ratio is $\sim$56. The two species are strongly correlated (e.g., $r^2 > 0.9$), as shown in Figure 6b, with very similar results for both flights 8 and 9. Since HNO$_3$ is not a primary volcanic species we consider that its abundance reflects the atmospheric chemistry of the volcanic plume. But also of note during flight 9 is the long-wavelength “whaleback” profile in the measured HNO$_3$, which peaks at $\sim$0.1 ppbv around 2220 UTC (Figure 6a). This is a peculiar feature characterized by HNO$_3$ values generally $>0.03$ ppbv, which, from inspection of the flight lines, extends up to 15 km upwind from Erebus, and throughout the 56 km flight downwind. It is clearly independent of the spikes in HNO$_3$ that correspond to the visible crater plume (Figure 2). As also discussed above, significant evidence was found for the Erebus plume also reaching the Polar Plateau above which the HNO$_3$ levels observed were 0.060 ppbv above background levels (which were $\sim$0.040 ppbv).

[24] The other species with a clear plume signal is HO$_2$NO$_2$ (which was measured on flight 9 only). The peak in its mixing ratio is $\sim$0.13 ppbv (Figure 6b). The HO$_2$NO$_2$/HNO$_3$ molar ratio is $\sim$0.6, and the SO$_2$/[HNO$_3$ + HO$_2$NO$_2$] ratio is $\sim$40. However, there was no evidence for volcanogenic NO$_x$ in the plume based on the NO measurements. Although spikes in the NO concentration up to $\sim$0.08 ppbv were recorded, inspection of the GPS track indicates these can all be attributed to aircraft engine exhaust reaching the sampling line as a result of 180° turns.

3.3. Impacts of Erebus Plume on Ozone Abundance

[25] Ozone levels recorded during flight 9 reveal significant perturbations associated with the plume. These were particularly noticeable when the comeasured SO$_2$ abundance reached its highest values (Figure 7). This can be seen best at 2306 UTC when the SO$_2$ mixing ratio exceeds 25 ppbv and O$_3$ falls from a mean of $23.6 \pm 2.0$ (1σ) ppbv to a low of 14.8 ppbv (i.e., more than 4σ below the mean).

Figure 4. Observations from flight 9 on 11 December showing correspondence between SO$_2$ (red line) and H$_2$SO$_4$ (blue line with triangles) mixing ratios. Note different units (pptv for H$_2$SO$_4$ and ppbv for SO$_2$).

Figure 3. (a) Flight lines from GPS record; arrows show flight entries and exits. Erebus is the red triangle; flights 8 and 9 are indicated by dotted green and solid red lines, respectively. Yellow diamonds indicate observed SO$_2$ mixing ratios above 0.05 ppbv. Using this as a plume discriminator, the emissions have been tracked up to 56 km from source. The gray ovals indicate very approximately the location of the plume during the two encounters. (b) SO$_2$ mixing ratios observed during flights 8 (green triangles) and 9 (red circles) plotted as a function of plume age (estimated from an early morning wind speed observation for the approximate altitude of the Erebus plume taken from one rawinsonde observation at McMurdo). During flight 8, the plume became virtually invisible at distances greater than 10 km; thus more flight time was required to locate the plume.
Figure 5

a) Airborne downwind observations
Crater FTIR observations

OCS/CO = 0.0033
R² = 0.99

OCS/CO = 0.0035
R² = 0.80

b) Airborne downwind observations
Crater FTIR observations

SO₂/CO = 0.42
R² = 0.52

SO₂/CO = 0.082
R² = 0.78
Another fall in O₃ to 18.4 ppbv at 2253 UTC is less pronounced but still represents a drop ~2.5σ below the mean. There is no evidence for O₃ loss in the measurements from flight 8 but we note that SO₂ values measured during this flight never exceeded 20 ppbv.

4. Discussion

4.1. Sulfur Chemistry

[26] The close correspondence of CO and OCS levels (molar OCS/CO ~0.0033–0.0035) based on both airborne and intracrater plume observations provides unambiguous evidence that the ANTCI mission succeeded in sampling the Erebus plume up to 56 km from the source (Figure 3). It further shows that CO and OCS were not appreciably oxidized during the corresponding atmospheric transport (or at least that there was no differential loss of the two species). This result is consistent with their known tropospheric lifetimes (months in the case of CO, years for OCS). By contrast, the SO₂/CO ratio in the distal plume was substantially lower than that observed at the crater (Figure 5b). Although we cannot completely exclude complications arising from calibration differences between the measurements, these results strongly suggest that significant loss of plume SO₂ occurred during transport. Future aircraft studies (with rigorous instrument intercalibration) will be required to confirm this effect and to identify variability that might be associated with atmospheric and meteorological conditions.

[27] It is noteworthy that both the crater rim and distal plume measurements for CO versus OCS are strongly correlated (Figure 5a). This most likely reflects the thermodynamic equilibrium reached for the magmatic conditions prior to emission to the atmosphere and subsequent quenching. In the magmatic gas, the following equilibrium is relevant:

\[ 3\text{CO} + \text{SO}_2 \leftrightarrow 2\text{CO}_2 + \text{OCS}. \]  

The CO/CO₂ is fixed according to the oxygen fugacity and temperature of the magma, thus thermodynamically controlling the SO₂/OCS proportion.

[28] A final question addressed that relates to plume sulfur chemistry concerns the source of H₂SO₄ in the Erebus plume. Possible sources of H₂SO₄ could include in situ production within the plume by gas kinetic processes or volatilization of H₂SO₄ from aerosol species where the acid was formed earlier in the young, hot gas mixture leaving the lava lake surface. In the latter case one can hypothesize that this primal H₂SO₄ in a more dilute plume would reach an equilibrium between adsorbed H₂SO₄ on particulates and its gas phase. To address this question, we present calculations here that explore the gas kinetic hypothesis in somewhat greater detail. We begin by accepting the well established three step oxidation process for SO₂ via OH; that is,

\[ \text{OH} + \text{SO}_2 + \text{M} \rightarrow \text{HSO}_3, \]  

\[ \text{HSO}_3 + \text{O}_2 \rightarrow \text{SO}_3 + \text{HO}_2, \]  

\[ \text{SO}_3 + (\text{H}_2\text{O})_2 \rightarrow \text{H}_2\text{SO}_4 + \text{H}_2\text{O}. \]  

The rate controlling step in this scheme is [2]. Thus, using an upper limit value for measured OH of \(4 \times 10^3 \text{ cm}^{-3}\) (estimated from limited ANTCI 2005 measurements of OH at 3.8 km above sea level), an average SO₂ plume abundance of 10 ppbv, and a k₂ value of \(1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) (estimated for the air temperature at plume altitude), the net formation rate for H₂SO₄ is \(~0.8 \times 10^5 \text{ molecule cm}^{-1} \text{ s}^{-1}\). Given this value, calculation of the plume H₂SO₄ concentration becomes tractable provided the first-order loss of H₂SO₄ to particulates is known. Unfortunately, aerosol parameters were not recorded during our plume intercepts with the Twin Otter. Thus we estimate the aerosol impact based on previous studies by Eisele and Tanner [1993] and Mauldin et al. [2004]. In this case, the stated loss rates for the different aerosol settings range from \(10^{-3} \text{ s}^{-1}\) for very clean background conditions to \(1 \text{ s}^{-1}\) for highly polluted environments. Given the visual appearance of the Erebus plume during our observations (e.g., Figure 2), we consider the intermediate value of \(~10^{-2}\) (e.g., typical of the aerosol loading in background continental air) to be the most appropriate [Eisele and Tanner, 1993]. Thus, the abundance of H₂SO₄ can be estimated at \(~0.4 \text{ ppbv}\), a value comparable to that observed in the Erebus plume of 0.1–0.6 ppbv. This suggests that the most likely source of in-plume H₂SO₄ was that resulting from gas kinetic processes.

4.2. NOₓ Chemistry

[29] Previous observations of high NO₂ abundance above the Erebus crater [Oppenheimer et al., 2005] along with the ANTCI 2005 measurements that reveal the total absence of NOₓ in the distal plume (even within 1 km of the crater) strongly suggest that NO₂ formed in the crater is rapidly oxidized during plume transport. Importantly, the detection of HNO₃ and HO₂NO₂ provides further confirmation that NO₂ was present in the very early evolution of the plume.

Figure 5. Comparison of airborne samples (red circles: flights 8 and 9 combined) and intracrater plume sensed by FTIR spectroscopy (green triangles) for (a) CO versus OCS and (b) CO versus SO₂. Note that FTIR measurements represent 8 s averages over a 300 m path, whereas the aircraft measurements are 1 min averages that represent an average over 4 km. The OCS/CO molar ratio (~0.0033–0.0035) is comparable for both proximal and distal plume, while the SO₂ versus CO measurements show that the distal plume is strongly depleted in SO₂. Note the differences in units: volume mixing ratios for the airborne sampling versus column amounts for the retrievals of open-path FTIR spectra. The distal plume data do not plot through the origin but trend to the background tropospheric mixing ratios of CO (~50 ppbv) and OCS (~0.4 ppbv). Note also the tighter correspondence in the aircraft observations between OCS versus CO than for SO₂ versus CO. The scatter in the FTIR-spectra derived SO₂ versus CO plot reflects the dynamics of degassing in the magma conduit [Oppenheimer et al., 2009]. Relative errors shown for FTIR spectra represent ±1σ of the residual for each spectral fit. The spread of values represents plume dilution.
Stated differently, the observation of highly elevated HNO₃ abundance in the plume is chemically required given the crater observations of highly elevated NOₓ along with the absence of NOₓ in the downwind plume. The fact that there were elevated levels of HO₂NO₂ in the plume also strongly suggests that the conversion of NO₂ to HNO₃ and HO₂NO₂ occurred in the gas phase, since we know of no heterogeneous process that can generate the thermodynamically unstable HO₂NO₂ species.

Interestingly, the persistence of HO₂NO₂, even out to distances corresponding to a few hours, reflects the low ambient temperatures that were present in the Antarctic.
atmosphere at that time (~250 K), leading to a relatively low rate of thermal decomposition (e.g., 3–9 h),

\[
\text{HO}_2\text{NO}_2 \rightarrow \text{HO}_2 + \text{NO}_2. \tag{5}
\]

As far as we are aware, this is the first observation of \(\text{HO}_2\text{NO}_2\) in a volcanic plume. The \(\text{HO}_2\) required in the reaction with \(\text{NO}_2\) may have been generated from the hot gas mixture above the lava lake [Gerlach, 2004; Martin et al., 2006, 2009] or possibly even by conventional atmospheric photochemical processes involving \(\text{O}_3, \text{H}_2\text{O}, \text{or} \text{H}_2\text{O}_2\) [e.g., Finlayson-Pitts and Pitts, 1997]. For example, high levels of \(\text{H}_2\text{O}\) within the crater in the presence of \(\text{O}_3\) and sunlight may have resulted in a major source of \(\text{HO}_x\) radicals. However, any \(\text{HO}_2\) formed in this way would be consumed rather quickly by its reaction either with \(\text{NO}\), \(\text{NO}_2\) or possibly with halogen species, for example,

\[
\text{HO}_2 + \text{NO} \leftrightarrow \text{NO}_2 + \text{OH}. \tag{6}
\]

Significant levels of NO most likely were generated by fixation of atmospheric \(\text{N}_2\) at the hot lava lake [e.g., Huebert et al., 1999; Mather et al., 2004a] or as a result of mixing of hot magmatic gases and ambient air [Martin et al., 2006]. As noted above, the reaction of NO with \(\text{HO}_2\) or halogen oxides would have quickly led to \(\text{NO}_2\) formation. The subsequent reaction of this species with either \(\text{OH}\) or \(\text{HO}_2\) radicals would then provide one possible explanation for both the observed \(\text{HNO}_3\) and \(\text{HO}_2\text{NO}_2\); that is,

\[
\text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 \tag{7}
\]

\[
\text{HO}_2 + \text{NO}_2 + \text{M} \rightarrow \text{HO}_2\text{NO}_2. \tag{8}
\]

More speculative, is the possibility of generation of elevated \(\text{HNO}_3\) via a combination of gas phase and heterogeneous reactions [Oppenheimer et al., 2006; Roberts et al., 2009]:

\[
\text{BrO} + \text{NO}_2 \rightarrow \text{BrONO}_2, \tag{9}
\]

\[
\text{BrONO}_2 + \text{HBr}_{(aq)} \leftrightarrow \text{HNO}_3 + \text{Br}_2, \tag{10}
\]

\[
\text{BrONO}_2 + \text{H}_2\text{O}_{(aq)} \leftrightarrow \text{HNO}_3 + \text{HOBr}. \tag{11}
\]

In 2004, the use of UV differential optical absorption spectroscopy to observe the summit plume rising above the crater indicated a \(\text{SO}_2/\text{NO}_2\) molar ratio of \(\sim 10\) [Oppenheimer et al., 2005]. This is substantially lower than the molar ratio of \(\text{SO}_2/\text{HNO}_3\) that we observe in the core of the distal plume \((\sim 56 \text{ km})\) or the observed \(\text{SO}_2/\text{[HNO}_3 + \text{HO}_2\text{NO}_2]\) ratio of \(\sim 40\); and suggests that much of the \(\text{NO}_2\) observed above the crater was converted into undetected \(\text{N}\)-bearing species within a short time (<1 h) of exiting the crater. Possibilities include nitrate in the form of aerosol, and/or gas phase halonitrates. Indeed, Radke [1982] reported nitrate in aerosol sampled 13 km downwind from the crater of Erebus, with a sulfate:nitrate proportion of 9.4:2.2 by mass.

[31] Importantly, there is no evidence for fractionation during transport between gas phase \(\text{NO}_2\) and \(\text{SO}_2\) in the visible summit plume. This is reflected in the stable \(\text{SO}_2/\text{HNO}_3\) ratio as shown in Figures 6b and 8. Equally significant is the fact that the nitrogen/sulfur results are essentially identical on two days of observations. However, the long-wavelength, “whaleback” profile apparent in the \(\text{HNO}_3\) record for flight 9 (Figure 6a) cannot be directly related to the visible plume: it extends cross wind and even upwind of

**Figure 7.** Correspondence between observed \(\text{SO}_2\) (red line) and \(\text{O}_3\) (blue line with triangles) during part of flight 9. Note depletion of \(\text{O}_3\) in two intercepts of the plume involving the highest loadings of \(\text{SO}_2\).
the crater. There is a similar but less pronounced feature apparent in the HNO3 measurements for flight 8 but it only extends downwind and more closely envelopes the visible plume. The associated HNO3 values typically exceed 0.03 ppbv, still substantially above background levels. One interpretation of this phenomenon is that it represents a “pool” of aged plume that accumulated around the volcano as a result of the continuous degassing, comparatively low wind speeds during the two flight days (3.1 and 1.8 m s⁻¹ during flights 8 and 9, respectively), and the complex topography of the crater and upper flanks of the volcano, which typically lead to turbulent airflow around the mountain. Still an even more likely scenario is that the longer atmospheric lifetime of HNO3 versus SO2 at altitudes above the planetary boundary layer [Slusher et al., 2010] in conjunction with significant fluctuations in wind speed and wind direction during the earlier morning hours preceding the launch of flight 9 (see earlier meteorological discussions, section 2.2) produced the upwind HNO3 elevations. This would also explain the lack of correlation between SO2 and HNO3 in the distributed plume “pool”; that is, SO2 was lost more rapidly than HNO3 through chemical conversion to H₂SO₄. In the latter regard, it is significant that even within the visible plume there was some evidence for differential mixing and chemical processing along the fringes of the plume. This is apparent where high values of H₂SO₄ are seen at both very high levels of SO2 as well as very low.

4.3. Ozone Chemistry

As revealed for flight 9, we see clear evidence of O3 loss in parts of the Erebus plume but only when SO2 abundance exceeded ~20 ppbv (Figure 9). (Recall, during flight 8, SO2 never reached levels in excess of this amount.) There is surprisingly little by way of comparable observations reported in the literature. The identification of near complete O3 destruction in the plume from the 2000 eruption of Hekla [Hunton et al., 2005; Millard et al., 2006; Rose et al., 2006], while striking, is not comparable to the Erebus observations. The Hekla plume was the result of an explosive eruption, was situated in the stratosphere, and was largely isolated from sunlight in the boreal polar winter. Thus, the Hekla case offers little insight into the chemistry relevant to Erebus volcano.

There are a handful of reports of O3 loss in tropospheric volcanic plumes. Reporting on the results from airborne measurements in six different volcanic plumes (five of them in Alaska), Stith et al. [1978] briefly noted “ozone concentrations were depressed below ambient levels in plumes with relatively high gaseous sulfur,” but no further details are provided (even the specific volcanoes are not identified). Fruchter et al. [1980] reported an airborne study of the fringes of an ash-rich plume emitted from Mount St. Helens the day after its major explosive eruption of 18 May, 1980. At 200 km from the volcano, they detected H₂S and SO2 concentrations <100 and <39 ppbv, respectively, and an O3 abundance that was down by at least a third compared with background values. Hobbs et al. [1982] also measured the Mount St. Helens plume, using an instrumented aircraft flying at ~3 km above sea level, and, like Fruchter et al. [1980], observed low O3 levels. In one case, a “puff” of an ash-rich plume generated by a hydrovolcanic eruption (sampled on 28 March 1980) contained O3 levels that were just 10% of ambient background abundances. O₃ depletions were recognized on three subsequent missions (between June and September 1980) while the volcano was passively degassing from its lava.

Figure 8. Molar SO₂/HNO₃ ratio plotted versus estimated plume age, for measurements in which SO₂ abundance exceeds 0.05 ppbv.
dome. In one of these flights, on 18 June 1980, bromide was identified in the volcanogenic aerosol.

[34] It is significant that all of the above measurements were made prior to the identification of reactive halogens (especially BrO) in volcanic plumes [Bobrowski et al., 2003]. In light of our more recently acquired understanding of the origins and role of reactive halogen chemistry in tropospheric volcanic plumes [Roberts et al., 2009; von Glasow et al., 2009], along with the known presence of bromine species in the aerosol and gas phases in the Erebus plume [Zreda-Gostynska et al., 1997; Ilyinskaya et al., 2010], we consider it likely that reactive bromine was among the key chemical players in the O3 depletion we observed in the Erebus plume. It is also likely that a significant role was played by preexisting, as well as newly formed aerosol in the Erebus plume. Although no aerosol measurements were made during this study, we expect that the very elevated levels of SO2 were accompanied by correspondingly elevated aerosol abundance. This would have provided a heterogeneous pathway for the production of reactive halogens via the formation and release of gas phase Br2, which then would photolyze to form BrO, leading to a reaction with O3 to form 2 BrO.

The most likely reaction of BrO (e.g., in the absence of plume NOx) would be with HO2 radicals thereby generating HOBr, thus leading to an autocatalytic cycle that would rapidly destroy O3 [Oppenheimer et al., 2006; Bobrowski et al., 2007; Roberts et al., 2009]. This then points to the removal of NO2 from the plume as a critical step in that it is this species that most frequently leads to chain termination of BrO or ClO by forming the corresponding nitrate species [McElroy et al., 1992; Schoeberl et al., 1993]. Even if the latter were formed, however, in the case of the Erebus plume, the species BrONO2 and/or ClONO2 could also initiate O3 destruction via direct photolysis (e.g., for mid-December the two channels for ClONO2, Jtot is 4.3 × 10^-5 s^-1 at high noon and that for BrONO2 is 1 × 10^-3 s^-1).

[35] But why did ozone loss not show up in all the Erebus plume transects? The answer most likely has to do with the effect of aerosols. As previously stated, excessively high levels of aerosols make possible the generation of reactive halogen species. It seems reasonable that some of the highest aerosol loadings for the plume would coincide with some of the highest SO2 concentrations, thereby leading to the highest reactive halogen production and O3 loss.

5. Conclusions

[36] We detected the magmatic gases SO2, CO and OCS in the distal Erebus plume, as expected from ground-based measurements by FTIR spectroscopy. The OCS/CO molar ratio (~0.0033) in the distal plume (up to a plume age estimated at ~5 h) corresponds very closely with the intracrater composition, consistent with the relatively long lifetimes of these species (>>months). By contrast, the SO2/CO ratio in the distal core plume (aged >1 h) is around one fifth that of the intracrater plume. However, the aircraft measurements suggest that if a major heterogeneous loss in SO2 did occur, it took place near the crater itself, and most likely involved conversion via “cloud processing” in liquid phase aerosol in the proximal plume.

[37] We have convincingly shown that nitrogen is a key component of the Erebus plume. We identified both HNO3 and HO2NO2 in the plume, consistent with the previous identification of large quantities of NO3 directly above the Erebus crater [Oppenheimer et al., 2005] but the absence of
NO₃ in the downwind plume. HNO₃ and HO₂NO₂ represent oxidation products of NO₂ formed initially through thermal fixation of atmospheric molecular nitrogen close to the hot lava lake surface. However, the combined HNO₃ and HO₂NO₂ abundance measured was found to be less than a tenth of that expected based on the CO/NO₂ ratio measured in 2003. This suggests that additional N-bearing species might have been present in the distal plume either in the form of the halogen species ClONO₂, and BrONO₂, or as aerosol nitrates. We also identified a “pool” of aged plume abundant in HNO₃ and with elevated H₂SO₄ levels but depleted in SO₂, which extended around the summit, separate from the visible crater plume. We believe this “pool” accumulated either through the steady degassing of the volcano and separation and stagnation of parts of the plume or as a result of shifts in wind speed and direction hours before the launching of the Erebus flights and outside of the small temporal sampling window of the rawinsonde wind observations.

[38] We identified significant O₃ loss in some of the plume transects. In one case, O₃ abundance was ~35% of ambient levels. This is likely the result of reactive halogen (especially Br) chemistry, which could have been initiated by heterogeneous processes given that the key ingredients are known to have been present (bromine, sunlight and acid aerosol [e.g., Roberts et al., 2009]). Firm objectives for future work on Erebus are to determine if and when BrO is present in the distal plume either in the form of the halogen species ClONO₂, and BrONO₂, or as aerosol nitrates. We also identified a “pool” of aged plume abundant in HNO₃ and HO₂NO₂ representing a global model analysis, J. Geophys. Res., 10(1)(D13), 18,691–18,699, doi:10.1029/96JD01222.


