

# Sulfate in air and snow at the South Pole: Implications for transport and deposition at sites with low snow accumulation

Susan Harder

Department of Geology, Washington State University, Vancouver

Stephen G. Warren and Robert J. Charlson

Department of Atmospheric Sciences, University of Washington, Seattle

**Abstract.** Air and surface snow were sampled at Amundsen-Scott Station at the South Pole from July through December of 1992. Four-day averages of non-sea-salt sulfate (nss-SO<sub>4</sub><sup>2-</sup>) aerosol show a strong seasonal trend, increasing by a factor of about 30 from winter to summer as oceanic biogenic sources become more active and atmospheric transport pathways change. Three-dimensional sampling of small-scale surface topography (sastrugi) provides evidence supporting wind pumping and filtration of aerosol by snow as a significant mechanism for dry deposition at this site. The estimated monthly flux of nss-SO<sub>4</sub><sup>2-</sup> to the snow surface also increases from winter to spring, but by only a factor of 2, suggesting that the efficiency of deposition for this aerosol-borne species from the near-surface air to the snow is greater in winter. The strong surface-based temperature inversion in winter inhibits vertical motion and may limit the rate of delivery of aerosol to the boundary layer from the free troposphere. Because the snow surface is a sink for aerosol, near-surface measurements of aerosol in the stable inversion layer may not be representative of the free troposphere. Air and snow data in summer (when the inversion is weak) are used to estimate a tropospheric residence time of 4–20 days for nss SO<sub>4</sub><sup>2-</sup>.

## 1. Introduction

Non-sea-salt sulfate (nss-sulfate) aerosol contributes to the planetary heat balance by influencing the amount of solar radiation reaching the Earth directly through backscattering [Charlson *et al.*, 1992] and indirectly as cloud condensation nuclei [e.g., Anderson *et al.*, 1992]. Ice core records of sulfate may provide insight into how changes in the atmospheric concentration relate to changes in climate. The sulfate records clearly show evidence of volcanic eruptions, increases in anthropogenic emissions, and concentration decreases from glacial to interglacial periods [Delmas, 1992]. However, determining absolute concentrations of chemical constituents in the past atmosphere from concentrations measured in ice is frequently a complex problem. Incorporation of constituents from the atmosphere into the snow, and finally the ice, depends not only on the atmospheric concentration at the time of deposition but also on physical and chemical processes that occur during and following deposition (aerodynamic transport, air-snow exchange, snow accumulation rate, firm-to-ice transformation, and chemical reactions, among others) [Waddington *et al.*, 1996; Davidson *et al.*, 1996]. Understanding of how these processes work to produce the chemical signals seen in ice is needed if a transfer function is to be developed to infer paleoatmospheric concentrations from ice core measurements.

Particle-borne species such as sulfate are incorporated into surface snow by wet and dry deposition [Davidson, 1989; Bergin *et al.*, 1995a; Davidson *et al.*, 1996]. Wet deposition dominates in

most locations, but dry deposition may become significant in environments where precipitation is low such as the ice core drilling sites on the Antarctic plateau. Dry deposition may also be enhanced by wind pumping, a process by which the porous snow surface is ventilated as ambient air is forced through it by pressure differentials occurring when a steady wind flows over a rough surface [Gjessing, 1977; Colbeck, 1989; Cunningham and Waddington, 1993; Waddington *et al.*, 1996]. As air moves into the pore space within the snow, the surface area available for dry deposition becomes much greater than that of a planar nonporous surface, thereby enhancing dry deposition. The Antarctic plateau is an environment where significant wind pumping may occur because it exhibits surface roughness with a vertical scale of 0.1–0.5 m in the form of longitudinal erosional features called sastrugi [Kotlyakov, 1961; Kruchinin, 1965; Gow, 1965] and persistent winds averaging about 6 m s<sup>-1</sup> [Schwerdtfeger, 1970]. Cunningham and Waddington [1993] modeled wind pumping at the South Pole and calculated a volume flux of air through snow of about 3 × 10<sup>4</sup> m<sup>3</sup> m<sup>-2</sup> yr<sup>-1</sup>, resulting in an estimated dry flux for nss-sulfate of about 3 kg SO<sub>4</sub><sup>2-</sup> km<sup>-2</sup> yr<sup>-1</sup>, suggesting that dry deposition accounts for two thirds of the total deposition at this location. Harder *et al.* [1996] determined that ventilated snow efficiently traps submicrometer aerosol particles, indicating that if sufficient volume flux occurs, dry deposition will be significantly enhanced.

Interpretation of records for aerosol-borne chemical species in ice cores requires knowledge of the contribution of dry deposition to the total deposition. To clarify this issue, the role played by wind pumping must be determined. During 1992 we attempted to measure sulfate in air, falling snow, and surface snow at the South Pole to ascertain the relative amounts of dry and wet deposition.

We were unable to collect falling snow without simultaneously collecting drifting and blowing snow, so we were not able to complete that study. We did, however, collect aerosol samples and surface snow samples for several months, which we present here with our first attempt to calculate flux and residence time of  $\text{nss-SO}_4^-$  at the South Pole. We also sampled two sastrugi and present a map of  $\text{SO}_4^-$  concentration in these features which shows a concentration pattern consistent with that expected from wind pumping.

## 2. Methods

### 2.1. Air Sampling

Aerosol samples were collected from the end of July through December 1992. Filters were mounted about 1.5 m above the roof of the Clean Air Facility located upwind from the station. Aerosol was collected for sulfate and sodium analysis using a cyclone with a size cut of 1  $\mu\text{m}$ , on 47-mm Gelman Teflo filters with a pore size of 2  $\mu\text{m}$  and a stated collection efficiency for 0.3- $\mu\text{m}$  particles of 99.99%. A flow rate of 50  $\text{L min}^{-1}$  was maintained and measured using an American Meter volume flowmeter.

### 2.2. Snow Sampling

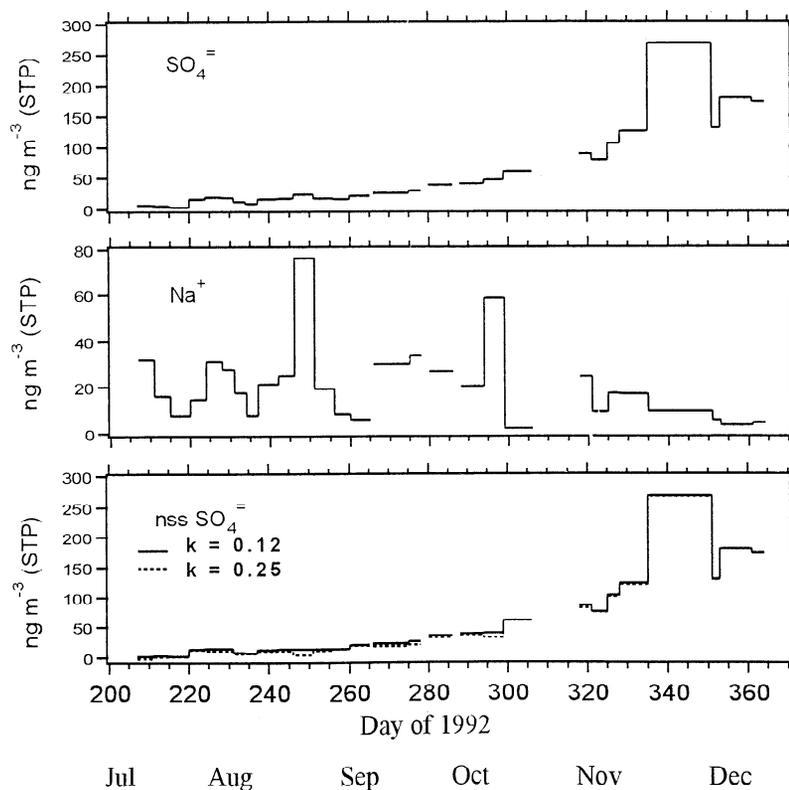
The surface snow used for calculations here was the top 1.5 cm layer of snow pits located 1 km upwind of the Clean Air Facility in the Clean Air Sector along 45°E longitude. Stainless steel partitioned sampling frames were used which collected 10 layers simultaneously, each 1.5 cm in thickness. These frames were designed for rapid sampling (necessary for the extreme cold in winter) with minimal contamination. In each pit, duplicate sets of

samples were collected, separated horizontally by 1 m. The two sets were analyzed separately and the average of their concentrations is reported here. Antistatic clean suits, including hoods and mittens, were worn during sample collection. The filled sampling frames were returned to the station, where the snow from each layer was repackaged into a cleaned polyethylene bottle using a stainless steel scoop in a Class 100 clean hood. This procedure took 3-5 min but melting was insignificant. The bottles were immediately placed outdoors where the temperature never exceeded -20°C.

After sampling the snow pit was refilled. The next pit was dug about 8 weeks later. Each consecutive pit was located 10 m upwind of the previous pit, so as to be close enough to have a similar deposition history but far enough away that the previous pit would not affect deposition processes in the snow to be sampled in the new pit. The spatial variability of chemical concentrations results in significant variability in our results and is discussed later.

The sastrugi were sampled 6.4 km from the South Pole on the 128° E longitude line along the edge of the Clean Air Sector in January 1991. Samples were collected in cleaned polyethylene bottles with stainless steel spatulas. Each sastruga was sampled at three locations in each of three dimensions, resulting in a total of 27 sections. One 125-mL bottle was filled with snow for each section. Additionally, three samples were collected on the flat surface in front of each sastruga at 3-cm intervals.

All samples remained frozen during storage at the South Pole and transport to the United States, and were kept in frozen storage at -20°C or colder until the time of chemical analysis. A detailed discussion of sampling techniques is given by Harder [1996].



**Figure 1.** Time series of air measurements at South Pole Station. The concentrations are given as nanograms per cubic meter of air at standard temperature and pressure (STP, 15°C and 1013 mbar).

### 3. Analytical Methods

Air filters were extracted in 1 mL of methanol and 30 mL of distilled deionized (Milli-Q) water in Teflon beakers. The beakers are shaken manually for 1 min at regular intervals over a 15-min period. This method has been shown to be more than 95% efficient for ion removal [Jaffrezo *et al.*, 1994]. The extractions were performed in a Class 100 clean hood. Samples were extracted in groups of 10 and were immediately analyzed for sulfate and sodium.

Ionic analysis was performed using Dionex 2000i or 4000i ion exchange chromatographs with conductivity detectors. Samples are injected using Millipore Millex-HV<sub>13</sub> syringe tip filters (0.45- $\mu\text{m}$  pore diameter). A Dionex AS4A analytical column with 1.44-mM Na<sub>2</sub>CO<sub>3</sub>/1.36-mM NaHCO<sub>3</sub> eluent was used for sulfate analysis, and a Dionex CS12 analytical column with an 8-mM methanesulfonic acid eluent was used for sodium analysis. The precision of the technique for duplicate measurements of a given sample was 1-5%. The instrumental detection limit, defined as the sum of the mean blank and 3 times the standard deviation of the mean blank [Skoog, 1985], was determined by measuring distilled deionized water, as 4 ppb for SO<sub>4</sub><sup>2-</sup> and 1 ppb for Na<sup>+</sup> at a 95% confidence level. Process blanks for air samples were collected at the South Pole by loading a filter into the filter rack for several minutes without pumping, removing it, and storing it in the same manner as the sample filters until analysis. Blanks for snow samples were collected by filling sample bottles with Milli-Q water at the South Pole and storing them frozen together with the snow samples until analysis. These blanks do not reflect contamination that may have been introduced during snow sampling using the stainless steel samplers and transfer of snow from the samplers to polyethylene bottles. The mean air process blanks for SO<sub>4</sub><sup>2-</sup> and Na<sup>+</sup> were 5.1 and 7.8 ppb, respectively (corresponding to about 0.6 and 0.9 ng m<sup>-3</sup> (STP) for a day sampling period). The mean snow process blanks were 0.5 ppb for SO<sub>4</sub><sup>2-</sup>, which is below the limit of detection defined above for the instrument, and 1.5 ppb for Na<sup>+</sup>.

### Seasonal Variation of Sulfate Aerosol

Time series of atmospheric concentrations of submicrometer SO<sub>4</sub><sup>2-</sup> and Na<sup>+</sup> for the period from late July to late December 1992 are shown in Figure 1. Total sulfate increases from about 5 ng m<sup>-3</sup> in winter to about 250 ng m<sup>-3</sup> (STP) in summer. This trend is expected, because total particle counts increase seasonally by about a factor of 20 [Bodhaine *et al.*, 1986], and is in general agreement with the results of Tuncel *et al.* [1989, Table 5] who found seasonal mean sulfate concentrations at the South Pole to increase by factors of 5-10 from winter to summer. Sodium increases from near zero to almost 40 ng m<sup>-3</sup> (STP) with spikes in September and October of about 80 and 60 ng m<sup>-3</sup> (STP). These spikes are probably due to frontal weather systems from the coast carrying sea salt to the South Pole. Sodium also shows a seasonal trend with concentrations decreasing from winter to summer.

Non-sea-salt SO<sub>4</sub><sup>2-</sup> is commonly estimated from measurement of total SO<sub>4</sub><sup>2-</sup> and Na<sup>+</sup>:

$$[\text{nssSO}_4^{2-}] = [\text{SO}_4^{2-}] - k[\text{Na}^+], \quad (1)$$

where  $k = 0.25$  is the SO<sub>4</sub><sup>2-</sup>/Na<sup>+</sup> mass ratio for bulk seawater [Delmas, 1992]. However, use of this ratio frequently produces negative values of nss-SO<sub>4</sub><sup>2-</sup> in coastal Antarctica [Wagenbach *et al.*, 1988; Gjessing, 1977; Mulvaney *et al.*, 1992; Minikin *et al.*, 1994], suggesting that fractionation is occurring between seawater and sea salt aerosol. Using  $k = 0.25$ , we also found negative

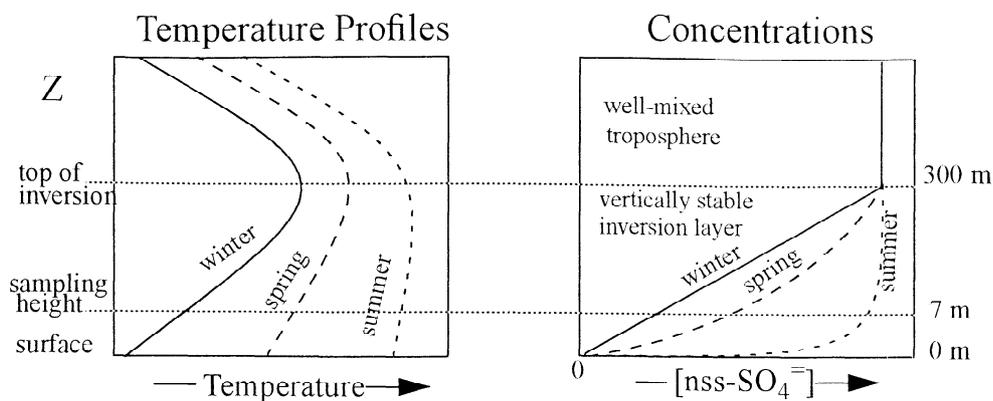
nss-SO<sub>4</sub><sup>2-</sup> in July. We therefore determined a  $k$  from the data set as follows. A sample with high sodium content (days 246-251 in Figure 1) was compared to the two samples bracketing it in time, so that the systematic seasonal change in nss-SO<sub>4</sub><sup>2-</sup> would be insignificant. We then plotted total SO<sub>4</sub><sup>2-</sup> versus Na<sup>+</sup> for those three samples to obtain  $k = 0.12$  [Harder, 1996]. This value is close to that of Ducroz [1996] ( $k = 0.1$ ) and greater than that of Minikin *et al.* [1994] ( $k = 0.05$ ) for coastal sites. (Sea salt indicators other than Na<sup>+</sup> have sometimes been used to determine nss-SO<sub>4</sub><sup>2-</sup>, but Legrand and Delmas [1988] demonstrated that Na<sup>+</sup> is most appropriate for inland Antarctic sites). Non-sea-salt SO<sub>4</sub><sup>2-</sup> is plotted in Figure 1 using both values for  $k$  to indicate the uncertainty in this calculation. During the summer (November-December) when Na<sup>+</sup> is low and SO<sub>4</sub><sup>2-</sup> is high, the difference in estimated nss-SO<sub>4</sub><sup>2-</sup> is small (0.5-4%). During winter and spring when SO<sub>4</sub><sup>2-</sup> is small (as low as 3 ng m<sup>-3</sup>, STP), use of  $k = 0.25$  instead of the data-derived  $k$  decreases computed nss-SO<sub>4</sub><sup>2-</sup> on average by about one third. However, since SO<sub>4</sub><sup>2-</sup> is very low at this time, even the large relative difference does not greatly increase the computed absolute concentration or change the seasonal trend.

Non-sea-salt sulfate accounts for most of the total SO<sub>4</sub><sup>2-</sup> during the spring and summer (greater than 99% in December). During the winter both nss-SO<sub>4</sub><sup>2-</sup> and total SO<sub>4</sub><sup>2-</sup> are low. Sea salt becomes relatively more important at this time; contributing 10-60% of the total in July. This seasonal change in source is supported by the results of single-particle analysis of South Pole aerosol [Ohtake, 1993], which showed sulfuric acid particles to be the dominant species in spring, summer, and autumn, while during winter sea-salt SO<sub>4</sub><sup>2-</sup> predominated.

These seasonal trends are most likely due to changes in atmospheric dynamics and source strength. The source of nss-SO<sub>4</sub><sup>2-</sup> is primarily biogenic emission from the ocean of dimethylsulfide and other reduced sulfur gases, which are greater in summer. The sea-salt source, as indicated by the trend in Na<sup>+</sup>, is greater in winter, as previously noted by Tuncel *et al.* [1989], when the stronger winter winds produce more aerosol which may originate from both the open ocean and from brine pools on sea ice. Another factor that may influence the seasonal trend is the strong temperature inversion at the surface that is almost continuously present during autumn, winter, and spring over the Antarctic plateau. This inversion produces a stable boundary layer typically 100-400 m thick. Little dynamic mixing occurs within this layer. Because the snow surface is a sink for particles [Harder *et al.*, 1996] and the troposphere is a source, a concentration gradient due to diffusion of particles should exist from the tropospheric concentration above the inversion to close to zero at the surface. Such a gradient was observed by Hogan [1979] for vertical profiles of aerosol particles measured over the South Pole during early November. As the strength of the inversion decreases from spring to summer, the surface concentration should increase even if the concentration in the free troposphere remains constant (Figure 2). Therefore as the marine source of nss-SO<sub>4</sub><sup>2-</sup> increases during summer, the weakening of the inversion might act to amplify the increase seen at the surface where measurements are made. Sanak *et al.* [1985] proposed that this effect accounted for seasonal trends they found at Dumont d'Urville in atmospheric measurements of aerosol-borne <sup>7</sup>Be and <sup>32</sup>P for which the primary source, cosmogenic production in the stratosphere, is constant throughout the year.

### 4. Sastrugi and Wind Pumping

Wind pumping causes air to flow into the snow at the upwind end (the nose) of a sastruga. If significant wind pumping occurs,



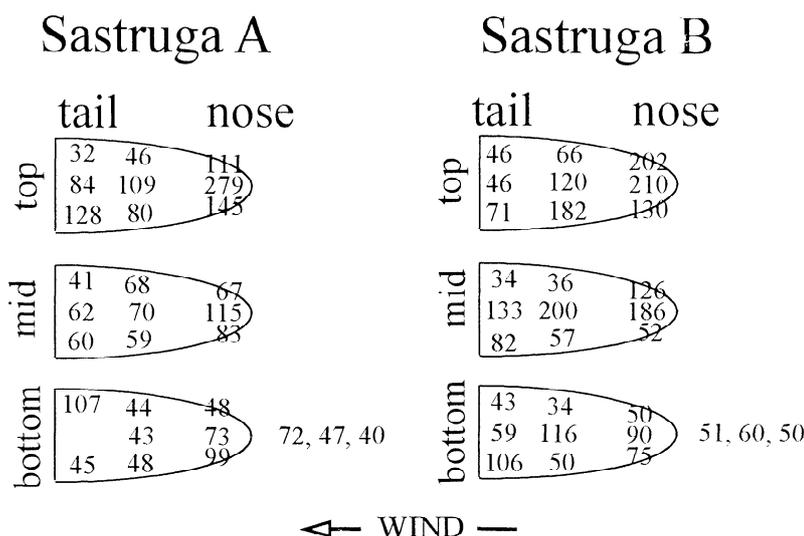
**Figure 2.** Influence of atmospheric stability in the lowest 300 m on  $[\text{SO}_4^=]$  measured at a height of 7 m, showing (left) inversion strength (and thus stability) decreasing from winter to summer, and (right) the consequent gradient of  $[\text{SO}_4^=]$  from the bottom of the free troposphere at 300 m (assumed well mixed), to the aerosol sink at the snow surface. The weaker inversion in summer permits mixing of free tropospheric air to lower altitudes than in winter.

$\text{SO}_4^=$  should be deposited preferentially in the nose, resulting in higher concentrations there than in the downwind tail and in the level surface immediately upwind of the nose [Gjessing, 1977; Cunningham and Waddington, 1993]. Two sastrugi were sampled to test this hypothesis. They were located 6.4 km from the South Pole along  $128^\circ$  E longitude on the edge of the Clean Air Sector. Maps of the  $\text{SO}_4^=$  concentration within the sastrugi are shown in Figure 3. The average concentration in the upper nose for both sastrugi is about 3 times that of the tail and the upwind surface. The average concentration in the middle of the upper nose is about 4 times that of the tail and the upwind surface. This is the pattern expected from wind pumping. Sublimation might also act to increase  $\text{SO}_4^=$  concentration in snow. However, the relative humidity near the surface is high at the South Pole. It was measured at 97% in November and is likely near 100% throughout the winter since clear sky precipitation (diamond dust) is continuous during this period. Therefore movement of air across the molecular boundary layer is not likely to cause sublimation. Sublimation does occur in summer due to differences in temperature caused

by solar heating. This process occurs primarily along the steep sides of the sastrugi due to the low solar elevation [Gow, 1965; Fujii and Kusunoki, 1982] and should produce a pattern of increased concentration on all sides rather than solely in the nose. We conclude that the pattern of sulfate concentrations in Figure 3 provides evidence of wind pumping.

These results imply that the  $\text{SO}_4^=$  concentration in surface snow has high spatial variability. However, because of the seasonal erosion and deflation of sastrugi, and the redistribution that occurs with the frequent drifting of surface snow in Antarctica, the variability in the average surface concentration is likely to be much less than that seen in the sastrugi maps if care is taken to avoid sampling directly from the sastrugi themselves.

These measurements indicate that sastrugi do collect aerosol, but they do not allow us to quantify the contribution of wind pumping to the ultimate concentration of aerosol-borne species in firn and ice. As shown by Cunningham and Waddington [1993] and Harder et al. [1996], the magnitude of deposition due to this mechanism is a function of snow characteristics (porosity, grain



**Figure 3.** Sulfate concentration is mapped in three dimensions for two sastrugi. The values are given in nanograms per gram and are accurate to  $\pm 6\%$ . Sastruga A was 0.15 m high at the nose, 1.5 m long, and 1.1 m wide. Sastruga B was 0.1 m high, 1 m long, and 1 m wide.

ize, pore space dimensions), wind speed and duration, and saskugi size, shape, and areal density, as well as atmospheric concentration. Modeling studies, such as those of *Albert* [1993], which determine volume flux of air within firm due to pressure changes induced by wind blowing over a rough surface, combined with filtering efficiencies for snow [*Harder et al.*, 1996], and using field measurements of the above mentioned parameters, at various sites, would be helpful in clarifying the importance of dry deposition due to wind pumping. In section 5.2 we do, however, make a rough estimate of this deposition using air and snow pit measurements.

## 5. Flux and Residence Time for nss-Sulfate

### 5.1. Flux

Although the variability of surface snow concentration is large and our surface snow sampling area is small, we can make a rough estimate of the monthly flux of nss-SO<sub>4</sub><sup>=</sup> to the surface at the South Pole. Total flux  $F$  (wet + dry) can be calculated from measurement of snow accumulation rate  $\dot{b}$  (g m<sup>-2</sup> time<sup>-1</sup>) and the concentration of the constituent in the surface snow  $C_s$  (ng SO<sub>4</sub><sup>=</sup> g<sup>-1</sup> (snow)) as

$$F = C_s \dot{b}. \quad (2)$$

The snow accumulation rate was obtained monthly by the South Pole Weather Office (SPWO) from measurements of snow depth at an array of 50 stakes located about 0.3 km northeast of

the station near the Clean Air Sector. The monthly accumulations for 1992 are given in Table 1. Because of redistribution due to blowing snow, the local variability is large and the standard error of the mean is typically 40%. Accumulation near the station is greater than on the surrounding plateau due to drift caused by the buildings. Therefore the measurements made at the snow stakes must be corrected before calculating SO<sub>4</sub><sup>=</sup> fluxes. The correction factor, 0.82, was determined using oxygen isotope analyses of snow collected from a snow pit in November 1992, in which a peak of isotopically heavier water corresponding to January 1992 was located in the subsurface snow [*Harder*, 1996]. The 1992 annual accumulation at the snow sampling site was 25 cm of snow or 7.2 cm of liquid equivalent (Table 1), whereas at the stake array it was 30.4 cm of snow.

Concentrations of nss-SO<sub>4</sub><sup>=</sup> from surface snow samples and the monthly snow accumulation from Table 1 are used to calculate 30-day mean fluxes in Table 2. Because of uncertainty in how much mixing of snow of different ages is caused by drifting, we assume that the top 1.5 cm of snow may represent any time period from the previous 1 month to the previous 3 months of accumulation. To account for this uncertainty, time-weighted monthly means and standard deviations are calculated for the 30, 60, and 90 days of accumulation prior to each sampling. The mean of these three values is used for the snow accumulation in the flux calculation. The uncertainty in flux, given in the rightmost column of Table 2, is due to three sources: (1) spatial variability in measured chemical concentrations, (2) uncertainty in monthly snow accumulation, and (3) uncertainty in how many months are represented in the top 1.5 cm.

**Table 1.** Monthly Snow Accumulation for 1992 at the South Pole

| Month (1992) | Accumulation at Snow Stakes <sup>a</sup> , cm month <sup>-1</sup> | Accumulation at Pit Site <sup>b</sup> , cm month <sup>-1</sup> | Accumulation at Pit Site <sup>c</sup> , g cm <sup>-2</sup> month <sup>-1</sup> |
|--------------|---|--|--|
| January      | 0.41  | 0.33   | 0.10   |
| February     | 2.01  | 1.65   | 0.48   |
| March        | 1.17  | 0.96   | 0.28   |
| April        | 6.05  | 4.96   | 1.44   |
| May          | 2.06  | 1.69   | 0.49   |
| June         | 3.45  | 2.83   | 0.82   |
| July         | 2.95  | 2.42   | 0.70   |
| August       | 1.40  | 1.15   | 0.33   |
| September    | 5.41  | 4.44   | 1.29   |
| October      | 3.51  | 2.87   | 0.83   |
| November     | 1.83  | 1.50   | 0.43   |
| December     | 0.20  | 0.17   | 0.05   |
| Annual       | 30.43   | 24.95  | 7.24   |

<sup>a</sup>Accumulation measured monthly by personnel of the South Pole Weather Office on 50 stakes. These values are higher than those at the snow pit site, because the accumulation stake array is closer to the station buildings and subject to more wind drifting. The uncertainty in monthly snow accumulation at the array (standard error of the mean) is typically 40%.

<sup>b</sup>Accumulation corrected for the difference between accumulation stake array and snow pit site, using a scale factor of 0.82 based on the annual average (25.0 / 30.4 = 0.82).

<sup>c</sup>Liquid water equivalent is calculated using the average density of 0.29 ± 0.01 g cm<sup>-3</sup> for the snow in the 1992 layer of a snow pit dug on November 17, 1992, from eight samples spaced 2.5 cm apart in depth.

### 5.2. Interpretation of Sulfate Fluxes

The fluxes given in Table 2 can be compared to that calculated by *Legrand* [1995] for the South Pole, 38 ng cm<sup>-2</sup> month<sup>-1</sup>. Our fluxes are somewhat higher for most months. This difference may be due to an increase in the stratospheric burden of nss-SO<sub>4</sub><sup>=</sup> in 1992 resulting from the 1991 eruptions of Mount Pinatubo and Mount Hudson [*Cacciani et al.*, 1993; *Saxena et al.*, 1995]. An increase in nss-sulfate concentration found in snow pit profiles for this period has also been attributed to these eruptions by *Dibb and Whitlow* [1996] and *Cole-Dai et al.* [1997].

We can define efficiencies  $k_w$  (m<sup>3</sup>(air) g<sup>-1</sup>(snow)) and  $k_d$  (m<sup>3</sup> cm<sup>-2</sup> month<sup>-1</sup>) for wet and dry deposition, respectively, as follows:

$$F = F_w + F_d, \quad (3)$$

$$F_w = k_w C_a \dot{b}, \quad (4)$$

$$F_d = k_d C_a, \quad (5)$$

where  $F_w$  is the wet deposition flux of SO<sub>4</sub><sup>=</sup> (ng cm<sup>-2</sup> month<sup>-1</sup>),  $F_d$  is the dry deposition flux of SO<sub>4</sub><sup>=</sup>,  $C_a$  is the concentration of SO<sub>4</sub><sup>=</sup> in air (ng m<sup>-3</sup>), and  $\dot{b}$  is the snow accumulation rate (g cm<sup>-2</sup> month<sup>-1</sup>). If dry deposition is totally due to wind pumping, then  $k_d$  can be interpreted as the volume of air passing through 1 cm<sup>2</sup> of the surface in 1 month.

*Legrand* [1995] plotted total SO<sub>4</sub><sup>=</sup> flux  $F$  versus snow accumulation rate for several sites in Antarctica and found a linear relationship. Assuming  $C_a$ ,  $k_w$ , and  $k_d$  are the same at all sites, the intercept (≈16 ng cm<sup>-2</sup> month<sup>-1</sup>) is  $F_d$  for Antarctica. The sites with lowest total flux, Dome C and Vostok, with 19 and 21 ng cm<sup>-2</sup> month<sup>-1</sup>, respectively, are then dominated by dry deposition ( $F_d \sim 0.85F$ ). The average flux for South Pole, 38 ng cm<sup>-2</sup> month<sup>-1</sup>, implies that deposition there was 60% wet and 40% dry. Applying those same percentages to the year 1992, when the total

**Table 2.** Non-Sea-Salt  $\text{SO}_4^-$  Flux, South Pole 1992

| Date of Snow Sampling | Snow Accumulation in Previous 1-3 Months, $\text{g cm}^{-2} \text{ month}^{-1}$ | nss- $\text{SO}_4^-$ Concentration <sup>a</sup> , $\text{ng g}^{-1}$ | Flux of $\text{SO}_4^-$ , $\text{ng cm}^{-2} \text{ month}^{-1}$ |
|-----------------------|---|--|--|
| March 22              | 0.32  | 148 ± 15   | 47 ± 21  |
| May 17                | 0.85  | 59 ± 2   | 50 ± 21  |
| July 10               | 0.77  | 46 ± 1   | 35 ± 15  |
| September 8           | 0.61  | 62 ± 6   | 38 ± 16  |
| October 31            | 0.90  | 97 ± 6   | 87 ± 38  |
| December 4            | 0.58  | 143 ± 28   | 84 ± 48  |

<sup>a</sup>The uncertainty in the nss- $\text{SO}_4^-$  snow concentrations is the standard error for the mean of two surface measurements. The uncertainty in the flux is computed by combining the uncertainty in measurement of concentration with the uncertainty in snow accumulation (40%) and the uncertainty of how many months are represented in the top 1.5 cm of snow due to mixing by drifting.

$\text{SO}_4^-$  flux was greater but the snow accumulation rate was normal, we obtain  $F_w(\text{annual}) = 36 \text{ ng cm}^{-2} \text{ month}^{-1}$ ;  $F_d(\text{annual}) = 24 \text{ ng cm}^{-2} \text{ month}^{-1}$ . (For these estimates we use Table 2, but because of scarcity of summer snow pit data we have allowed the December data to represent the entire summer.) In the following we distinguish just two seasons, a 4-month summer (November-February) and an 8-month winter (March-October).

We estimate the seasonal variation of  $k_d$  using values from Figure 1 and Table 1:  $\dot{b}$  (summer) =  $0.9 \text{ g cm}^{-2} \text{ month}^{-1}$ ;  $\dot{b}$  (winter) =  $2.7 \text{ g cm}^{-2} \text{ month}^{-1}$ ;  $C_a(\text{summer}) = 200 \text{ ng m}^{-3}$ ; and  $C_a(\text{winter}) = 7 \text{ ng m}^{-3}$ . Assuming  $k_w$  is the same for winter and summer, we obtain

$$F_w(\text{annual}) = k_w(4C_a(\text{summer})\dot{b}(\text{summer}) + 8C_a(\text{winter})\dot{b}(\text{winter}))/12, \quad (6)$$

so  $k_w = 0.50 \text{ m}^{-3}(\text{air}) \text{ g}^{-1}(\text{snow})$ ;  $F_w(\text{winter}) = 9 \text{ ng cm}^{-2} \text{ month}^{-1}$ ; and  $F_w(\text{summer}) = 90 \text{ ng cm}^{-2} \text{ month}^{-1}$ .

Taking the value  $F = 84 \text{ ng cm}^{-2} \text{ month}^{-1}$  from Table 2 for December as representative of the entire summer, we find that for summer  $F \approx F_w$  and dry deposition is negligible. But for winter,  $F \approx 51$  and  $F_w \approx 9 \text{ ng cm}^{-2} \text{ month}^{-1}$ . This indicates that dry deposition is responsible for about 80% of the total deposition, and the dry deposition efficiency is estimated as  $k_d = 6 \text{ m}^3 \text{ cm}^{-2} \text{ month}^{-1}$ , a factor of 30 larger than the annual average rate of air flux estimated by *Cunningham and Waddington* [1993]. However, this calculation of  $F_w$  assumed that the measured concentration  $C_a$  in winter is representative of the troposphere. If the tropospheric concentration is greater than that measured at 7 m height, as suggested by Figure 2, then wet deposition could contribute more in winter than we have estimated here, and both  $k_w$  and  $k_d$  would be smaller than our estimate. In any case it is likely that  $k_d$  is larger in winter than in summer, because of stronger winds ( $k_d$  is proportional to the square of wind speed [*Cunningham and Waddington*, 1993]) and greater surface roughness [*Gow*, 1965].

### 5.3. Residence Time

The mean atmospheric residence time  $\tau$  of a chemical component can be estimated from the column burden  $B$  ( $\text{g m}^{-2}$ ) and the flux  $F$  to the surface ( $\text{g m}^{-2} \text{ s}^{-1}$ ) [*Rodhe*, 1992]:

$$\tau = B/F. \quad (7)$$

The flux is calculated as described above. The tropospheric column burden of a well-mixed chemical constituent in the troposphere is obtained using the hydrostatic equation and the ideal gas law as

$$B = \left( \frac{C_a RT}{p_s} \right) \left( \frac{p_s - p_t}{g} \right), \quad (8)$$

where  $C_a$  is the concentration of the component in near-surface air ( $\text{g m}^{-3}$ , at local temperature and pressure),  $R$  ( $\text{J kg}^{-1} \text{ K}^{-1}$ ) is the gas constant for dry air,  $T$  is the surface air temperature,  $g$  is the acceleration due to gravity,  $p_s$  is surface pressure, and  $p_t$  is tropopause pressure.

As previously discussed, our measurements of sulfate, collected near the surface, are likely to be representative of the free troposphere only in summer, because the inversion inhibits mixing

**Table 3.** Calculation of Residence Time (Summer)

| Variable <sup>a</sup> | Value  | Source                      |
|-----------------------|--|-----------------------------|
| $C_a$                 | 85 ± 5 $\text{ng m}^{-3}$                          | this work, 1992             |
| $C_s$                 | 143 ± 28 $\text{ng g}^{-1}$                        | this work, 1992             |
| $\dot{b}$             | 0.019 $\text{g cm}^{-2} \text{ d}^{-1}$            | SPWO snow stakes (1992)     |
| $T$                   | 234 K  | <i>Schwerdtfeger</i> [1970] |
| $p_s$                 | 681 mbar   | <i>Schwerdtfeger</i> [1970] |
| $p_t$                 | 300 ± 80 mbar                                      | this work, Table 4          |
| Calculation           | Value  | Error                       |
| $B$                   | $3.3 \times 10^5 \text{ ng m}^{-2}$                | ~ 30%                       |
| $F$                   | $2.8 \times 10^4 \text{ ng m}^{-2} \text{ d}^{-1}$ | ~ 57%                       |
| $\tau$                | 12 ± 8 days  |                             |

<sup>a</sup>Air concentrations are for ambient air, not converted to standard temperature and pressure.  $C_a$  is  $\text{SO}_4^-$  concentration in air,  $C_s$  is  $\text{SO}_4^-$  concentration in surface snow,  $\dot{b}$  is snow accumulation,  $T$  is surface air temperature,  $p_s$  is surface pressure,  $p_t$  is pressure at the tropopause,  $B$  is the atmospheric burden of  $\text{SO}_4^-$ ,  $F$  is the  $\text{SO}_4^-$  flux, and  $\tau$  is atmospheric residence time.

**Table 4.** Tropopause Height at the South Pole as Determined by Four Different Criteria<sup>a</sup>

| Criterion                                     | Tropopause Height <sup>b</sup> |         |           |
|---|--------------------------------|---------|-----------|
|   | January                        | May     | October   |
| $dT/dz$ (change in sign)                      | 8 (325)                        | --      | --        |
| $dT/dz$ (abrupt change in magnitude)          | 8 (325)                        | 8 (315) | 7.5 (340) |
| Water vapor (abrupt decrease in mixing ratio) | 12 (180)                       | 9 (270) | 13 (135)  |
| Ozone (abrupt increase in mixing ratio)       | 7.5 (350)                      | 9 (270) | 7 (370)   |

<sup>a</sup>Based on radiosonde, ozonesonde, and water-vapor sonde measurements made at the South Pole in 1992 [Walden *et al.*, 1998].

<sup>b</sup>Values are in units of kilometers (millibars).

during the rest of the year. Therefore in this calculation we use only the surface samples collected in December and the air samples from November. The values used for the variables in equations (2) and (3) are listed in Table 3. A tropospheric residence time of 12 days is calculated for  $\text{SO}_4^{2-}$ . Although surface stability decreases greatly in summer, weak temperature inversions do occur occasionally, so air near the surface may sometimes be poorly mixed with that of the free troposphere. Therefore, even in summer, measurements of surface air may be lower in concentration than the concentration in the free troposphere, causing our estimate of residence time to be too short. The estimated uncertainty in the residence time (6 days) is propagated from the uncertainties in the fluxes (from Table 2) and the burden. The variations in air concentrations, monthly mean surface temperature and pressure, and the height of the tropopause all contribute to the uncertainty in the calculated burden. The relative error in the measured air concentrations is about 6% and the variabilities in both the surface temperature and pressure are about 1.5% during summer, based on measurements made by the South Pole Weather Office. However, all these variations are small compared to the uncertainty in  $(p_s - p_t)$ , which may be as large as 30% (Table 4), so it is the largest contributor to uncertainty in the burden. There is some additional error due to our assumption that the concentration measured at 7 m is representative of the entire troposphere, that is, that the troposphere is well mixed in summer (Figure 2). This error is difficult to evaluate; vertical profiles of  $[\text{SO}_4^{2-}]$  are needed to address this issue.

## 6. Conclusions

To interpret ice core records of  $\text{nss-SO}_4^{2-}$ , the relative amounts of wet and dry deposition must be determined. The low precipitation rate, persistent winds, and microtopography of the interior plateau of Antarctica suggest that dry deposition in general, and wind pumping in particular, may be important at this location. Three-dimensional sampling of sastrugi shows a pattern of sulfate concentrations consistent with significant deposition by wind pumping. This result indicates that determining a transfer function for aerosol-borne chemical species at such locations may require an understanding of the factors that control wind pumping (particularly surface microtopography, snow structure, and winds) and of how these factors change in different climate regimes.

Non-sea-salt  $\text{SO}_4^{2-}$  aerosol collected near the surface shows strong seasonal variation, with summer values 30 times winter values. The calculated monthly flux of  $\text{nss-SO}_4^{2-}$  to the snow surface also increases from winter to summer, but only by a factor of

about 2. The less dramatic trend for flux must be due to a decrease in efficiency of delivery of  $\text{nss-SO}_4^{2-}$  to the surface during the period of highest near-surface atmospheric concentration. The factors that influence wind pumping (winds and microtopography) vary accordingly, such that dry deposition should increase in winter and decrease in summer. Furthermore, if removal of aerosol at the surface by wind pumping is efficient enough, aerodynamic resistance may become the limiting factor for dry deposition. This may be especially relevant for cold periods when a strong surface-based temperature inversion is present which limits the delivery of aerosol from the free troposphere to the surface.

If dry deposition is a function of microtopography, snow structure, wind, and atmospheric dynamics, a transfer function for sulfate and other aerosol-borne constituents may be difficult to construct since changes in these factors for past times are difficult to determine. Although field measurements may be relevant for estimating atmospheric concentrations from ice core measurements during the recent past or even for the entire Holocene [Bergin *et al.*, 1995b; Wolff *et al.*, 1998], further investigation of the processes controlling deposition is necessary to interpret data from glacial periods when these processes may have varied greatly. Sites with relatively little wind (e.g. Dome C) may provide records that can be more easily interpreted and perhaps should be considered preferentially as future coring sites, although the factors influencing wind pumping might still have changed significantly over glacial-interglacial transitions even at such sites.

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R. J. Charlson and S. G. Warren, Department of Atmospheric Sciences, University of Washington, Seattle, WA 98195.

S.L. Harder, Department of Geology, Washington State University, 14204 N.E. Salmon Creek, Vancouver, WA 98686. (harders@vancouver.wsu.edu)

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