Atmospheric chemistry of an Antarctic volcanic plume

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Received 12 February 2009; revised 15 September 2009; accepted 22 September 2009; published 27 February 2010.

[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 volcanogenic H2SO4, HNO3 and, recognized for the first time in a volcanic plume, HO2NO2. We did not find NOx 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.

Citation: Oppenheimer, C., et al. (2010), Atmospheric chemistry of an Antarctic volcanic plume, J. Geophys. Res., 115, D04303, doi:10.1029/2009JD011910.

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 NOx chemistry in volcanic plumes following previous observations of NO2 emissions above the Erebus crater [Oppenheimer et al., 2005]. This NO2 was thought to have been formed from oxidation of atmospheric N2 at the hot surface of the volcano’s active lava lake. It was also suggested that Erebus represents the largest point source of NOx 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].

[4] 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 ~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 volcano contributes 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 glacioclimatology of ice cores drilled at Law Dome, Wilkes Land (~2000 km from Erebus). More recently, Shirsat and Graf [2009] demonstrated the preeminence of Erebus’ contribution to the Antarctic atmospheric SO2 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 pptv to the tropospheric SO2 burden in the Ross Sea region and is a significant source of sulfate deposition on the Royal Society mountain range.

[6] The new measurements we report 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 ~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, HNO3, HO2NO2, SO2, COS, CO, O3 and H2O. More limited observations were also available during flight 9 for H2SO4 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, 2σ 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 (H2SO4 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 O3 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 SO2, HNO3, HO2NO2 and H2SO4 involved two versions of the select ion chemical ionization mass spectrometry technique. For SO2, HNO3 and HO2NO2, sampling was achieved through a heated inlet that extended ~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 SO2, HNO3 and HO2NO2 was SF6, which was generated in an ion source chamber by associative electron capture. A typical measurement sequence consisted of integrating the signal at 148 amu (SF6) for 25 ms, 82 amu (NO3·HF) for 2 s, 98 amu (NO2·HF) for 2 s, and 102 amu (F2SO2) 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
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.

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
stickiness of these compounds and the need to use longer sampling lines, most of it is likely related to a background shift in the instrument upon entering the densest volcanic gas/aerosol areas of the plume. Though, in principle, this affect could have been removed by rezeroing the instrument while in the plume, this was not practical under the sampling conditions presented by the Erebus plume. Most importantly, this perturbation was quite small when compared to the real signal while in the plume, and it had no significant influence on the interpretation of the data.

[12] In the measurement of H$_2$SO$_4$ and OH the reagent ion employed was NO$_3^-$, which was generated in an ion source where the air stream had HNO$_3$ injected into it. The detection of OH involved first allowing ambient OH in the sampled gas stream to react with $^{34}$SO$_2$ to form $^{34}$SO$_3$. This product was then allowed to react with H$_2$O in the gas stream, forming H$_2$$^{34}$SO$_4$. After reaction with the reagent ion NO$_3^-$, the final detected ion was H$_2$$^{34}$SO$_4$. Thus, both ambient H$_2$SO$_4$ as well as OH were ultimately measured mass spectrometrically via the detection of the HSO$_4^-$ ion [see Tanner et al., 1997; Mauldin et al., 1998, 2004]. Unfortunately, due to instrument difficulties, OH abundance could only be evaluated semiquantitatively, based on measurements from a later ANTCI flight.

2.2. Airborne Plume Intercept Details

[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 (MDAC M-4402-1) fitted with ZnSe beam splitter and a liquid nitrogen-cooled

| Flight Number | Flight Intercept Time (UTC) | Local Time | Distance to Crater (km) | Maximum Plume Age (h) | Solar Elevation | Flight Altitude Above Sea Level (m) | Air Temperature (K) | Dew Point (K) | Wind Speed (m s$^{-1}$) |
|---------------|----------------------------|------------|------------------------|-----------------------|-----------------|-----------------------------------|---------------------|--------------|------------------|
| 8             | 0450–0600, 9 December 2005 | 1750–1900  | 4–20                   | ~2                    | 21°–25°         | ~3815                             | 248–251             | 246–249      | 3.1              |
| 9             | 2230–2310, 10 December 2005 | 1130–1210  | 1–56                   | ~9                    | 33°–34°         | ~3815                             | 246–251             | not available | 1.8              |

Table 2. Timing, Location, and Meteorology for Plume Intercepts by Aircraft
InSb detector. Seven volcanic species were determined: 
H$_2$O, CO$_2$, CO, SO$_2$, HCl, HF and OCS. The instrument's
10 inch Newtonian telescope (field of view of 3 mrad) was
trained on the active lava lake (the IR source), such that the
plume was sampled within seconds or a few tens of seconds
after release into the atmosphere along a path of $\sim$300 m
from the crater rim to the lava surface. All spectra were
recorded with a nominal optical path difference (retardation)
of 2.0 cm, corresponding to $\sim$0.5 cm$^{-1}$ spectral resolution.
Consecutive batches of 8 interferograms were averaged
(i.e., 8 sweeps of the mirror, which took $\sim$8 s) to enhance the
signal.

[16] The resulting interferograms were inverse Fourier
transformed with a Mertz phase correction and triangular
apodization, and the resulting single-beam spectra were ana-
yzed 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 volca-
nic 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 spec-
trum 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 abun-
dance 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].

[17] 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

[18] Of the species measured during the Twin Otter
flights, several showed enhancements in the volcanic
plume. We report first the observations of the magmatic
gases, then results for NO$_x$ and O$_3$. 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.

3.1. SO$_2$, CO, OCS, and H$_2$SO$_4$

[19] The SO$_2$ 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 SO$_2$ mixing ratios, up to
30 ppbv, were measured on flight 9. However, as much as
0.238 ppbv of SO$_2$ was detected at $\sim$56 km from the
crater, an abundance that was $\sim$25–50 times background
values ($\sim$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 $\sim$600 km from the volcanic source
[Slusher et al., 2010]. During this mission, the aircraft
flew from McMurdo to the automatic weather station at
Mid-Point (75°S, 145°E). The plume was recognized by
increases in both HNO$_3$ and SO$_2$. The former species
reached levels that were $\sim$0.06 ppbv above background;
whereas SO$_2$ was 0.005–0.01 ppbv above stable back-
ground levels. Confirming the SO$_2$ results, there were
corresponding elevations in H$_2$SO$_4$ levels. Further analyses
of these data based on forward trajectory modeling con-
ﬁrmed Erebus as the most likely source and that the plume
had been airborne for around 3–4 days by the time it was sampled.

[20] In clear association with SO$_2$, we find elevated gas
phase H$_2$SO$_4$ in the plume encounters for flight 9 (Figure 4).
The molar ratio of SO$_2$/H$_2$SO$_4$ is $\sim$4.1 $\times$ 10$^{-4}$. However,
there is also variability in the proportions of the two species,
notably several samples with much higher H$_2$SO$_4$ relative to
SO$_2$. 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.

[21] 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 $\sim$300 is strikingly similar for both the
airborne measurements and the summit FTIR observations.
On the other hand, the SO$_2$/CO proportions for gas within
the crater and distal plume differ markedly: the SO$_2$/CO
molar ratio was $\sim$0.42 at the source compared with $\sim$0.082
downwind. Accepting comparability of the two techniques,
this suggests significant depletion of SO$_2$ in the plume
during advection. Also of note in the aircraft data, the
observations for CO versus OCS are more strongly corre-
lated than those for CO versus SO$_2$ ($r^2 = 0.99$ versus $r^2 =
0.78$, respectively).

[22] The molar abundance of CO in the magmatic gas is
$\sim$2% [Oppenheimer and Kyle, 2008] so the CO maxima
observed in the downwind plume ($\sim$200–350 ppbv)
correspond to a dilution of the plume by ambient air on the
order of 1:10$^4$ to 1:10$^5$. 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 1:10$^3$ to 1:10$^4$), 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 $\sim$4 km, thus there was the potential for sampling
in and out of the plume during an individual measurement.
Figure 3
3.2. Volcanogenic NO$_y$

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).

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

Ozone levels recorded during flight 9 reveal significant perturbations associated with the plume. These were particularly noticeable when the cmeasured 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).

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**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) Scatter plot showing the correlation between CO and OCS.

- Airborne downwind observations
- Crater FTIR observations

OCS/CO = 0.0033
R² = 0.99

OCS/CO = 0.0035
R² = 0.80

(b) Scatter plot showing the correlation between CO and SO₂.

- 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:

\[3CO + SO₂ ↔ 2CO₂ + OCS.\]  

(1)

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 dissolved 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 primordial 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,

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

(2)

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

(3)

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

(4)

The rate controlling step in this scheme is [2]. Thus, using an upper limit value for measured OH of \(4 \times 10^5 \text{ cm}^{-3}\) (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 \(k_2\) 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 \(\sim0.8 \times 10^5 \text{ molecule cm}^{-3} \text{ s}^{-1}\). 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 \(1 \times 10^{-3} \text{ s}^{-1}\) 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 \(\sim10^{-2}\) (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 \(\sim0.4 \text{ pptv}\), a value comparable to that observed in the Erebus plume of 0.1–0.6 pptv. This suggests that the most likely source of plume H₂SO₄ was that resulting from gas kinetic processes.

4.2. NO₂ 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 HO\(_2\)NO\(_2\) in a volcanic plume. The HO\(_2\) required in the reaction with 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 O\(_3\), H\(_2\)O, or H\(_2\)O\(_2\) [e.g., Finlayson-Pitts and Pitts, 1997]. For example, high levels of H\(_2\)O within the crater in the presence of O\(_3\) and sunlight may have resulted in a major source of HO\(_x\) radicals. However, any HO\(_2\) formed in this way would be consumed rather quickly by its reaction either with NO, 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 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 HO\(_2\) or halogen oxides would have quickly led to NO\(_2\) formation. The subsequent reaction of this species with either OH or HO\(_2\) radicals would then provide one possible explanation for both the observed HNO\(_3\) and HO\(_2\)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 HNO\(_3\) via a combination of gas phase and heterogeneous reactions [Oppenheimer et al., 2006; Roberts et al., 2009]:

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

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

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

In 2004, the use of UV differential optical absorption spectroscopy to observe the summit plume rising above the crater indicated a SO\(_2\)/NO\(_2\) molar ratio of ~10 [Oppenheimer et al., 2005]. This is substantially lower than the molar ratio of SO\(_2\)/HNO\(_3\) that we observe in the core of the distal plume (~56 km) or the observed SO\(_2\)/[HNO\(_3\) + HO\(_2\)NO\(_2\)] ratio of ~40; and suggests that much of the NO\(_2\) observed above the crater was converted into undetected 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 NO\(_x\) and SO\(_2\) in the visible summit plume. This is reflected in the stable SO\(_2\)/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 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](image-url).

**Figure 7.** Correspondence between observed SO\(_2\) (red line) and O\(_3\) (blue line with triangles) during part of flight 9. Note depletion of O\(_3\) in two intercepts of the plume involving the highest loadings of 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

[32] 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.

[33] 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.
dome. In one of these flights, on 18 June 1980, bromide was identified in the volcanogenic aerosol.

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 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, $J_{tot}$ is $4.3 \times 10^{-5}$ s$^{-1}$ at high noon and that for BrONO2 is $1 \times 10^{-3}$ s$^{-1}$).

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

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.

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 NOx directly above the Erebus crater [Oppenheimer et al., 2005] but the absence of
NO$_2$, in the downwind plume. HNO$_3$ and H$_2$O$_2$ represent oxidation products of NO$_2$ formed initially through thermal fixation of atmospheric molecular nitrogen close to the hot lava lake surface. However, the combined HNO$_3$ and H$_2$O$_2$ abundance measured was found to be less than a tenth of that expected based on the CO/NO$_2$ 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 ClONO$_2$, and BrONO$_2$, or as aerosol nitrates. We also identified a “pool” of aged plume abundant is known to have been present (bromine, sunlight and acid (especially Br) chemistry, which could have been initiated 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 O$_3$ loss in some of the plume transects. In one case, O$_3$ 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 plume using UV spectroscopy, and to model the chemistry of an Erebus-like plume containing reactive nitrogen and halogen species as well as an assortment of aerosol species. We emphasize that plumes can be complex, particularly with respect to their mixing dynamics.

[39] We also encourage future airborne campaigns including both crewed aircraft and unmanned aerial vehicles, as these are likely to shed further light on the critical chemical and physical processes occurring in the plume, leading to improved understanding of the nature and extent of the impact of Erebus emissions on the atmospheric and cryospheric environments. In particular, future work should be undertaken to characterize the aerosol phase in the downwind plume, and to trace the plume over greater distances (hundreds of km). That this should prove fruitful is strongly suggested by a subset of the measurements made during the ANTCT 2005 field study, which revealed remnants of the Erebus plume ~600 km from the volcano [Slusher et al., 2010]. Thus, we propose that far more ambitious airborne plume studies of Erebus are warranted in the future.

[40] Acknowledgments. This work was generously supported by grants from the Office of Polar Programs, National Science Foundation, to P.R.K. and D.D. and by a “study abroad fellowship” awarded to C.O. by the Leverhulme Trust. C.O. also acknowledges support from the EU Framework 6 project “NOVAC” and the NERC National Centre for Earth Observation. D.D. is grateful to William Neff for his retrieval of MET data used to help characterize plume drift velocity, to Darlene Slusher for her efforts in drafting early versions of several figures and providing modifications to these, and to several students and technicians who contributed to the data collection process, namely, Will Wallace and Ed Kocsich. We thank the three referees for thorough reviews, Yinon Rudich for editorial evaluation and advice, Tjarda Roberts, Rob Martin, Rod Jones, and Tony Cox for discussions, and Mike Burton for providing the FTIR spectral retrieval code.

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