A 200 year sulfate record from 16 Antarctic ice cores and associations with Southern Ocean sea-ice extent

Daniel DIXON, Paul A. MAYEWSKI, Susan KASPARI, Karl KREUTZ, Gordon HAMILTON, Kirk MAASCH, Sharon B. SNEED, Michael J. HANDLEY

Climate Change Institute, Department of Earth Sciences, University of Maine, 303 Bryant Global Sciences Center, Orono, ME 04469-5790, USA
E-mail: daniel.dixon@maine.edu

INTRODUCTION

Reliable instrumental records of Earth's climate have only been collected since the late 19th century; of these, high-resolution records of Southern Hemisphere climate are geographically sparse and rarely extend back more than 50 years. A longer perspective on climate variability can be obtained by studying natural archives that provide proxies for past climate, such as tree rings, sediment cores and ice cores.

Antarctic ice cores are a valuable resource for reconstructing the climate of the past because they can provide sub-annually resolved, continuous proxy records of atmospheric temperature, atmospheric circulation, precipitation, and resulting in enhanced levels of ultraviolet-B (UV-B) radiation at the Earth's surface (Berresheim and others, 1990). SO$_4^{2-}$ aerosols play a significant role in the heat budget of the global atmosphere, mainly through the scattering of incoming solar radiation and through indirect effects involving clouds (Charlson and others, 1990). SO$_4^{2-}$ from large explosive volcanic eruptions significantly affects stratospheric chemistry, inducing a higher catalytic destruction rate of ozone and resulting in enhanced levels of ultraviolet-B (UV-B) radiation at the Earth's surface (Berresheim and others, 1995).

The isolated Antarctic continent is an ideal place to study natural atmospheric SO$_4^{2-}$ variability, thanks to its remoteness from major anthropogenic SO$_4^{2-}$ sources that can confound the investigation of natural variability compared to more populated regions (Shaw, 1982; Legrand and Mayewski, 1997).

Sulfate sources and transport pathways

Sea-salt (ss) SO$_4^{2-}$ reaches West Antarctica almost exclusively through the lower troposphere, and as a result can contribute over 25% of the total SO$_4^{2-}$ budget to coastal and low-elevation sites (Dixon and others, 2004). Interpreting the significance of excess (xs) SO$_4^{2-}$ concentrations in Antarctica is complicated because the xsSO$_4^{2-}$ arrives from a variety of sources. The major source is biogenic xsSO$_4^{2-}$ that results from vigorous biological activity in the surrounding oceans during the Southern Hemisphere summer months (Bates and others, 1992; Legrand and Mayewski, 1997). The strong seasonality of biogenic xsSO$_4^{2-}$ production and transport results in well-defined annual peaks in all of the ice-core records used in this study (Dixon and others, 2004). Biogenic source xsSO$_4^{2-}$ reaches a peak from November to January (Minikin and others, 1998) and arrives in West Antarctica via two major transport pathways. Biogenic xsSO$_4^{2-}$, produced south of 60°S (Minikin and others, 1998), is transported mainly through the lower troposphere, whereas biogenic xsSO$_4^{2-}$, primarily from low–mid-latitude sources, is transported through the mid–upper troposphere (Shaw, 1982; Legrand and others, 1992; Minikin and others, 1998). The ssSO$_4^{2-}$ fraction reaches a peak during the winter/spring transition, when intense cyclonic activity and intrusions of lower-tropospheric marine air masses are
common (Legrand and others, 1992; Whitlow and others, 1992; Hogan, 1997).

Other important sources of West Antarctic xsSO$_4^{2-}$ are volcanic eruptions and the multiple-source stratospheric SO$_4^{2-}$ layer that is comprised of background volcanic, biogenic and potentially anthropogenic contributions. Volcanic xsSO$_4^{2-}$ input to West Antarctica from large explosive eruptions is episodic. The major transport pathway for this source of xsSO$_4^{2-}$ is the mid–upper troposphere and stratosphere (Legrand and Delmas, 1987; Dibb and Whitlow, 1996; Legrand and Wagenbach, 1999). The stratospheric contribution of SO$_4^{2-}$ is generally assumed to be minimal (Legrand, 1997; Bergin and others, 1998) except after large explosive volcanic eruptions (Legrand and Delmas, 1987; Dibb and Whitlow, 1996). Volcanic xsSO$_4^{2-}$ from small volcanic eruptions may travel through the lower troposphere but usually does not travel far from the eruption source.

The influence of lower-tropospheric air masses diminishes with increasing elevation and distance from the coast, causing ssSO$_4^{2-}$ to decrease concomitantly. The influence of mid–upper tropospheric and stratospheric air masses on coastal sites is minor (Minikin and others, 1998; Legrand and Wagenbach, 1999) compared to higher-elevation interior areas. As a result, large explosive volcanic eruptions are most clearly distinguished in ice-core xsSO$_4^{2-}$ records from higher-elevation interior areas.

Polynyas are an important local source of ssSO$_4^{2-}$ and xsSO$_4^{2-}$ in coastal Antarctic precipitation. Although relatively small in area, coastal polynyas are areas of considerable sea-ice production and salt flux in winter, and regions of greatly enhanced primary and secondary production in summer (Arrigo and Van Dijken, 2003; Kaspary and others, 2005). The largest polynya in the Southern Ocean is the Ross Sea Polynya, which is one of the most biologically productive regions around Antarctica (Arrigo and others, 1998). It forms annually as a result of the strong katabatic winds flowing off the Ross Ice Shelf into the southwestern Ross Sea (Bromwich and others, 1992).

Traditionally, bubble bursting at the open-ocean water surface was considered to be the sole source of sea-salt aerosols in Antarctic precipitation, but more recently Southern Ocean sea-ice extent (SIE) has been shown to play an important role in controlling concentrations of ssSO$_4^{2-}$ in coastal Antarctic precipitation through the formation of highly saline frost flowers on the surface of new sea ice (Wagenbach and others, 1998; Rankin and others, 2000, 2002). Highly saline brine forms at the surface of new sea ice, and below ~8 °C sodium sulfate decahydrate (mirabilite: Na$_2$SO$_4$·10H$_2$O) precipitates from the brine (Richardson, 1976). This process produces aerosols strongly depleted in SO$_4^{2-}$ relative to Na$^+$ from the brine (Rankin and others, 2002). Several studies report negative winter xsSO$_4^{2-}$ values from aerosol, snow and ice-core samples at coastal sites (Mullvany and Peel, 1998; Wagenbach and others, 1998), indicating that the brine associated with frost flowers is a dominant source of marine aerosols to coastal sites in winter. However, Kreutz and others (2000b), using the Siple Dome ice core, and Kaspari and others (2005), using International Trans-Antarctic Scientific Expedition (ITASE) cores, show that the ice-core sea-salt record is a proxy for the strength and position of the Amundsen Sea low, indicating that wind strength is still a major control of sea-salt aerosols in Antarctic precipitation whether the aerosols are derived from frost flowers or the open-ocean surface.

SIE is also linked to concentrations of xsSO$_4^{2-}$ in the Antarctic atmosphere (Welch and others, 1993; Peel and others, 1996; Meyerson and others, 2002; Curran and others, 2003) via its strong, consistent association with the methanesulfonate (MS) seasonal cycle of marine productivity (Minikin and others, 1998). Peel and others (1996) show that in areas adjacent to the Weddell Sea, extensive sea-ice cover appears to suppress emissions of the xsSO$_4^{2-}$ precursor dimethylsulfide (DMS). However, other studies reveal a positive relationship between increased MS at coastal sites and increased SIE in adjacent longitudinal ocean sectors (Welch and others, 1993; Curran and others, 2003). Meyerson and others (2002) note a positive relationship between South Pole MS concentrations and Amundsen–Ross region SIE.

In this study, chemistry data from 16, 50–115 m deep, sub-annualy dated ice-core records (Fig. 1) are used to investigate recent spatial and temporal concentration variability of the soluble ssSO$_4^{2-}$ and xsSO$_4^{2-}$ in ice cores over West Antarctica. We investigate associations between the xsSO$_4^{2-}$ and ssSO$_4^{2-}$ concentration time series from each core and SIE and we discuss the importance of the SIE–ssSO$_4^{2-}$ correlations in terms of the 1940 background xsSO$_4^{2-}$ rise observed in our previous study (Dixon and others, 2004).

**METHODOLOGY**

The ice cores used in this study were collected during Antarctic field seasons 1994–2001. The eight older cores (SP-95, SDM-94, RIDS-A, -B and -C, CWA-A and -D and Up-C) were sectioned using the ultra-clean procedures described in Buck and others (1992). The eight new US ITASE cores were sampled at high resolution using the University of Maine melt system (up to 50 samples m$^{-1}$; Table 1) to develop sub-annually resolved time series (Dixon and others, 2004). To prevent contamination, only the inner portion of each core was sampled, and, prior to melting, the ends of each core section were scraped using a sterile surgical stainless-steel blade. Each sample was analyzed for its soluble major-ion content (Na$^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$, Cl$^-$, NO$_3^-$, SO$_4^{2-}$) using a Dionex$^\text{TM}$ DX-500 ion chromatograph coupled to a Gilson$^\text{TM}$ autosampler, and concentrations are reported in µg L$^{-1}$ (ppb). To determine anion (Cl$^-$, SO$_4^{2-}$ and NO$_3^-$) concentrations, the chromatograph was set up with an AS-11 column with 6 mM NaOH eluent. For cation (Na$^+$, Ca$^{2+}$, Mg$^{2+}$ and K$^+$) concentrations, a CS-12a column with 25 mM MSA eluent was used. All ion concentrations are determined with an accuracy of better than 0.1 ppb.

The high-resolution section of every ice core is dated by matching seasonal peaks from each of the major-ion time series in accord with seasonal timing identified by previous research (e.g. Whitlow and others, 1992; Wagenbach, 1996; Legrand and Mayewski, 1997; Kreutz and Mayewski, 1999; Dixon and others, 2004). The counting of annual peaks between known large explosive volcanic events in our ion records, such as the 1815 eruption of Tambora, Indonesia, the 1883 eruption of Krakatau, Indonesia, the 1963 eruption of Agung, Indonesia, and the 1991 eruption of Pinatubo, Philippines, confirms that each year is preserved in each high-resolution ice-core record and allows a dating accuracy of better than 1 year (Dixon and others, 2004).
Each ice-core SO₄²⁻ time series is separated into its primary constituents, ssSO₄²⁻ and xsSO₄²⁻, using the technique described by O’Brien and others (1995). The ssSO₄²⁻ fraction is calculated by applying a standard sea-water ratio of 30.61(Na⁺), 1.11(K⁺), 3.69(Mg²⁺), 1.16(Ca²⁺), 55.04(Cl⁻) and 7.68(SO₄²⁻) to the ion concentrations in each sample (Holland, 1978). The concentration values are reduced incrementally according to this ratio until a value of zero is reached in one of the six ion concentrations. The ion that reaches zero concentration first is considered to be the conservative ion for that sample, and the concentration values for the other five ions are recorded. These become the excess (xs) concentrations for that sample. This technique is used in preference to the total-Na⁺ conservative method because it takes all of the sea-salt ions into account when calculating sea-salt concentrations and therefore lessens the likelihood of a possible ssSO₄²⁻ to Na⁺ ratio bias caused by frost flower fractionation (Rankin and others, 2002). Previous research reveals no significant correlations between snow ion concentration and accumulation rate for Antarctic glaciochemical series in general (e.g. Mulvaney and Wolff, 1994; Kreutz and Mayewski, 1999; Kreutz and others, 2000a) or for the glaciochemical series used in this study (Dixon and others, 2004), so flux corrections for accumulation were not applied.

In order to characterize and compare the total ssSO₄²⁻ and xsSO₄²⁻ concentration at each ice-core site, we calculate mean values for the period 1952–91 (Fig. 2). We use 1952–91 because this is the longest time period for which we have a large number of continuous ice-core time series (mean value for site 01-6 is calculated from 1978–91, the full length of the record). Raw ssSO₄²⁻ and xsSO₄²⁻ time series for the last 200 years are plotted to determine the seasonal and longer-term variance in each of the ice-core SO₄²⁻ records (Fig. 3).

Linear correlations of annually averaged ssSO₄²⁻ and xsSO₄²⁻ concentrations from each core vs SIE data from 1973 to 1996 (Jacka, 1983) are performed (the Up-C core is not used because of data gaps) to determine how SIE is related to SO₄²⁻ concentrations at the South Pole and across West Antarctica. The annual xsSO₄²⁻ concentration is calculated for each year from June to June (referred to as type A), and the annual ssSO₄²⁻ concentration is calculated from January to January (type B), as these periods best cover the annual concentration peak in each SO₄²⁻ time series. The SIE data were compiled from satellite-derived maps (US Navy and US National Oceanic and Atmospheric Administration Joint Ice Center) which by definition have the ice edge determined by a sea-ice concentration of >15% (Jacka, 1983, and monthly updates). For each month (January 1973–
December 1996), a latitudinal position of the sea-ice edge is available for every 10° of longitude (Simmonds and Jacka, 1995), yielding 36 separate time series. The only missing data are for August 1975 for all longitudes. The August average (1973–96) for each longitude series was substituted for these missing values. The SIE data are annually averaged from June to June (A) and from January to January (B) resulting in annual SIE records that span the time periods 1974–96 and 1973–96 respectively. Correlations are performed between the $\text{xsSO}_4^{2–}(A)$ and SIE (A) data and the $\text{ssSO}_4^{2–}(B)$ and SIE (B) data. Longitudinal SIE segments that correlate above 95% significance are plotted on polar stereographic maps of Antarctica (see Table 2 for corresponding $r$ values).

### RESULTS AND DISCUSSION

#### 50 Year mean concentrations

Sites 01-6, 01-5, 01-3, 01-2, 00-1, 00-4 and 00-5 are located along transect A–B from eastern to central to western West Antarctica (Fig. 1). The sites increase in elevation from ~1200 m to ~1800 m from east to west. Mean $\text{xsSO}_4^{2–}$ concentrations along this transect display relatively uniform values from eastern to central West Antarctica, and an increase from central to western West Antarctica (Fig. 2). The increase in mean $\text{xsSO}_4^{2–}$ concentration towards the west is believed to be the result of increased downward flow of sulfate-laden air from the mid–upper atmosphere over the Executive Committee Mountain Range, inferred from atmospheric flow models in this area (Guo and others, 2003).

#### Table 1. Information for each ice core used in this study

<table>
<thead>
<tr>
<th>Location</th>
<th>Lat.</th>
<th>Long.</th>
<th>Elev.</th>
<th>Mean acc.</th>
<th>Distance from open water (1952–91)</th>
<th>$\text{xsSO}_4^{2–}$ conc. (1952–91 mean)</th>
<th>$\text{ssSO}_4^{2–}$ conc. (1952–91 mean)</th>
<th>$\text{ssSO}_4^{2–} : \text{xsSO}_4^{2–}$ (1952–91 mean)</th>
<th>Depth</th>
<th>High-res. time period</th>
<th>Sampling resolution a$^{-1}$ (high-res. mean)</th>
<th>Samples</th>
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<tbody>
<tr>
<td>ITASE 01-6</td>
<td>76.0968</td>
<td>89.0147</td>
<td>1232</td>
<td>cm w.e. a$^{-1}$ km</td>
<td>39.7</td>
<td>320</td>
<td>7.1</td>
<td>29.9</td>
<td>0.24</td>
<td>18</td>
<td>2000–1978</td>
<td>2.1–3.6</td>
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<td>ITASE 01-5</td>
<td>77.0593</td>
<td>89.1375</td>
<td>1246</td>
<td>36.5</td>
<td>400</td>
<td>6.8</td>
<td>29.4</td>
<td>0.23</td>
<td>114</td>
<td>2002–1781</td>
<td>1.5–3.5</td>
<td>23</td>
</tr>
<tr>
<td>ITASE 01-3</td>
<td>78.1202</td>
<td>95.6463</td>
<td>1633</td>
<td>32.7</td>
<td>370</td>
<td>4.2</td>
<td>24.9</td>
<td>0.17</td>
<td>71</td>
<td>2002–1859</td>
<td>1.5–3.2</td>
<td>20</td>
</tr>
<tr>
<td>ITASE 01-2</td>
<td>77.8436</td>
<td>102.9103</td>
<td>1335</td>
<td>42.5</td>
<td>295</td>
<td>6.4</td>
<td>30.8</td>
<td>0.21</td>
<td>71</td>
<td>2002–1890</td>
<td>1.7–4.1</td>
<td>27</td>
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<tr>
<td>ITASE 00-1</td>
<td>79.3831</td>
<td>111.2286</td>
<td>1791</td>
<td>22.3</td>
<td>475</td>
<td>5.7</td>
<td>30.0</td>
<td>0.19</td>
<td>105</td>
<td>2001–1651</td>
<td>1.6–3.5</td>
<td>13</td>
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<tr>
<td>ITASE 00-4</td>
<td>78.0829</td>
<td>120.0764</td>
<td>1697</td>
<td>19</td>
<td>460</td>
<td>7.9</td>
<td>37.2</td>
<td>0.21</td>
<td>58</td>
<td>2001–1799</td>
<td>1.4–3.1</td>
<td>13</td>
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<tr>
<td>ITASE 00-5</td>
<td>77.6821</td>
<td>123.9914</td>
<td>1828</td>
<td>14.6</td>
<td>400</td>
<td>8.1</td>
<td>53.7</td>
<td>0.15</td>
<td>60</td>
<td>2001–1708</td>
<td>2–6.4</td>
<td>8</td>
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<td>RIDS-A</td>
<td>78.7300</td>
<td>116.3300</td>
<td>1740</td>
<td>23.6</td>
<td>440</td>
<td>6.2</td>
<td>28.0</td>
<td>0.22</td>
<td>150</td>
<td>1996–1831</td>
<td>3 &amp; 60</td>
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<td>RIDS-B</td>
<td>79.4600</td>
<td>118.0500</td>
<td>1603</td>
<td>14.8</td>
<td>535</td>
<td>5.9</td>
<td>39.1</td>
<td>0.15</td>
<td>60</td>
<td>1996–1926</td>
<td>3, 20, &amp; 30</td>
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<td>RIDS-C</td>
<td>80.0100</td>
<td>119.5600</td>
<td>1530</td>
<td>11.1</td>
<td>580</td>
<td>5.8</td>
<td>45.7</td>
<td>0.13</td>
<td>60</td>
<td>1996–1905</td>
<td>2, 3, &amp; 259</td>
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<td>Up-C</td>
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<td>135.9720</td>
<td>525</td>
<td>11.5</td>
<td>640</td>
<td>21.5</td>
<td>85.7</td>
<td>0.25</td>
<td>28</td>
<td>1996–1870</td>
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<td>CWA-(A)</td>
<td>82.3671</td>
<td>119.2855</td>
<td>950</td>
<td>14.5</td>
<td>850</td>
<td>13.1</td>
<td>46.1</td>
<td>0.28</td>
<td>93.5</td>
<td>1994–1939</td>
<td>3 &amp; 40</td>
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<td>ITASE 99-1</td>
<td>80.6200</td>
<td>122.6300</td>
<td>1350</td>
<td>13.6</td>
<td>640</td>
<td>11.8</td>
<td>40.3</td>
<td>0.29</td>
<td>58</td>
<td>2000–1713</td>
<td>2–4.3</td>
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<td>CWA-(D)</td>
<td>81.3723</td>
<td>107.2750</td>
<td>1930</td>
<td>21.3</td>
<td>735</td>
<td>5.5</td>
<td>30.3</td>
<td>0.18</td>
<td>50.5</td>
<td>1994–1952</td>
<td>3 &amp; 60</td>
<td>13</td>
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<td>South Pole-95</td>
<td>90.0000</td>
<td>0.0000</td>
<td>2850</td>
<td>8.2</td>
<td>1300</td>
<td>2.6</td>
<td>52.6</td>
<td>0.05</td>
<td>71</td>
<td>1992–1487</td>
<td>2</td>
<td>6</td>
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</table>

Fig. 2. Mean excess (red) and sea-salt (blue) sulfate concentrations in ppb for the years 1952–91 for each ice core used in this study. Green dots represent elevation in meters. Purple dots represent distance from nearest open water in kilometers. Red lines (A–B, C–D and E–F) are transects from Figure 1 (not to scale).
Ice-core sites RA, RB and RC are located in a ~300 km northeast–southwest transect (C–D) descending from the ice divide into the Ross Ice Shelf catchment area (Fig. 1). Concentrations of $\text{xSO}_4^{2-}$ along this transect exhibit an increasing trend toward site RC (Fig. 2), most likely as a consequence of closer proximity to the turbulent atmosphere over the Ross Ice Shelf area (Kreutz and Mayewski, 1999) and the biological productivity of the Ross Sea Polynya. Concentrations of $\text{ssSO}_4^{2-}$ remain relatively constant over the spread of sites 01-6, 0-5, 0-3, 0-2, 0-1, 0-4, 0-5, RA, RB and RC.
Sites SDM-94, Up-C, CWA-A, 99-1, CWA-D and SP-95 lie on transect E–F and range in elevation from 620 m at the edge of the Ross Ice Shelf to 2850 m at South Pole (Fig. 1). Concentrations of \( \text{ssSO}_4^{2-} \) decrease with increasing elevation up to site CWA-D, and the trend reverses between CWA-D and SP-95 (Fig. 2) as a result of multiple input sources (tropospheric and stratospheric) for \( \text{ssSO}_4^{2-} \) in this area (Proposito and others, 2002; Dixon and others, 2004). Concentrations of \( \text{ssSO}_4^{2-} \) along the same transect decrease steadily toward South Pole with increasing elevation and distance from the coast, indicating a single lower-tropospheric source for marine ions that reach the polar plateau.

Raw concentrations

Plots of raw (unprocessed) \( \text{ssSO}_4^{2-} \) and \( \text{xsSO}_4^{2-} \) concentrations against time (Fig. 3) illustrate the large (more than an order of magnitude in some cases) increases in \( \text{ssSO}_4^{2-} \) immediately following several global-scale large explosive volcanic eruptions (Tambora (1815), Cosiguina, Nicaragua (1835), Krakatau (1883), Agung (1963) and Pinatubo (1991)) in the sub-annually resolved data from all cores except SDM-94, Up-C and CWA-A (Dixon and others, 2004).

The majority of the West Antarctic ice-core sites in this study (01-6, 01-5, 01-3, 01-2, 00-1, 00-4, 99-1, RA, RB, RC, Up-C, CWA-A and CWA-D) have high annual \( \text{ssSO}_4^{2-} \) variance, commonly displaying low winter \( \text{ssSO}_4^{2-} \) concentrations, but it contains numerous large \( \text{xsSO}_4^{2-} \) peaks that are not related to global-scale volcanic eruptions because they do not appear at any other site and do not correspond to historic global-scale volcanic events. The large peaks in 01-5 may be a result of local volcanism, biogenic \( \text{ssSO}_4^{2-} \) input from nearby polynyas, or evaporite dust input from the nearby Ellsworth Mountains. The most likely cause for the majority of these large peaks is evaporite dust because of coincident large \( \text{Ca}^{2+} \) peaks.

Site SP-95 (Fig. 3) maintains a relatively high \( \text{ssSO}_4^{2-} \) baseline (~50 ppb) and low (~30–70 ppb) variance throughout the year compared to other sites. It also contains unusually large (sometimes more than an order of magnitude above the mean) \( \text{xsSO}_4^{2-} \) signatures from global-scale volcanic eruptions. The SP-95 \( \text{xsSO}_4^{2-} \) volcanic signatures are a result of its high (~2850 m) elevation and direct access to upper-tropospheric/stratospheric air masses (Dixon and others, 2004).

Non-volcanic \( \text{xsSO}_4^{2-} \) concentrations at site 00-5 (Fig. 3) are similar in structure to those at SP-95 (high background, low variance) during several short periods over the last 200 years (e.g. 1942–47, 1908–13) but are similar to the majority of West Antarctic sites for the remainder of the record (low winter values, high variance). The change in \( \text{ssSO}_4^{2-} \) deposition style at site 00-5 may reflect changes in the strength of downward airflow over the Executive Committee Range (as discussed earlier). Periods of strengthened downward flow may cause the \( \text{ssSO}_4^{2-} \) signature at site 00-5 to be more similar to that at SP-95.

The mean \( \text{ssSO}_4^{2-} \) concentrations at SDM-94 (Fig. 3) frequently decrease to ~30 ppb, comparable to, or, lower than, the mean \( \text{ssSO}_4^{2-} \) concentration at that site, suggesting a high event frequency of at least one of the major \( \text{ssSO}_4^{2-} \) sources to the site, probably marine biogenic \( \text{ssSO}_4^{2-} \). The low elevation and proximity to the coast of the SDM-94 site signify that its major \( \text{ssSO}_4^{2-} \) sources are sea salt and marine biological productivity from the adjacent ocean area. Therefore, a likely cause for the observed \( \text{ssSO}_4^{2-} \) fluctuations is variability of Ross Sea climatic conditions. Interestingly, the \( \text{ssSO}_4^{2-} \) fluctuations in the SDM-94 record are not observed at Up-C or CWA-A as would be expected from events of this magnitude. Another reason for the independent behavior of SDM-94 \( \text{ssSO}_4^{2-} \) concentrations may be the location of the site. The SDM-94 core site is located on the top of a 600 m high dome; this protruding geography may prevent certain air masses from reaching the ice-core drill site and could well be a factor regarding the unique character of the glaciochemical concentrations.

Almost every core in this study has a mean \( \text{ssSO}_4^{2-} \) to \( \text{ssSO}_4^{2-} \) ratio between 0.13 and 0.29 (Table 1); the exceptions are SP-95 with a ratio of 0.05, and SDM-94 with a ratio of 0.40. The low ratio at SP-95 is caused by a combination of extremely low \( \text{ssSO}_4^{2-} \) concentrations resulting from its high elevation and distance from the coast, and the fact that \( \text{ssSO}_4^{2-} \) concentrations at this site maintain a relatively constant baseline (~50 ppb) and low

### Table 2. Pearson’s r values for the 95% and 99% significance level in correlations between annually averaged sea-ice extent and annually averaged \( \text{ssSO}_4^{2-} \) and \( \text{xsSO}_4^{2-} \) concentrations

<table>
<thead>
<tr>
<th></th>
<th>( \text{ssSO}_4^{2-} )–SIE (B) correlation</th>
<th></th>
<th>( \text{xsSO}_4^{2-} )–SIE (A) correlation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( r = 95% )</td>
<td>( r = 99% )</td>
<td>( r = 95% )</td>
</tr>
<tr>
<td>01-6</td>
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The high ssSO$_4^{2-}$:xsSO$_4^{2-}$ ratio at SDM-94 is a result of extremely high ssSO$_4^{2-}$ concentrations resulting from proximity to the Ross Ice Shelf edge and Ross Sea Polynya.

**Sea-ice correlations**

Linear correlation between monthly values of SIE and monthly values of SDM-94 xsSO$_4^{2-}$ (from 1973–94) was performed to determine if SIE exhibited any significant associations with xsSO$_4^{2-}$ concentrations in precipitation (Fig. 4). We chose SDM-94 to begin with because it is the nearest to open water of our low-elevation sites. The monthly values were calculated by resampling the original time series to 12 samples per year based on the assumption that the annual xsSO$_4^{2-}$ peak occurs near the December/January transition (Minikin and others, 1998). The results show that the strongest correlations are obtained when records are lead/lagged 2–3 months. This is because the maximum and minimum SIE occurs in September/October and March/April respectively and the xsSO$_4^{2-}$ peak falls on the December/January transition. To overcome any further possible autocorrelation problems, we resampled both time series to annual resolution. The results for SDM-94 xsSO$_4^{2-}$ and SIE reveal that the most robust correlation ($r > 0.6 > 99\%$ significance) occurs with no leads or lags. Figure 5 shows that the strongest correlations occur with SIE from longitudes 70–80°, 130–150° and 200–240°.

Linear correlations with annually averaged SIE from 1973–96 were also performed on the annually averaged xsSO$_4^{2-}$ and ssSO$_4^{2-}$ records from each core (Figs 6 and 7) for the full period of data overlap. With SIE calculated as a function of latitude in Figures 6 and 7, a positive correlation means decreased SIE when SO$_4^{2-}$ concentrations are high, and a negative correlation means increased SIE when SO$_4^{2-}$ concentrations are high. The statistically significant ($>95\%$) results show that in general the SIE closest to West Antarctic ice-core sites, in the Ross, Amundsen and Bellingshausen Seas, is negatively correlated with ssSO$_4^{2-}$ ($r \geq 0.405–0.537$) and positively correlated with xsSO$_4^{2-}$ ($r \geq 0.414–0.561$) concentrations.

West Antarctic ice-core sites (SDM-94, 00-1, 00-4, 01-3 and RIDS-A) exhibit increased concentrations of xsSO$_4^{2-}$ when SIE in the Bellingshausen–Amundsen–Ross (Pacific) region is reduced (Fig. 6). At the same time, when xsSO$_4^{2-}$ concentrations at site 01-3 are higher, the SIE in the Pacific region is reduced and the SIE in the Weddell (Atlantic) region is increased. If the primary xsSO$_4^{2-}$ source for site 01-3 is the Weddell region, our result is in agreement with several previous studies (Welch and others, 1993; Meyerson and others, 2002; Curran and others, 2003); but if, as is more likely, the primary xsSO$_4^{2-}$ source for site 01-3 is the Bellingshausen–Amundsen–Ross region, our results suggest that the SIE-xsSO$_4^{2-}$ relationship is opposite to that of SIE-MS. The associations present in the Weddell region may be related to the Antarctic dipole, which manifests itself as out-of-phase retreat (advance) of sea ice in the Atlantic (Pacific) ocean basins (Yuan and Martinson, 2000). Assuming the latter to be true, differences between our results and those of previous studies (Welch and others, 1993; Curran and others, 2003) may be due to the fact that none of our sites are truly coastal locations (although SDM-94 has some coastal characteristics). Also, we examine xsSO$_4^{2-}$ concentrations rather than MS, and the ice-core locations for all previous studies are in East Antarctica.

Linear correlation between ssSO$_4^{2-}$ and SIE (Fig. 7) reveals that concentrations of ssSO$_4^{2-}$ are higher at several West Antarctic sites (CWA-A, 00–1, 00–4, 00–5, RIDS-A, RIDS-B and CWA-D) when there is greater SIE in the Amundsen, Ross and Bellingshausen Seas. There could be several possible mechanisms for this association. One is increased sea-ice production leading to greater frost flower growth and resulting in greater volumes of highly saline aerosols (Rankin and others, 2002; Kaspari and others, 2005). Another is increased meridional transport and higher wind speeds over the open-ocean surface during colder years, causing greater concentrations of ss aerosols to reach the ice sheet (Curran and others, 1998; Kreutz and others, 2000b). The most likely explanation is that both of these mechanisms are responsible to varying degrees for the observed relationship between ssSO$_4^{2-}$ and SIE.
Our study of $\text{xsSO}_4^{2-}$ does not reveal strong associations between longitudinal bands of SIE in the Amundsen–Ross region and SP-95 $\text{xsSO}_4^{2-}$ concentrations, but it does show a positive association between increased SP-95 $\text{xsSO}_4^{2-}$ concentrations and reduced SIE in the Weddell Sea region. The SP-95 SIE correlation of Meyerson and others (2002) is based upon smoothed (seven-point running mean) monthly MS and SIE values and an average SIE calculated from 185 to 245 $^\circ$ longitude; this may explain why we do not see similar correlation patterns in our study. The positive association we observe between increased SP-95 $\text{xsSO}_4^{2-}$ concentrations and reduced SIE in the Weddell Sea region suggests that the source region for SP-95 $\text{xsSO}_4^{2-}$ is probably different to that of the West Antarctic cores in this study.

An important consideration on the sulfur budget of West Antarctica is the effect of coastal polynyas. Three of the four most productive Antarctic polynyas surround West Antarctica, and the dominant polyna with respect to total area-weighted production is in the Ross Sea, accounting for half of the total polyna production on the entire Antarctic continental shelf (Arrigo and Van Dijken, 2003). The peak production in January averaged over all polynya waters is more than three times higher than the average for the entire offshore Southern Ocean (Arrigo and Van Dijken, 2003). As a result, polynyas may be a significant source of both $\text{ssSO}_4^{2-}$ (in winter) and $\text{xsSO}_4^{2-}$ (in summer) to West Antarctic sites.

**Background sulfate concentrations**

There are no significant trends apparent in the robust spline-smoothed $\text{ssSO}_4^{2-}$ concentrations over the last 200 years (Fig. 8). In a previous study (Dixon and others, 2004) we showed that a significant rise in background $\text{xsSO}_4^{2-}$ concentrations occurs from 1940 to the present in central

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Fig. 6. Correlations between annually averaged sea-ice extent and excess sulfate. All plotted sites represent correlations above 95% significance. A ‘+’ indicates a positive correlation and a ‘–’ indicates a negative correlation for each associated ice-core site. Latitudinal position of text has no significance. RA, RB and RC represent core sites RIDS-A, RIDS-B and RIDS-C, respectively. SD, CWA, CWD and SP represent SDM-94, CWA-A, CWA-D and SP-95 respectively. Map created using the RAMP digital elevation model (Liu and others, 2001).
West Antarctic ice-core sites (00-1, 00-4, 00-5, RIDS-A, RIDS-B and RIDS-C; Fig. 8). We argued that the rise could not be attributed to anthropogenic activities since it does not show up in all our high-elevation xsSO$_4^{2-}$ concentration records. Here we suggest that the 1940 xsSO$_4^{2-}$ rise cannot be attributed to changes in sea-ice extent since xsSO$_4^{2-}$ concentrations at sites 00-5, RIDS-B and RIDS-C are not statistically related to SIE (in the Ross, Amundsen and Bellingshausen Seas) above 95% significance, and sites 00-1, 00-4 and RIDS-A are not related to SIE (in the Ross, Amundsen and Bellingshausen Seas) above 99% significance. Figures 6 and 7 show that the core sites displaying the strongest xsSO$_4^{2-}$ association with SIE are SDM-94 and 01–3; conversely sites 00-4, RIDS-A and CWA-D display the strongest ssSO$_4^{2-}$ association with SIE. This suggests that central West Antarctica is not significantly affected by lower-tropospheric coastal air masses during the summer months but is significantly affected by these air masses during the winter period.

A study by Kaspari and others (2004) shows that central West Antarctic precipitation is statistically linked to the mid–low latitudes. This may suggest that the 1940 rise in xsSO$_4^{2-}$ is related to a change in production in the mid–low latitudes and/or increased transport from the mid–low latitudes to central West Antarctica.

**CONCLUSIONS**

In this study, we present the ssSO$_4^{2-}$ and xsSO$_4^{2-}$ records from 16 sub-annually resolved ice cores from West Antarctica. There are several sources and transport pathways of ssSO$_4^{2-}$ and xsSO$_4^{2-}$ and these vary from site to site and can only be resolved from a multiple core study.

Linear correlations between SIE and the ssSO$_4^{2-}$ and xsSO$_4^{2-}$ records from 15 of the cores in this study reveal that for several sites ssSO$_4^{2-}$ concentrations are higher with increased SIE, and xsSO$_4^{2-}$ concentrations are higher when SIE is decreased. It is important to note that although our results demonstrate a strong association between SIE and
SO$_4^{2-}$ concentrations in West Antarctica, they do not necessarily imply direct causal links. The two parameters (SIE and SO$_4^{2-}$) may be teleconnected to a third parameter that forces both simultaneously. Our SIE–ssSO$_4^{2-}$ association supports the concept that frost flower growth on sea ice may be an important source of ssSO$_4^{2-}$ aerosol to inland West Antarctic sites as noted by Rankin and others (2002) and Kaspari and others (2005). Conversely, our SIE–xsSO$_4^{2-}$ association suggests that during periods of decreased SIE in the Bellingshausen–Amundsen–Ross region, more xsSO$_4^{2-}$ is deposited in West Antarctica. This latter result does not agree with the results of previous studies that find a positive association between elevated MS concentrations and increased SIE (Welch and others, 1993; Curran and others, 2003) but it is consistent with the observations of Peel and others (1996) who find that extensive sea-ice cover tends to suppress emissions of DMS. The association between SIE and SP-95 xsSO$_4^{2-}$ in this study shows that the SP-95 site receives more xsSO$_4^{2-}$ when SIE in the Weddell region is decreased, the opposite relationship to our West Antarctic sites that receive more xsSO$_4^{2-}$ when SIE in the Bellingshausen–Amundsen–Ross region is decreased.

The out-of-phase behavior between SIE in the Weddell region and the rest of Antarctica is a common pattern for Southern Ocean sea ice and is evident in our SIE–SO$_4^{2-}$ associations. It is most likely related to the structure of the Antarctic dipole (Yuan and Martinson, 2001) and it highlights the strong links between Antarctic climate and the climate of the tropical and mid-latitude Southern Hemisphere. Yuan and Martinson (2000) found consistent and statistically significant teleconnection patterns linking Antarctic SIE variations (including an out-of-phase relationship between Pacific and Atlantic polar regions) to those of mid- and low-latitude climate that are verified by our study.

The 1940 rise in xsSO$_4^{2-}$ background concentrations in our central West Antarctic ice cores cannot be attributed to changes in SIE. The most likely explanation for this trend is an increase in xsSO$_4^{2-}$ production in the mid–low latitudes around 1940 and/or an increase in transport efficiency from the mid–low latitudes to central West Antarctica at that time.

The influence of coastal polynyas on the West Antarctic SO$_4^{2-}$ budget is of utmost importance to the understanding and interpretation of ice-core records. Future work should focus on the associations between summer and winter polynya activity and the ssSO$_4^{2-}$ and xsSO$_4^{2-}$ time series in ice cores, particularly from western West Antarctica.

REFERENCES


(AUTHOR: Is this the correct reference?)


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