Major ions and radionuclides in aerosol particles from the South Pole during ISCAT-2000

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Abstract

As part of ISCAT 2000, bulk, high-volume, aerosol samples were collected at the South Pole (SP) nominally over 24-h intervals, and they were analyzed for major ions, several trace elements, and three naturally occurring radionuclides. The mean concentrations of Na (< 17 ng m\textsuperscript{-3}), sulfate (98 ng m\textsuperscript{-3}), and methanesulfonate (MSA, 4.4 ng m\textsuperscript{-3}) all were lower in ISCAT 2000 compared with ISCAT 1998, suggesting weaker marine influences during the latter study. In contrast, the \textsuperscript{210}Pb activity (0.20 mBq m\textsuperscript{-3}) was more than two-times higher in ISCAT 2000 than in 1998, and nitrate concentrations (150 ng m\textsuperscript{-3}) were approximately four-times higher, suggesting stronger continental influences in the second study. These differences between experiments are consistent with an analysis of meteorological transport and exchange. \textsuperscript{7}Be activities were generally comparable for ISCAT-1998 and 2000, suggesting that there were, on average, similar upper tropospheric/lower stratospheric influences on surface air during the two experiments: long-term records of \textsuperscript{7}Be, however, show pronounced annual and lower-frequency cycles. The concentration ratios of MSA to nss-sulfate (R) were similar in the two campaigns, and a regression analysis suggests that a non-biogenic source or sources account for up to \textasciitilde 30\% of the nonsea-salt sulfate. Various possible explanations for the low values of R (= 0.08) relative to other Antarctic sites are discussed, including differences in R due to where the oxidation of DMS takes place (that is, in the marine boundary layer or in the buffer layer/free troposphere), chemical fractionation during transport, and the transport of sulfur compounds from lower latitudes and possibly from Mt. Erebus.

Keywords: Sulfur cycle; Major ions; Trace elements; Radionuclides; Aerosols; Antarctica; Geochemistry

1. Introduction

The ISCAT (Investigation of Sulfur Chemistry in the Antarctic Troposphere) Program was initially developed to investigate atmospheric sulfur chemistry over the South Pole (SP). This focus was tied to the use of sulfur compounds in Antarctica ice cores as proxy species for evaluating major geophysical events as well as shifts in climate (Dibb and Whitlow, 1996; Legrand and Delmas, 1987; Petit et al., 1990; De Angelis et al., 1984; Wagenbach, 1996; Indermühle et al., 1999, see also Davis et al., 2004). Of particular significance in studies...
of the chemical coupling between the atmosphere and ice cores is nonsea-salt sulfate (nssSO₄²⁻, that is, the sulfate in excess of that attributable to sea-salt aerosol particles). In the austral summer, nssSO₄²⁻ is by far the dominant aerosol constituent, accounting for 70% or more of the aerosol mass at the SP (total sulfate is 80–90% of the aerosol mass according to Maenhaut et al. (1979) and nssSO₄²⁻ is 90–95% of the total measured SO₄²⁻ (Harder et al., 2000; Arimoto et al., 2001).

In the atmosphere over remote marine regions, the main sources for aerosol nssSO₄²⁻ are reactions involving either dimethylsulfide (DMS) or primary SO₂. The former is produced by phytoplankton while the latter is typically the result of either volcanic emissions or human activities (Andreae, 1986; Berresheim and Jaeschke, 1983; Buat-Ménard, 1990). Numerous studies have shown that the amounts of nssSO₄²⁻ aerosol as well as the relative source contributions vary significantly with respect to time and location. Inferences about source contributions often have been drawn from statistical relationships among the sulfur species. For example, besides nssSO₄²⁻, another sulfur compound of great interest has been methanesulfonate (MSA), another of the oxidation product resulting from the DMS/OH reaction pathway(s). Data for MSA have been used to provide a first-order estimate of the relative amounts of sulfate from biogenic versus anthropogenic sources, but the application of this approach is complicated due to temperature effects (Bates et al., 1992) and uncertainties in the oxidation pathways and kinetics (Davis et al., 1998). In an effort to overcome some of these difficulties, Savoie et al. (2002) recently used antimony and nitrate together with MSA to simultaneously evaluate anthropogenic as well as marine biogenic sources for aerosol sulfate.

Based on unexpected results from the first ISCAT mission (ISCAT-1998, Davis et al., 2001; Chen et al., 2001; Crawford et al., 2001), the second ISCAT campaign (ISCAT-2000) shifted much of its emphasis to photochemistry (see Davis et al., 2004). In spite of this, several lines of aerosol research were continued in ISCAT 2000, including studies designed to better relate the aerosol and plateau ice core data. Specific objectives for the studies presented here were to investigate the sources for nssSO₄²⁻ and to assess the atmospheric chemical, physical, and meteorological factors influencing the concentrations and speciation of sulfur-containing aerosols. Other aerosol data for the study included: Na, filterable nitrate, and three naturally occurring radionuclides (⁷Be, ²¹⁰Pb, and ²¹⁰Po; half lives of 53 days, 22 year, 138 days, respectively). Sodium was used as an indicator of sea-salt; nitrate is dealt with briefly here, but discussed in detail elsewhere (Huey et al., 2004); ⁷Be was used as a tracer of upper tropospheric/lower stratospheric air (Dutkiewicz and Husain, 1985); ²¹⁰Pb a tracer of continental air (Turekian et al., 1989; Balkanski et al., 1993); and ²¹⁰Po a volcanic tracer (Polian and Lambert, 1979). The concentrations of these substances have been interpreted with particular attention to their transport pathways to the SP.

2. Experimental

2.1. Sampling

The field studies for ISCAT-2000 took place from November 2000 to January 2001. Two sets of aerosol samples were collected using procedures essentially the same as those in the ISCAT 1998 (Arimoto et al., 2001). From 18 November 2000 to 4 January 2001, 43 bulk ~24 h aerosol samples for elemental and ion chromatographic (IC) analyses were collected from the roof of the Clean Air Facility (89.997°S, 102.0°W, elevation: 2841 m). Several additional samples were collected over longer intervals (typically 2 days, but in one case 8 days) from 4 January to 26 January 2001.

All sample handling was done by persons wearing particle free gloves and all reasonable precautions were taken to minimize contamination, these included handling of the samples with plastic forceps and individually bagging the samples after collection. As in the prior experiment, the winds were predominantly from the station’s clean air sector (0°–120°), and sampling was interrupted when aircraft or ground operations, the most likely sources of contamination, were in progress. The only difference in sampling for two ISCAT experiments of any potential significance was that one set of the ISCAT-2000 samples was collected on 20 × 25 cm Whatman 41 filters (Whatman Ltd., Maidstone, UK) whereas all samples from the earlier study were collected using Dynaweb DW7301L® filters (Web Dynamics, East Stroudsburg, PA).

The reason for switching filters was that the Whatman 41®’s are more easily prepared for studies of trace elements than the Dynaweb®. The Whatman 41® blanks for Na and Cl are somewhat higher those for the Dynaweb®, but for most other ions of concern the differences between blanks are small (Table 1). The use of Whatman 41® filters for aerosol sampling has been questioned in the past, but their use is widespread. More important, data in Savoie et al. (1989) indicate that Whatman 41® collection efficiencies are ≥ 90–99% for sulfate, MSA, nitrate, sea salt, and mineral dust.

As in the ISCAT first field experiment, a second high-volume aerosol sampler was used to collect samples for studies of ⁷Be, ²¹⁰Pb and ²¹⁰Po in bulk aerosols. The radionuclide sampler drew air from an inlet used for long-term studies conducted by the Environmental
Measurements Laboratory of the US Department of Energy (http://www.eml.doe.gov), and those samples were collected on the same type of Dynaweb® filters in both ISCAT field missions. A total of 33 samples was collected for the radionuclide studies.

2.2. Major ion and elemental analyses

For the major ion studies, each Whatman 41® sample filter was cut into quarters using plastic scissors in a chemical clean bench. For the IC analysis, one quarter of each filter was extracted in three steps with 18 MΩ de-ionized water (10, 5, and 5 mL). A Dionex 500 ion chromatography system (Dionex Corp, Sunnyvale, CA) was used for all aerosol ion analyses. Nitrate, sulfate and Cl⁻ were separated using an AS-14 column and MSA with an AS-11 HC microbore column. Non-sea salt sulfate was calculated based on a seawater SO₄²⁻/Cl⁻/Na⁺ mass ratio of 0.2515 (Millero, 1996).

Sodium was determined in separate aliquots of the Whatman 41® filters. For these analyses, quarter-filter aliquots were placed in Teflon® vessels, and to each vessel was added 5 mL ultrapure H₂O₂, 7 mL concentrated HNO₃, 3 mL concentrated HCl, 5 mL concentrated HF, and 1 mL H₂O₂. The vessels were sealed and heated to 180°C in a microwave digestion unit (Model MDS 2100, CEM Corporation, Matthews, NC) for 30 min. Instrumental analyses were performed using a Perkin-Elmer Elan 6000 inductively coupled plasma mass spectrometer, following EPA Method 200.8. In those cases where Na could not be quantified, the detection limit for Na was used to calculate nssSO₄²⁻. While this would lead to an underestimate of nssSO₄²⁻, the effect would be small because even when using the Na detection limit, sea salt only accounted for ~5% of the total SO₄²⁻, consistent with prior studies (Harder et al., 2000).

2.3. Radionuclides

⁷Be and ²¹⁰Pb were determined by a non-destructive method as described in Arimoto et al. (2001). For this procedure, an entire Dynaweb® filter was folded in half, and the activities of ⁷Be and ²¹⁰Pb were quantified using gamma-ray spectroscopy through the emissions of 477.6 and 46.5 keV photons, respectively. A high-purity germanium spectrometer was used for the measurement of ⁷Be, and a dual scintillation-detector spectrometer was used for the measurement of ²¹⁰Pb. The nominal detection limit for ⁷Be is 0.7 mBq m⁻³, and for ²¹⁰Pb a representative detection limit is 0.070 mBq m⁻³.

Following the gamma-spectroscopy, the ²¹⁰Po activities were determined for the Dynaweb® filters. For these analyses, quarter filter aliquots were placed in individual beakers and an isotopic tracer, ²⁰⁹Po, was added to determine the ²¹⁰Po recovery. Concentrated HNO₃ (100 mL) was added to the filters to solubilize refractory materials. These samples were heated at ~95°C to near dryness. This step was repeated four times, using 100 mL of ultrapure water as a diluent to help drive off the HNO₃. After digestion, 30 mL of ultrapure water, 1 mL of concentrated HCl and 1 mL of a saturated ascorbic acid solution was added to each sample. The samples were then heated to ~50°C, and the ²¹⁰Po spontaneously plated onto Ni planchettes overnight. The planchettes were counted for ~24 h using an Oxford Oasis alpha-spectroscopy system (Oxford Instruments Inc., Oak Ridge, TN). Activities

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Volume (m³)</th>
<th>Concentration (ng m⁻³)</th>
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<td>Number of samples</td>
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<td>29</td>
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<td>45</td>
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<tr>
<td>Sample standard error</td>
<td>13.8</td>
<td>5.9</td>
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Table 1

Comparison of concentrations of aerosol constituents for ISCAT-2000 versus ISCAT-1998

<table>
<thead>
<tr>
<th>Parameter</th>
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<th>Concentration (ng m⁻³)</th>
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</tr>
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<td>Sample standard error</td>
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<td>5.9</td>
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</table>

aBlank means and standard errors calculated from laboratory reagent blanks assuming volumes of 1700 and 1600 m³ for ISCAT-1998 (7 blanks) and ISCAT-2000 (6 blanks), respectively.

bNA stands for not applicable.
were mathematically back corrected to the time of collection, allowing for both grow-in and decay of $^{210}$Po.

3. Results and discussion

3.1. ISCAT-1998 versus ISCAT-2000

The chemical composition of the SP aerosol differed markedly between the two ISCAT campaigns. Relationships between aerosol composition, meteorology, and transport conditions during ISCAT-2000 were investigated in some detail, and because those analyses have broad implications for the other ISCAT studies, the results are summarized in the project’s overview (Davis et al., 2004). In this context, it is noteworthy that Lettau (1969); Parungo et al., (1979); Shaw (1988); Hogan and Gow (1993) have all described meteorological events that transport trace species from the surrounding seas to the SP. Moreover, the number concentrations of aerosol particles at SP increase roughly twenty-fold during the austral spring when air from lower latitudes is advected to the Polar Plateau (Hogan, 1975; Hogan and Barnard, 1978). The greatest monthly mean number concentrations at SP occur in November (Samson et al., 1990), which is the month when sampling for both ISCAT field studies began.

In attempting to relate the differences in aerosol composition for the two experiments to meteorology and transport, we first consider atmospheric sea salt, as represented by Na. As noted above, sulfate is the dominant aerosol species in summer, but sea-salt elements, such as Na, Cl, Mg, etc., make up the second most abundant aerosol component by mass in that season. Based on a 12-year record of chemical composition and aerosol mass at the SP, Tuncel et al. (1989) apportioned the composition of the aerosol particles in summer as follows: sulfate = 77.5%; marine elements = 16.6%; crustal material = 4.0%; with several additional minor components. In winter, the relative proportions of the marine elements and sulfate are very nearly reversed: sulfate then accounted for only 18.0% and sea salt elements 78.6% of the aerosol mass, respectively, with the other components showing much smaller relative differences between seasons.

The Na concentrations during ISCAT-2000 were substantially less than in ISCAT-1998 (Table 1), indicating a much weaker maritime influence on the atmosphere during the latter experiment. During December 2000 there were distinct periods during which marine air stagnated over the Antarctic continental ice prior to arriving at SP. The fact that the Na concentrations in most of the samples from ISCAT-2000 were below a nominal minimum limit of quantitation makes it impossible to precisely calculate the concentration difference between the two experiments. Nevertheless, one can determine a lower bound for the difference by substituting the Na detection limit for those samples with concentrations below detection. Comparisons of the arithmetic means for the two experiments show that the average Na concentration, determined by ICP-MS, decreased by at least 60% from the first experiment to the second. Although there is evidence that chloride may be volatilized from sea salt particles at SP (Maenhaut et al., 1979; Arimoto et al., 2001), aerosol Cl$^-$ is largely from sea salt, and it was lower by $\geq 70\%$ in ISCAT-2000. These results indicate that during the main sampling period for ISCAT-2000, the air was considerably less marine in character than in ISCAT 1998.

To investigate in more detail the cause(s) for the difference in sea salt concentrations between the two campaigns, a flow analysis was made in which 5160 geopotential meters (gpm) was chosen to represent the 500 hPa height. This approach was used to evaluate the transport of marine air associated with low-pressure systems about Antarctica, considering the level of the jet surrounding the continent. Comparisons of the meteorological fields during the two experiments (Fig. 1) suggest that the Ross Sea/ice shelf low-pressure system...
was relatively strong in 1998 (500 hPa heights frequently below 5160 gpm), with correspondingly frequent and vigorous marine flow to the SP. In comparison, the effects of the Ross Sea low-pressure system were weaker during 2000/2001, that is, the 500 hPa heights were more often above 5160 gpm compared with the earlier study. Thus fewer days of marine flow to the Pole occurred during ISCAT-2000; and this is consistent with the low aerosol Na and Cl concentrations observed during the latter experiment.

The concentrations of MSA and nssSO$_4^{2-}$, the two main particulate sulfur species of interest, also differed between the two ISCAT campaigns, with the respective arithmetic mean concentrations about 65% and 60% lower in ISCAT-2000 (Table 1). As is true for sea salt aerosol, the oceans are the dominant source for MSA, and therefore lower concentrations of this marine biogenic compound during ISCAT-2000 are consistent with the lower sea-salt aerosol concentrations. Prior studies have shown that the concentrations of MSA and nssSO$_4^{2-}$ in aerosols from the SP are correlated and that the ratio of these two species in the SP aerosols is similar to that found in Antarctic ice (Arimoto et al., 2001; and Legrand et al., 1991, respectively). This relationship between MSA and nssSO$_4^{2-}$ thus explains why the lower nssSO$_4^{2-}$ concentrations during ISCAT-2000 are consistent with weaker marine influences during that campaign.

Higher concentrations of NO$_3^-$ and $^{210}$Pb during the second ISCAT experiment compared with the first, suggest a stronger influence of continental material during ISCAT-2000. In contrast to the marine-derived substances discussed above, the mean concentration of aerosol NO$_3^-$ in ISCAT-2000 was more than 4-fold higher compared with the earlier data set (Table 1), and $^{210}$Pb was slightly more than twice as high in the second experiment (the arithmetic mean was 0.089 mBq m$^{-3}$ for ISCAT-1998 versus 0.20 mBq m$^{-3}$ for ISCAT-2000, see Fig. 2). It bears noting, however, that only about a third of the samples were above the minimum detectable $^{210}$Pb activity in the ISCAT-1998 samples, thus biasing the mean for that study high.

While the bulk of the $^{210}$Pb is indisputably continental in origin, it is more difficult to identify the primary sources for aerosol nitrate owing to the complex chemical cycling of reactive nitrogen on the Antarctic plateau (Davis et al., 2004, Davis et al., 2001 and Jones et al., 1999). Possible primary sources include: lightning (Wolff, 1995); NO$_3$ (NO and NO$_2$), inputs from the lower stratosphere (Legrand and Kirchner, 1990); and long-range transport of peroxyacetyl nitrate (PAN) generated from surface sources in the southern hemisphere (Davis et al., 2004). Efforts to obtain more detained information on the density of lightning during the two campaigns have not been successful for latitudes $>40^\circ$S (e.g., Southern Ocean), but to the north of this latitude, the available data reveal no major differences for the months of November and December. Results of a chemical ionization study of HNO$_3$ and SO$_2$ conducted for ISCAT-2000 are presented in Huey et al. (2004). These authors found relatively high mixing ratios of HNO$_3$ and low NO when air was mixed downward, but the source for the HNO$_3$ could not be definitively ascertained.

The activities of $^7$Be, the tracer for upper tropospheric/lower stratospheric air (Dutkiewicz and Husain, 1985), indicate that stratosphere/troposphere exchange was on average similar during the two studies, and therefore, the observed differences in NO$_3^-$ between the two field studies cannot be tied to this source of variability. The $^7$Be activities were comparable during the two ISCAT experiments (number of observations, $n = 29$, arithmetic mean $\pm$ standard error, SE = $6.7 \pm 0.5$ mBq m$^{-3}$ for ISCAT-1998 versus $n = 32$, mean $= 7.5 \pm 0.4$ mBq m$^{-3}$ for ISCAT-2000, one sample in the second experiment was compromised). Even so, it is to be noted that the 1998 study did have a sudden burst in $^7$Be activity over a few days early in December at the onset of summer; this was not seen in 2000.

While $^7$Be does provide a measure of stratospheric/upper tropospheric exchange, a variety of processes cause low-frequency variability in $^7$Be activities in surface air (Gerasopoulos et al., 2003). A plot of the ISCAT data along with long-term records of $^7$Be produced by the Environmental Measurements Laboratory (using methods described by Larsen, 1993), shows a pronounced annual cycle in $^7$Be, with a minimum in $^7$Be activity around 1990 corresponding to a maximum in sunspot activity. Long-term trends in $^7$Be in surface air have, in fact, been linked to the modulation of galactic cosmic rays by the solar wind. That is, when sunspot
activity is high, the flux of galactic cosmic rays is low, and hence there are fewer spallation reactions producing $^7$Be (Larsen, 1993). Although controversial, connections between cosmic rays and climate recently have been proposed. In this regard Yu (2002) has suggested that cosmic rays could globally alter cloud properties, especially in the lower troposphere, and thus cosmic rays could conceivably indirectly affect atmospheric chemistry as well. Superimposed on the major effect of the cosmic rays and solar wind are longer-term trends induced by the solar magnetic field; intermediate-term cycles caused by Earth system processes, such as the quasi-biennial oscillation (at least in more temperate latitudes); and shorter-term variability due to deposition.

3.2. Relationship between aerosol MSA and nonsea-salt sulfate

The data for Na and several of the other analytes are too sparse for a meaningful analysis of trends, but the concentrations of MSA and nssSO$_4^{2-}$ did show trends consistent with an analysis of meteorological conditions (A Hogan, unpublished results). Briefly, the meteorological analyses showed that the inflow to SP was fairly vigorous on most days in November, with air from beyond the Antarctic Convergence, that is extra-Antarctic air, flooding the continent on 25–28 November 2000. This transition from spring- to summertime flow patterns ended on 5 December. From 5 to 13 December, the air stagnated over the polar plateau, and for the remainder of December, the circulation was relatively weak, with some brief periods of inflow on 16–17 and 21–22 December. There also were some brief periods of inflow from 25 to 31 December, but the latter episodes were short in duration. These flow patterns are at least semi-quantitatively consistent with the high MSA in the second half of November, the low MSA and nssSO$_4^{2-}$ early in December, and the peaks in both compounds centered around 26 December (Fig. 3).

A plot of the combined data sets from the two ISCAT experiments shows a consistent relationship between MSA and nssSO$_4^{2-}$ (Fig. 4). As noted above, both of these sulfur compounds had lower concentrations in ISCAT-2000 compared with the 1998 campaign, but a scatterplot of these two databases shows that the concentrations tend to fall along the same trend line. An orthogonal linear regression for the seventy-seven samples from the two experiments with data for both sulfur species shows a correlation of $r = 0.85$ and the following regression parameters (MSA and nssSO$_4^{2-}$ in units of ng m$^{-3}$):

$$\text{MSA} = 0.08(\pm 0.004) \times \text{nssSO}_4^{2-} - 3.5(\pm 0.7). \quad (1)$$

This analysis shows that despite substantial uncertainties, the recent data from ISCAT-2000 support the earlier contention that a moderate fraction of the aerosol sulfate at the SP in summer can be ascribed to non-biogenic sources (Arimoto et al., 2001). We estimate that this component could be as much as one-third of the average nssSO$_4^{2-}$ observed for the two studies. The percentage of non-biogenic nssSO$_4^{2-}$ can be estimated using the average MSA and nssSO$_4^{2-}$ concentrations as follows:

$$6.9 \ \text{ng MSA m}^{-3} = 0.08 \times 131 \ \text{ng nssSO}_4^{2-} \text{m}^{-3} - 3.5,$$

$$\text{Percentage non-biogenic nssSO}_4^{2-} = (3.5/0.08)/131 \times 100 = 33\%.$$

The MSA/nssSO$_4^{2-}$ mass ratio (henceforth: $R$) of 0.08 calculated for the SP aerosol is lower than the $R$ values

![Fig. 3. Timeseries of nonsea-salt sulfate and MSA concentrations in aerosol particles from the SP.](image1)

![Fig. 4. Relationship between nonsea-salt sulfate and MSA in aerosol particles during ISCAT 1998 and 2000.](image2)
observed at the coastal Antarctic sites of Mawson ($R = 0.36$) and Palmer ($R = 0.58$) where biogenic sources could account for 75–81% of the nssSO$_4^{2-}$ (Savoie et al., 1993; Arimoto et al. (2001) have observed that it is variability in MSA concentrations more than sulfate that leads to differences in $R$ among sites. Even so, possible controls on the concentrations of nssSO$_4^{2-}$ are worth considering because this is by far the dominant sulfur species in terms of mass, with an average mass concentration during ISCAT 2000 nearly 20 times that of MSA (Table 1).

Mazzera et al. (2001), analyzed relationships between the concentrations of MSA and nssSO$_3^{2-}$ in aerosol samples from two stations in coastal Antarctica: the value of $R$ for their Radar Dome site was 0.101, which is quite similar to what we calculated for ISCAT. These investigators noted that the value for $R$ was lower than what one would predict from the empirical temperature relationship of Bates et al. (1992), and they proposed that excess aerosol nssSO$_3^{2-}$ was from Na$_2$SO$_4$ that had precipitated from brine pools and was mobilized by the melting and re-freezing of surface snow on a nearby glacier.

Similarly, Hall and Wolff (1998), Wagenbach et al. (1998), and Mulvaney et al. (1993) have emphasized the potential influence of “fractionated” sea-salt on the chemical composition of ice cores from coastal Antarctica. Moreover, these authors have suggested that the effects of fractionation could be significant inland even though one might expect the strength of the effect to diminish with distance from the coast. Aristarain and Delmas (2002) have found that reactions with gaseous species, especially H$_2$SO$_4$, can alter the composition of atmospheric sea salt, in some cases leading to enrichments of sulfate and chloride. If fractionated sea salt were transported to the SP, the quantities of sulfate from this source could be several times higher than what is calculated from the SO$_4^{2-}$/Na ratio in seawater, and this could account for some of what has been identified in ISCAT as non-biogenic nssSO$_3^{2-}$. If future studies should show that the SO$_3^{2-}$/Na ratio for fractionated sea salt is more appropriate than the seawater ratio for calculating nssSO$_3^{2-}$, the value of $R$ naturally would have to be adjusted accordingly.

In related studies, Kumai (1976) examined particle residues in about one hundred ice crystal residues from the SP, using transmission electron microscopy and X-ray diffraction analysis. He found a large fraction of the crystals contained particles with Na as the major detectable element, and he proposed that Na containing particles were active ice nuclei at temperatures less than $-30^\circ$C. Tropospheric air must be exchanged through an ice-saturated layer colder than $-30^\circ$C on almost all days to reach the surface at the SP (e.g., Lettau, 1969). Therefore it is reasonable to propose that nucleation of the ice-crystal layer above the SP could selectively modify particle chemistry at the polar surface, possibly invalidating the assumption that the composition of seawater is the appropriate reference for calculating nssSO$_4^{2-}$.

The low value for $R$ for the ISCAT data compared with coastal Antarctic sites also could be due to the preferential removal of MSA relative to nssSO$_3^{2-}$ as air parcels move to the interior of the continent, a possibility suggested by Savoie et al. (1993) and supported to a degree by studies of anions in snowfall by Minikin et al. (1994). In contrast, a model presented by Pszenny et al. (1989), suggests the opposite, that is, that the total deposition of SO$_3^{2-}$ on a molar basis is roughly five times that of MSA. This discrepancy highlights the need for better constraints on the Antarctic sulfur budget, but it is unlikely that preferential removal of non-biogenic sulfate has a major effect on $R$. For example, even if all of the non-biogenic sulfate were completely removed, $R$ at SP would still be $\approx 0.11$, which is still a factor of three or more lower than at coastal sites.

As noted previously, results from the SCATE project (Davis et al., 1998) and the earlier ISCAT study (Arimoto et al., 2001) suggest a third possibility for the low values of $R$ observed at the SP. That is, the oxidation pathways for DMS in the Antarctic boundary layer may differ from those is the overlying buffer layer and/or lower free troposphere, leading to different product distributions depending on where the DMS oxidation takes place. For DMS oxidized within the marine boundary layer (MBL), dimethylsulfoxide (DMSO), produced via the OH addition channel of the DMS oxidation pathway is rapidly scavenged by sea-salt aerosol particles, and MSA is then formed heterogeneously (Jefferson et al., 1998 and Davis et al., 1998). These reactions in the MBL lead to a relatively large concentration of MSA compared with nssSO$_3^{2-}$ because DMSO has little opportunity to react with OH.

In contrast, under the low sea-salt aerosol conditions characteristic of the buffer layer and lower free troposphere, DMS would again undergo a rapid addition reaction with OH to form DMSO, but under the much lower sea-salt conditions there, DMSO would undergo further reaction with OH (Hynes and Wine, 1996; Urbanski et al., 1998). Although the details of the subsequent chemistry are still lacking, Davis et al. (unpublished results) have provided theoretical evidence suggesting that the major end-product from this follow-on chemistry would be sulfate. A minor reaction channel at higher altitudes would involve MSA production, and thus the resulting MSA/nssSO$_3^{2-}$ ratio for buffer layer or lower free tropospheric air would be much lower than that for the coastal MBL.

DMS and DMSO also can be oxidized by substances other than OH, and reactions with halogens, for example, could conceivably affect $R$, but some initial
model calculations suggest that oxidation in droplets in the presence of \( \text{O}_3 \) is modest. In addition, as noted elsewhere (Arimoto et al., 2001) strong influences from halogens are not likely from late spring into summer because the halogens are not prevalent beyond the end of October. These alternative oxidation pathways, and their possible influence on \( \text{R} \), do deserve further consideration, however.

Finally, two transport-related hypotheses can be put forward to explain the low value of \( \text{R} \) at the SP. The first hypothesis is that a significant fraction of the sulfur arriving at high altitudes does so as a result of the long-range transport of low- and mid-latitude air parcels. It has been established that in the tropics, MBL values of \( \text{R} \) are low and reproducible, averaging \( \sim 7\% \) (Saltzman et al., 1983). Thus the values for \( \text{R} \) in aerosols from lower latitudes are quite similar to the value reported here for SP aerosols and also for Antarctic ice. In fact, Legrand et al. (1992) invoked long-range transport of material from source regions in low- and mid-latitudes as a possible explanation for the low \( \text{R} \) -values observed in ice from the Antarctic plateau. The second transport-related hypothesis is that the values of \( \text{R} \) could be driven down at the SP due to \( \text{nssSO}_4^2^- \) originating from volcanic sources, most likely Mt. Erebus. This possibility is explored in detail in Section 3.3 that follows.

In summary, it has become apparent that \( \text{R} \) is determined by a variety of factors in addition to the simple temperature dependence of the OH/DMS addition and abstraction channels; Prospero et al. (1991), Wagenbach et al. (1996) and Davis et al. (1998) have all reached this same conclusion. Other important influences on \( \text{R} \) include the effects from atmospheric dynamics, the concentrations of other aerosol species, and the temperature dependences of later steps in the DMS oxidation scheme which involve highly energetic unimolecular decomposition processes. Data for the mass-particle size distributions for MSA and \( \text{nssSO}_4^2^- \) at the SP would be useful for testing the theory of preferential removal of MSA relative to \( \text{nssSO}_4^2^- \). Despite some attempts at such measurements during ISCAT, the concentrations were too low for quantification for the methods used. Future studies should place renewed emphasis on such measurements.

3.3. Possible influences from Mt. Erebus on aerosol sulfate

In addition to the long-range transport of sulfate from lower latitudes, possible impacts from volcanic emissions, specifically Mt. Erebus (77°32’S, 167°09’E, 3794 m), on aerosol sulfate at the SP were evaluated using the ISCAT aerosol data. Early studies by Radke (1982) and Rose et al. (1985) suggested that Mt. Erebus could supply 10–30% of the total sulfur over Antarctica. More recent work by Zreda-Gostynska et al. (1997) shows that \( \text{SO}_4^2^- \), HCl, and Pb and other trace elements from Erebus can be detected at the SP and that Mt. Erebus contributes \( \sim 3\% \) of the sulfur to the entire Antarctic atmosphere. These authors were careful to note that emissions from the volcano were not likely to be evenly distributed over the continent and that locally stronger effects were possible. On the other hand, meteorological analyses (A Hogan, unpublished results) have shown that during ISCAT-2000 tropospheric air had relatively long residence and continuous circulation south of the Antarctic Convergence, and as a result, material from Mt. Erebus would have been relatively well-mixed throughout the Antarctic troposphere.

The assessment that follows is based on the use of \( ^{210}\text{Po} \) as an indicator of Erebus emissions. Polian and Lambert (1979) suggested that \( ^{210}\text{Po} \) would be a useful tracer of Erebus emissions because there are no other major sources for it in Antarctica. The activities of \( ^{210}\text{Po} \) were relatively similar during the two experiments (means \( \pm \text{SE} = 0.014 \pm 0.0009 \) and \( 0.022 \pm 0.0011 \text{mBq m}^{-3} \) for ISCAT1998 and 2000, respectively), suggesting that the amounts of material from volcanic emissions were similar during the two experiments, or possibly slightly higher during ISCAT-2000. With respect to the potential for transport from Mt. Erebus during ISCAT-2000, a meteorological analysis (A. Hogan, unpublished results) shows that the relatively weak low-pressure system over the Ross Sea area during 2000/2001 caused the flow to the SP to come from the Weddell Sea, rather than the Ross Sea, and so presumably there was a weaker influence of Erebus in 2000 compared to 1998. This finding leads to the first caveat in this interpretation, that is, the \( ^{210}\text{Po} \) activities at the SP may not be totally controlled by emissions from Mt. Erebus.

We note in passing an error in the \( ^{210}\text{Po}/^{210}\text{Pb} \) ratio presented in a prior paper (Arimoto et al., 2001, the reported value, which is unitless, was 0.48). The correct ratios for the \( ^{210}\text{Po}/^{210}\text{Pb} \) activities are 0.18 (9 samples) for the first experiment and 0.13 for the second experiment (33 samples). The \( ^{210}\text{Po}/^{210}\text{Pb} \) ratios observed at the SP are several orders of magnitude lower than those observed at Mt. Erebus (J. Crain, NM Tech, unpublished results). One interpretation of these results would be that Mt. Erebus emissions affect the activity concentrations of \( ^{210}\text{Po} \) at the SP more than they affect \( ^{210}\text{Pb} \).

The simplest way of examining the ISCAT data indicates that the volcano’s influence on aerosol sulfate at the SP during ISCAT was probably minor but not necessarily negligible. Unlike the results for \( ^{210}\text{Po} \), which suggest similar or stronger influences from Erebus during ISCAT 2000, the concentration of non-biogenic \( \text{SO}_4^2^- \) was 2-fold lower during 2000 relative to the prior experiment (see Section 3.1 above). Thus a simple comparison of the data for the two experiments implies
that no more than 50% of the non-biogenic sulfate, which itself is not all that well constrained, can be ascribed to emissions from Erebus. This means that the volcanic contribution would have to be less than ~16% of the total nssSO$_4^{2-}$.

A second approach for evaluating the potential for impacts from Mt. Erebus is to scale the estimated emission of SO$_4^{2-}$ from the volcano by the corresponding emission of $^{210}$Po and then compare that figure with the observed SO$_4^{2-}/^{210}$Po ratio for SP aerosols. Polian and Lambert (1979) estimated an annual flux of $^{210}$Po as 250 Ci per year, and this is the only published estimate for $^{210}$Po to date. More recently J. Crain and P. Kyle (NM Tech, unpublished results) estimated $^{210}$Po emissions from Erebus at 690 Ci yr$^{-1}$. The flux estimates for SO$_2$ (or SO$_4^{2-}$ estimated from SO$_2$) are no less disparate than those for $^{210}$Po, and the earliest estimates of sulfur fluxes from Mt. Erebus (Polian and Lambert, 1979; Radke, 1982) have large associated uncertainties. More reliable correlation spectrometer measurements (Kyle et al., 1994) show that SO$_2$ fluxes from Erebus vary with the size of the permanent degassing lava lake there and thus vary substantially from year-to-year. For 2000, Kyle (P. R. Kyle, New Mexico Tech, unpublished results) suggests an SO$_2$ flux of 50 Mg per day.

The ratio of the two substances in emissions from Mt. Erebus can thus be estimated as $39.7 \times 10^6$ g SO$_4^{2-}$/Ci $^{210}$Po. In comparison, the SO$_4^{2-}$/Cl $^{210}$Po ratio calculated for the aerosols sampled during ISCAT 2000 was $140 \times 10^6$ g SO$_4^{2-}$/Ci $^{210}$Po (for both experiments combined the ratio was $274 \times 10^6$ g SO$_4^{2-}$/Ci $^{210}$Po). Again assuming that the volcano is the dominant source for $^{210}$Po, these results suggest that emissions from Mt. Erebus could account for ~15–30% of the total nssSO$_4^{2-}$ at the SP, which is enough to account for most of the non-biogenic nssSO$_4^{2-}$.

We cannot overemphasize the large uncertainties in these comparisons of the aerosol data from the SP versus the $^{210}$Po and S flux estimates for Mt. Erebus. Accordingly, we caution against drawing any inferences beyond our conclusion that we cannot discount a possibly significant influence of Mt. Erebus on the non-biogenic component of sulfate aerosol at the SP. The ISCAT data do, in any case, provide a point of reference for future studies of emissions from Mt. Erebus. Such studies could most effectively address this issue by simultaneously measuring $^{210}$Po and either SO$_4^{2-}$ or SO$_2$ at the volcano and at a receptor site such as SP.

4. Conclusions

The ISCAT analysis of meteorological transport to the south polar surface is unique in that trajectory information, tropospheric height analyses, and the local atmospheric structure derived from the SP soundings, could be pseudo-synoptically compared with filter collections. Analysis of tropospheric height fields allowed a reconstruction of the synoptic flow occurring at the time of the aerosol sampling. These analyses showed that a ridge of increasing high pressure caused the influx of air from beyond the Antarctic convergence, and this was accompanied by the maximum aerosol mass observed in late November (A. Hogan, unpublished results). Maximum MSA concentrations also accompanied identifiable intrusions of extra-Antarctic marine air into the interior of Antarctica.

The ISCAT data illustrate the dominant influence of marine sources on the composition of the SP atmosphere, not only for MSA and trace elements such as Na and Cl associated with sea salt aerosol, as one would expect, but also for nssSO$_4^{2-}$. The influence of the marine sources at SP was linked to the strength of the Ross Sea/ice shelf low-pressure system. The assessment of MSA/nssSO$_4^{2-}$ ratios in SP aerosols highlights the fact that $R$ is determined by more than a simple temperature dependence of the OH/DMS addition and abstraction channels. Theoretical arguments (Davis et al., in preparation) suggest that the ratio $R$ should largely be determined by whether the oxidation of DMS takes place in the MBL or in the buffer layer/free troposphere, but other potential influences on $R$ include the chemical fractionation of sea salt, the preferential removal of MSA during transport, and the transport of sulfur compounds from lower latitudes and possibly from Mt. Erebus.

Ice cores provide a record of large-scale changes in the composition of the atmosphere over time, but deciphering these records requires an understanding of the ways in which the atmospheric composition becomes imprinted in ice-cores (Dick and Peel, 1985; Bergin et al., 1998). The observed differences in the concentrations of many aerosol species between ISCAT–1998 and 2000 highlight the difficulty in discerning decadal or shorter-scale trends in concentrations of trace substances. The interpretation of the ice core data can be affected by seasonal cycles in emissions, by changes in transport pathways as the ISCAT studies illustrate, and by shifts in source regions (Legrand and Pasteur, 1998). In some cases, post depositional migrations can alter the distributions of the species of interest in ice (Pasteur and Mulvaney, 2000), complicating the interpretation of the chemical records further. Other processes, such as, windpumping (Waddington et al., 1996) present additional complications for interpreting the air-to-snow transfer of chemicals. Similarly, processes occurring in the inversion layer can inhibit the transfer of free tropospheric aerosol particles to the snow surface during cold periods (Hogan, 1979) further complicating the reconstruction of atmospheric records from ice cores.
The ISCAT results illustrate the dynamic nature of the chemistry of the SP atmosphere. Far from being a cold, isolated, unreactive region of the atmosphere, long-range transport supplies chemical reactants, and photochemical and oxidation–reduction reactions drive rapid and dynamic cycles of NOx and a variety of other species. The ISCAT studies have only begun to uncover the intricacies of the complex systems operating in the troposphere over Antarctica.

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