Spatial variability of Antarctic surface snow glaciochemistry: implications for palaeoatmospheric circulation reconstructions

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Abstract: Ice core glaciochemical records provide detailed information on past changes in atmospheric chemical composition and circulation, which is essential for understanding the timing and phasing of climatic change in different regions. Atmospheric circulation reconstructions based on these records require knowledge of modern chemical concentration controls (chemical source, transport pathway and strength) and spatial variability. To gain insight into these processes, glaciochemical data collected during reconnaissance drilling in West Antarctica combined with all other existing Antarctic surface snow glaciochemical records are examined for trends in chemical concentration vs distance inland, elevation, and accumulation rate. Snowpit data from inland West Antarctica displays significant spatial variability, suggesting complex patterns of atmospheric circulation and moisture transport in the region. Siple Dome sea-salt and methanesulphonic acid (MSA) concentrations are similar to coastal sites, suggesting enhanced advection of marine air masses to the site. Statistical analysis of a 110-year high-resolution Siple Dome ice core record confirms that strong lower tropospheric circulation dominates the region, which is most likely related to the strength of the Amundsen Sea low pressure system. An atmospheric circulation reconstruction based on the ice core glaciochemical data displays significant interannual and decadal-scale variability, but there is no overall trend in atmospheric circulation strength at Siple Dome in the past 110 years.

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Introduction

Polar ice cores have proven to be valuable records of climatic change, illustrating both anthropogenic and natural forcings on the global climate system (e.g. Dansgaard & Oeschger 1989, Mayewski et al. 1994). In particular, glaciochemical records provide a unique resource for examining changes in the sources, pathways, and distribution of chemical species in the atmosphere (Mayewski et al. 1993). Several ice cores have been recovered and analysed for soluble ionic chemistry in Antarctica (Fig. 1). Time-series records from these cores have been used to interpret past atmospheric composition, transport, and sources over periods as long as several glacial/interglacial transitions (e.g. De Angelis et al. 1984, Palais & Legrand 1985, Mayewski et al. 1996), and document significant decadale scale variability in chemical composition during the last few centuries (Mayewski & Lyons 1982, Mosley-Thompson 1992, Welch et al. 1993). Two sites in West Antarctica (Siple Dome and inland West Antarctica) have been identified as locations for new US projects intended to provide well-dated, high resolution, long (100 000 year) ice core records that will be used to answer the following central questions,

1) how do rapid global climate changes occur? and

2) how will the potentially unstable West Antarctic ice sheet affect future sea level rise? (WAIS Document 1995).

In preparation for these projects, snowpit and shallow ice core glaciochemical data were collected from Siple Dome (Mayewski et al. 1995) and inland West Antarctica (Kreutz et al. 1996) (Fig. 1).

In order to make interpretations of past environmental conditions using glaciochemical data from Siple Dome and inland West Antarctica, we must first understand the major controls on modern surface snow chemistry in these regions. Spatial and temporal variability of atmospheric circulation, sea-ice extent, ocean productivity, and other factors play an important role in determining chemical concentrations at a particular site (Peel & Mulvaney 1992, Legrand et al. 1991).

In the absence of long-term meteorological and atmospheric chemistry monitoring at a site, controls on chemical concentrations must be investigated using other methods. One such method is to study the modern spatial distribution of chemical species over all of Antarctica and identify differences in chemical concentrations based on physical parameters (i.e. distance inland, elevation, and accumulation rate). In this way, an individual site or region can be compared to overall
trends to indicate dominant glaciochemical controls. Recently, Mulvaney & Wolff (1994, and references therein, hereafter referred to as MW) compiled selected Antarctic surface snow chemistry data to examine spatial variability on a continent-wide scale. Relationships in sea-salt (ss) (i.e. Na\(^+\), Cl\(^-\)), non-sea-salt (nss) SO\(_{4}^{2-}\), and NO\(_{3}^{-}\) concentrations versus elevation and distance from the coast, previously shown to exist on a regional basis (e.g. Herron & Langway 1979, Herron 1982, Legrand & Delmas 1985), were found to be the same on a continental scale. The effect of accumulation rate on nss SO\(_{4}^{2-}\) concentration was shown to be minimal and NO\(_{3}^{-}\) concentration was shown to decrease with increased accumulation rate. Trends such as these can be used to examine the major controls (i.e. chemical source area, tropospheric vs. stratospheric transport) on surface snow glaciochemistry at Siple Dome and inland West Antarctica.

Major ionic species (Ca\(^{2+}\), K\(^{+}\), Mg\(^{2+}\), NH\(_{4}^{+}\)) and methanesulphonic acid (MSA), which MW did not include in their compilation are important proxy indicators of atmospheric transport pathways and source areas. Ca\(^{2+}\), K\(^{+}\), and Mg\(^{2+}\) concentrations in Antarctic snow and ice, a portion of which are derived from terrestrial dusts, have been used to study transport from areas of exposed bedrock in Antarctica (Welch 1993) and South America (De Angelis et al. 1992). The often dominant fraction of these species, derived from sea salt, can indicate changes in atmospheric transport strength and sea-ice cover (Mayewski et al. 1994). MSA concentrations in snow and ice can be a proxy indicator of sea ice extent (Welch et al. 1993), dimethylsulphide (DMS) emissions (Legrand et al. 1991), and ocean productivity (Gibson et al. 1990). MSA may also be related to low latitude climatic events such as the El Niño–Southern Oscillation (ENSO) (Legrand & Feniet-Saigne 1991). In addition, the usefulness of a full suite of major ions (Na\(^{+}\), Ca\(^{2+}\), Mg\(^{2+}\), K\(^{+}\), NH\(_{4}^{+}\), Cl\(^-\), NO\(_{3}^{-}\), and SO\(_{4}^{2-}\)) in determining seasonal deposition patterns, acid/base relationships, and natural sources (e.g. sea salt, volcanoes, biogenic activity, nitrogen fixation) has been demonstrated by Legrand & Delmas (1984).

To examine the major atmospheric controls on glaciochemical concentrations at Siple Dome and inland West Antarctica, a complete evaluation of existing glaciochemical data over all of Antarctica must first be made. Therefore, this paper will build upon the compilation of MW by examining the spatial distribution of the full suite of major ions plus MSA, and by adding snowpit glaciochemical data not used in their study or collected since their study (e.g. South Pole (Whitlow et al. 1992), Dominion Range (Mayewski et al. 1995a), Taylor Dome (Welch 1993), Newall Glacier (Welch 1993)) to provide more extensive spatial coverage. Using this expanded database, trends in each chemical species distribution versus elevation and distance from the coast, as well as the dependence of species concentration on accumulation rate are examined. Based upon these relationships, new glaciochemical data from West Antarctica is examined relative to other Antarctic sites. In this way, atmospheric transport pathways, transport strength, and chemical source areas for Siple Dome and inland West Antarctica can be investigated, thus providing important information for interpreting deep ice core
VARIABILITY OF SNOW GLACIOCHEMISTRY

Chemical sources and input timing

The chemical composition of the Antarctic atmosphere and precipitation consists of various soluble and insoluble impurities. These impurities are introduced to the atmosphere either directly (as aerosols) or produced in the atmosphere along various oxidation pathways involving trace gases mainly derived from the sulphur, nitrogen, halogen and carbon cycles (Barrie & Delmas 1994). Under present climatic conditions, soluble species dominate the impurity content of Antarctic snow (e.g. Legrand & Delmas 1984, Legrand 1987). Sources and input timing of these soluble major ionic impurities can be summarized as follows (Legrand & Delmas 1984, Legrand 1987, MW, Legrand & Mayewski 1997):

1) Seawater ions (a portion of Na+, Mg2+, K+, Ca2+, Cl−, SO4^{2−}). Aerosol and surface snow seawater concentrations generally peak in winter due to increased storm intensity and/or frequency (i.e. Whitlow et al. 1992, Wagenbach 1996).

2) H2SO4 and methanesulphonic acid (MSA), both derived from the oxidation of marine biogenic emissions of dimethylsulphide (DMS). The annual cycle of both species peaks in summer, corresponding to maximum biologic productivity (Wagenbach 1996). In addition, volcanic emissions produce sporadic inputs of H2SO4 (and may also contribute to background levels in some areas).

3) HNO3, likely derived from the stratosphere and from tropical lightning (Legrand & Kirchner 1990, Mulvaney & Wolff 1993). Sources for another nitrogen-bearing compound, NH4+, are less clear but may involve a combination of continental and local (i.e. penguin colonies) biogenic sources (Wagenbach 1996). In most Antarctic regions, concentrations of both species peak in summer.

4) Terrestrially-derived salts (a portion of Ca2+, Mg2+, and Na+). Deposition in interior regions is likely from long-travelled crustal aerosols, however areas of exposed bedrock can affect the chemistry of local surface snow (Welch 1993). A seasonal pattern of deposition is usually unclear, but in some areas has been shown to peak in winter (Welch 1993).

Methods

Surface snow chemistry data

Surface snow chemistry data collected since the International Geophysical Year (IGY, 1957–58) in Antarctica were compiled

Fig. 2. Surface snow chemistry sites in Antarctica. a. All sample sites with surface snow glaciochemical data, b. sites with glaciochemical data representing more than one year of snow deposition, c. sites with glaciochemical data covering the time period 1970–75, d. sites with glaciochemical data covering the time period 1980–85. Solid lines represent traverse routes which contain several individual sample sites, while dots represent a single sample site.
into a database using certain criteria. First, sample collection and analytical techniques have evolved significantly in the past 40 years, such that the quality of trace concentration ion data has likely improved. We have therefore used data produced by either ion chromatography or atomic-absorption methods, and where appropriate sample collection techniques are believed to have been used. There are, however, sites where data exists which does not meet these criteria. We have accepted these data, but caution that the accuracy is uncertain. Second, we seek to use data which are representative of a particular site. Such data must average more than one year of deposition, as there can be large seasonal variations as well as post-depositional effects. Figure 2a shows the distribution of all samples collected and analysed for major ion content in Antarctica. Unfortunately, data from several of these sites and traverse route cannot be used (Fig. 2b) in our analysis because they represent only near surface snow. Different sampling methods (snowpits, shallow cores, and surface snow collection) were used to collect the samples used in this study. Therefore, data from each individual site do not necessarily cover the same time period. In order to test whether modern surface snow data covering different time periods can be compared, we examined three time intervals: 1970–75 (Fig. 2c) and 1980–85 (Fig. 2d), and the full database, which covers c. 1960–95 (Fig. 2b). The two 5 year time intervals were chosen due to the abundance of sampling during those years, and the predominance of 3–5 year averaging in published surface snow data. Comparison of the relationships between snow chemical concentration, distance inland, elevation, and accumulation rate reveals that the overall trends are nearly identical during each of the three periods. Therefore, we choose to present analysis of the entire surface snow glaciochemical data-set, which covers c. 1960–95.

Because published elevation information was not provided for all sampling sites, estimates were made using the United States Geological Survey Satellite Image Map of Antarctica (1996). Distance to coast values were calculated ignoring sea ice extent, as sea ice is highly variable in extent and timing, and often contains thin areas and shoreleads (MW). Accumulation rate reveals that the overall trends are nearly identical during each of the three periods. Therefore, we choose to present analysis of the entire surface snow glaciochemical data-set, which covers c. 1960–95.

To compare the spatial variability of surface snow chemistry on a regional level, areas with a high number of closely spaced sample sites were grouped together. Eight groupings were created according to their geographical area: Queen Maud Land, East Antarctic Plateau, Wilkes Land, Victoria Land, West Antarctic Ice Sheet, Antarctic Peninsula, Ronne Ice Shelf, and the Ross Ice Shelf. When chemical species are compared to various physical parameters (see sections below), it is found that trends are similar in each geographical area. Our findings agree with those previously reported by MW, who found that regional and continental-scale trends in certain species (Cl and nssSO\textsubscript{4}\textsuperscript{2-}) were similar. However, in this study we examine an additional six species, and find that trends are similar in each geographical region for these species as well. For clarity we present the data broken into two main regions (East and West Antarctica), with inland West Antarctic and Siple Dome data marked independently (Figs. 3–5).

### Influence of accumulation rate, distance inland, and elevation on species concentration

The major factors likely to influence species concentrations are the distance inland, elevation, and accumulation rate (MW, Yang et al. 1996). Several secondary factors, such as temperature, sunlight received, surface wind speeds, and seasonality of deposition, also likely affect average concentrations, albeit to a lesser degree. A problem with focusing on the three major factors is that they often vary together in Antarctica. For example, across most of Antarctica, as distance inland increases, elevation also increases while accumulation rates decrease (Giovinetto et al. 1990). To properly evaluate the relative contribution of each factor (distance inland, elevation, and snow accumulation rate) to species concentration, we use multiple linear regression analysis (Table I). Because the variance of several species concentration is not constant across the range of physical parameters considered, several species have been investigated using the log of concentration (Table I).

<table>
<thead>
<tr>
<th>Species</th>
<th>Distance</th>
<th>Distance\textsuperscript{2}</th>
<th>Elevation</th>
<th>Acc. Rate</th>
<th>$r^2$</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na\textsuperscript{+} (log)</td>
<td>-4.11</td>
<td>4.01</td>
<td>-10.01</td>
<td>0.27</td>
<td>0.54</td>
<td>178</td>
</tr>
<tr>
<td>Cl\textsuperscript{-} (log)</td>
<td>-4.21</td>
<td>4.39</td>
<td>-10.24</td>
<td>-0.07</td>
<td>0.51</td>
<td>189</td>
</tr>
<tr>
<td>Mg\textsuperscript{2+} (log)</td>
<td>-1.74</td>
<td>1.87</td>
<td>-6.76</td>
<td>-0.54</td>
<td>0.37</td>
<td>120</td>
</tr>
<tr>
<td>K\textsuperscript{+} (log)</td>
<td>-3.36</td>
<td>3.05</td>
<td>-5.54</td>
<td>-1.06</td>
<td>0.42</td>
<td>98</td>
</tr>
<tr>
<td>Ca\textsuperscript{2+} (log)</td>
<td>-4.25</td>
<td>3.20</td>
<td>-2.47</td>
<td>-2.53</td>
<td>0.35</td>
<td>84</td>
</tr>
<tr>
<td>NH\textsubscript{4} (log)</td>
<td>0.82</td>
<td>-1.00</td>
<td>-1.92</td>
<td>0.12</td>
<td>62</td>
<td></td>
</tr>
<tr>
<td>NO\textsubscript{3} (log)</td>
<td>-0.23</td>
<td>-0.41</td>
<td>-2.36</td>
<td>0.05</td>
<td>167</td>
<td></td>
</tr>
<tr>
<td>nssSO\textsubscript{4} (log)</td>
<td>-2.60</td>
<td>3.27</td>
<td>-1.69</td>
<td>-0.83</td>
<td>0.02</td>
<td>187</td>
</tr>
<tr>
<td>MSA (log)</td>
<td>0.02</td>
<td>-2.65</td>
<td>0.44</td>
<td>0.28</td>
<td>55</td>
<td></td>
</tr>
</tbody>
</table>
the apparent dilution effect seen in $Ca^{2+}$ concentrations can be explained in part by a source effect.

For species derived from marine sources, distance inland and elevation are expected to be the main controls on snow concentration. Accordingly, seasalt species have the most pronounced relationships with these two variables (Table I and Figs 4 & 5). Of those species, $Na^+$ and $Cl^-$ display the strongest association with elevation (Table I). Several authors have previously noted this trend in surface snow samples collected along coast to inland traverses (Herron 1982, Warburton & Linkletter 1978, Delmas & Boutron 1980, Minikin et al. 1994, MW). As suggested by Legrand & Delmas (1985), fall-out of coarse seasalt aerosols as an air mass moves inland appears to be the main deposition

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**Fig. 3.** Major ion concentrations in Antarctic snow vs accumulation rate.
mechanism. Other species with seasalt contributions (Ca$^{2+}$, K$^+$, and Mg$^{2+}$) also display a significant decreasing relationship with increasing distance inland. In all species (except Ca$^{2+}$), the decreasing trend versus elevation is significant at a higher confidence level than that vs distance inland. This is most likely due to steep coastal topography in East Antarctica and the Antarctic Peninsula, where sites are relatively close to the coast yet are at high elevation. Likewise, in areas of flat topography such as ice shelves, distance inland is less of a control than elevation (Herron 1982, Minikin et al. 1994).

When residual values from the multiple regression model are evaluated, a quadratic effect is apparent (Table I). In all cases, results suggest that beyond a threshold distance inland (c. 500 km), concentrations essentially remain nearly constant.
This effect creates the quadratic effect noted, which is opposite to the negative relationship observed between concentration and distance inland in the initial 500 km from the coast. This result implies that a majority of seasalt and continental aerosol deposition occurs in the zone of steep coastal topography, and once an air mass has reached the polar plateau aerosol transport is mainly controlled by wind speed.

Of the sulphur species, only nssSO$_4^{2-}$ concentrations have been previously studied versus accumulation rate. Both Herron (1982) and MW concluded that nssSO$_4^{2-}$ concentrations were independent of accumulation rate in Antarctic snow. Our compilation displays similar results (Fig. 3), with no significant statistical relationship between nssSO$_4^{2-}$ concentration and accumulation rate (Table I). These findings
suggest that either there is inefficient scavenging of \( \text{nssSO}_4^{2-} \) aerosols as they move inland, or an upper tropospheric source of \( \text{nssSO}_4^{2-} \) at high elevation sites exists. Likewise, MSA concentrations have no significant statistical relationship with accumulation rate (Table I).

As with seasalt species, MSA concentrations are expected to decrease with increasing distance inland and elevation due to the marine source of MSA. An overall decreasing trend is apparent in the data for both distance inland and elevation (Figs 4 & 5). However, the decrease is not exponential in nature as it is for seasalt (\( \text{Na}^+ \) and \( \text{Cl}^- \)) species, nor is there a significant relationship between MSA concentration and distance inland. While there is a significant negative relationship between MSA concentrations and elevation, MSA concentrations at high elevation sites (i.e. South Pole) are roughly comparable to those at coastal sites. Legrand & Feniet-Saigne (1991) have noted a correlation between time-series firn core MSA concentrations at South Pole and El Niño–Southern Oscillation (ENSO) events. This finding implies that there may be transport of MSA from low-latitudes through the upper troposphere to high elevation regions of Antarctica.

Previous work (Delmas & Boutron 1978, Herron 1982, MW) suggests \( \text{nssSO}_4^{2-} \) concentrations are independent of distance inland and elevation. Figures 4 & 5 display a similar situation, however there is a significant negative relationship between \( \text{nssSO}_4^{2-} \) concentrations and distance inland. As with seasalt species, a quadratic effect is noted in the \( \text{nssSO}_4^{2-} \) / distance inland analysis, suggesting that transport from marine regions is a major \( \text{nssSO}_4^{2-} \) source. There is no significant statistical relationship between \( \text{nssSO}_4^{2-} \) and elevation. If an upper tropospheric source is delivering MSA to high elevation sites, transport of \( \text{nssSO}_4^{2-} \) from lower latitude sources may also occur, and hence high elevation sites display roughly comparable \( \text{nssSO}_4^{2-} \) concentrations.

Previous studies in Antarctica have focused on the relationship between \( \text{NO}_3^- \) and accumulation rate, with different results. Herron (1982) and MW concluded that \( \text{NO}_3^- \) concentration decreased with increasing accumulation rate, while Legrand & Delmas (1986), Legrand (1987), and Legrand & Kirchner (1990) found \( \text{NO}_3^- \) concentrations to be independent of accumulation rate. Our analysis indicates a statistically significant inverse relationship between \( \text{NO}_3^- \) concentrations and accumulation rate (Table I). The high variability of \( \text{NO}_3^- \) concentrations at low accumulation sites (Fig. 3) may suggest either post-depositional loss of \( \text{NO}_3^- \) (Mayewski & Legrand 1990, Dibb & Whitlow 1996), or a high proportion of dry deposition at these sites (MW).

\( \text{NO}_3^- \) concentrations have been shown to be independent of distance inland and elevation in previous work (Herron 1982, Legrand & Delmas 1985, Minikin et al. 1994). However, these studies were either regional in nature (i.e. Adélie Land and the Filchner–Ronne Ice Shelf), or contained few data points. In their continental-scale compilation, MW found that \( \text{NO}_3^- \) concentrations increased with elevation. Our analysis indicates no relationship between distance inland or elevation and \( \text{NO}_3^- \) concentration (Table I, Figs. 4 & 5). The lack of relationship with distance inland and elevation suggests that there is not a significant marine \( \text{NO}_3^- \) source. Instead, upper atmosphere (stratosphere and tropical lightning (Legrand & Kirchner 1990)) sources are more likely. As noted by MW, our understanding of deposition and subsequent re-emission of \( \text{NO}_3^- \), especially at high elevation Antarctic sites, is limited and needs to be improved.

There is no significant statistical relationship between \( \text{NH}_4^+ \) concentrations and any of the three physical parameters studied (Table I). This result makes distinguishing upper tropospheric from marine sources difficult with the present data set. We again note that \( \text{NH}_4^+ \) measurement in Antarctic snow is difficult due to low concentration and ease of contamination. A more thorough investigation of \( \text{NH}_4^+ \) sources in Antarctic snow will need to be made when additional \( \text{NH}_4^+ \) data are available.

**Interpretation of West Antarctic glaciochemical data**

In a previous section, relationships between the full major ion suite (plus MSA) and accumulation rate, distance inland, and elevation were investigated, helping to define chemical sources and the control that each of these factors have in determining chemical concentration. These relationships, developed on a continental scale, also provide a context into which data from inland West Antarctica and Siple Dome can be placed to investigate major controls on chemical concentrations at these sites.

**Inland West Antarctica**

During the 1995/96 field season, ice cores and 2 m snowpits were sampled at three sites along a 160 km traverse from Byrd Surface Camp (575–625 km inland, 1500–1800 m elevation, Fig. 1, Kreutz et al. 1996). Average chemical values from the inland West Antarctic (IWA) snowpits are presented in Table II. Mean ion concentrations in the three pits are similar, and consistent with values obtained by other studies in the Byrd Station area (Herron 1982, Langway et al. 1994) and areas on the East Antarctic polar plateau (e.g. Legrand & Delmas 1985). IWA snowpits group together with other sample sites of similar distance inland (Fig. 4) and elevation (Fig. 5) for all major ions and MSA. This suggests that, at least for the plateau sites studied to date, the major controls on surface snow glaciochemistry are similar on the West and East Antarctic polar plateaus. Seasalt and MSA values in IWA snowpits are considerably lower than at coastal sites, suggesting that the influence of marine air masses on this region of the polar plateau is reduced. Infrequent penetration of cyclonic systems, which carry coarse-mode seasalt aerosols to the polar plateau, has been found to occur mainly during winter at South Pole (Bodhaine et al. 1986). Time-series ice core records from Byrd Station display similar sporadic input of seasalt (Langway et al. 1994). \( \text{NO}_3^- \) and \( \text{nssSO}_4^{2-} \) values from IWA snowpits are...
Table 11. Summary of soluble ionic components in snowpits from Siple Dome and inland West Antarctica. All concentrations are in meq kg$^{-1}$.

<table>
<thead>
<tr>
<th>Component</th>
<th>Inland West Antarctica</th>
<th>Siple Dome</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RIDSA (2 m, 78°44'S 116°20'W, 150 km NE of Byrd Station)</td>
<td>Pit 94-1 (4 m, at drillsite)</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>mean 0.57 0.09 0.03 0.16 0.05 0.86 0.75 0.74 0.13</td>
<td>mean 5.59 0.16 0.16 19.68 0.20 8.18 0.64 2.02 0.27</td>
</tr>
<tr>
<td></td>
<td>s.d 0.54 0.03 0.03 0.15 0.04 0.68 0.56 0.46 0.09</td>
<td>s.d 5.67 0.14 0.16 16.65 0.20 7.04 0.40 2.80 0.33</td>
</tr>
<tr>
<td></td>
<td>median 0.39 0.08 0.02 0.12 0.04 0.63 0.66 0.63 0.10</td>
<td>median 4.23 0.14 0.12 16.54 0.16 6.73 0.52 0.96 0.16</td>
</tr>
<tr>
<td></td>
<td>RIDSB (2 m, 79°27.66'S 118°02.68'W, 70 km NE of Byrd Station)</td>
<td>Pit 94-2 (2 m, NW corner of grid)</td>
</tr>
<tr>
<td></td>
<td>mean 0.68 0.08 0.02 0.20 0.06 1.01 0.76 0.98 0.12</td>
<td>mean 7.10 0.14 0.20 2.05 0.23 10.98 0.58 1.71 0.35</td>
</tr>
<tr>
<td></td>
<td>s.d 0.52 0.04 0.02 0.16 0.04 0.63 0.30 0.62 0.12</td>
<td>s.d 7.27 0.08 0.21 1.95 0.23 10.89 0.35 3.35 0.60</td>
</tr>
<tr>
<td></td>
<td>median 0.52 0.07 0.02 0.14 0.05 0.85 0.72 0.84 0.07</td>
<td>median 4.69 0.13 0.14 1.57 0.17 7.80 0.51 0.52 0.13</td>
</tr>
<tr>
<td></td>
<td>RIDSC (2 m, 80°S 120°W, 3 km NE of Byrd Station)</td>
<td>Pit 94-3 (2 m, SW corner of grid)</td>
</tr>
<tr>
<td></td>
<td>mean 0.97 0.11 0.04 0.29 0.07 1.36 0.69 1.21 0.14</td>
<td>mean 5.80 0.16 0.15 1.60 0.34 8.95 0.72 2.35 0.37</td>
</tr>
<tr>
<td></td>
<td>s.d 0.94 0.04 0.03 0.28 0.06 1.17 0.30 1.05 0.15</td>
<td>s.d 4.91 1.14 0.12 1.34 0.28 6.85 0.40 3.43 0.40</td>
</tr>
<tr>
<td></td>
<td>median 0.61 0.10 0.03 0.18 0.04 0.96 0.66 0.93 0.09</td>
<td>median 4.27 0.13 0.14 1.57 0.17 7.80 0.51 1.36 0.25</td>
</tr>
<tr>
<td></td>
<td>Siple Dome</td>
<td>Pit 94-4 (2 m, NE corner of grid)</td>
</tr>
<tr>
<td></td>
<td>mean 5.65 0.14 0.13 1.62 0.17 7.93 0.67 2.07 0.30</td>
<td>mean 5.65 0.07 0.15 1.57 0.21 6.77 0.41 3.12 0.46</td>
</tr>
<tr>
<td></td>
<td>s.d 5.56 0.07 0.15 1.34 0.28 6.85 0.40 3.43 0.40</td>
<td>s.d 4.27 0.13 0.08 1.18 0.12 6.26 0.57 0.63 0.12</td>
</tr>
<tr>
<td></td>
<td>median 4.27 0.13 0.08 1.16 0.22 5.88 0.61 1.29 0.16</td>
<td>median 4.93 0.16 0.14 1.36 0.28 6.70 0.66 1.91 0.22</td>
</tr>
<tr>
<td></td>
<td>Pit 94-5 (2 m, SE corner of grid)</td>
<td>mean 3.82 0.05 0.10 0.93 0.22 4.46 0.33 2.09 0.23</td>
</tr>
<tr>
<td></td>
<td>mean 4.16 0.16 0.12 1.16 0.22 5.88 0.61 1.29 0.16</td>
<td>median 4.16 0.16 0.12 1.16 0.22 5.88 0.61 1.29 0.16</td>
</tr>
</tbody>
</table>

Fig. 6. Concentrations of nssSO$_4^{2-}$ and MSA in inland West Antarctic (IWA A–C) and Siple Dome (SDM 94–1) snowpits.
of the area (D.H. Bromwich, personal communication 1996), suggesting a sharp transition between maritime and continental air masses. The cloud gradient may be in part due to the presence of ice divide topography. Further evidence for ice divide effects on regional meteorology comes from accumulation rate data, which change significantly along the traverse route. Langway et al. (1994) determined an accumulation rate of 8 g cm\(^{-2}\) yr\(^{-1}\) at Byrd Station, based on a peak in beta radioactivity at 8.4 m. A beta profile from IWA A contains a peak at 14.5 m, suggesting an accumulation rate of 23 g cm\(^{-2}\) yr\(^{-1}\) (Kreutz et al. 1996). The glaciochemical and accumulation rate contrast between the sites suggests that there are significant differences in transport pathways and moisture input in the area.

**Siple Dome**

Sampling at Siple Dome (81.65°S, 148.81°W, 600 m elevation, 600 km inland, Fig. 1) included the recovery of four 2 m snowpits at the corners of a 10 km x 10 km grid centred on the geographic dome summit, and a 4 m snowpit at the shallow core (150 m) drill site (Mayewski et al. 1995). Snowpit

![Image](https://example.com/snowpit.jpg)  
**Fig. 7.** Major ion time-series from the upper 24 m of the 1994 Siple Dome ice core.

Empirical orthogonal function analysis

Given the high concentrations of seasalt in modern Siple Dome surface snow, changing seasalt concentrations in Siple Dome ice core time-series records may be used to document fluctuations in marine aerosol transport and hence lower tropospheric cyclonic frequency and/or intensity in the region.
through time. With this in mind, the upper 24 m of the Siple Dome ice core was sampled at 2 cm intervals to provide a high-resolution glaciochemical record of the last 110 years (Fig. 7). The core was dated using annual chemical signals (nssSO\textsubscript{4}\textsuperscript{2-}, NO\textsubscript{3}, and MSA), beta radioactivity measurements, and volcanic marker horizons. Overall, there are no distinct trends in any of the chemical species in the past 110 years. There is, however, considerable annual- and decadal-scale variability that will be investigated in future publications once a longer record is available. In addition, there are several prominent events present in each of the chemical records. One event that is particularly apparent is the large spike in seasalt species during 1933–35. This event is comprised of five data points in each seasalt species, all of which are in marine ratio. Therefore, we rule out contamination as a cause of this large spike. A more likely explanation for this event is prolonged intensification of storm activity in the region over the 1933–35 period.

Chemical signals contained in the 110-year ice core multivariate time-series data provide a signature of their source, transport, and deposition style. Therefore, significant information can be gained by exploring the variation and covariation of the individual chemical series to determine relationships that reflect the various ionic modes of production and transport. One tool commonly used to accomplish this is empirical orthogonal function (EOF) analysis (Peixoto & Oort 1992, Meeker \textit{et al.} 1995), that is based on principal component analysis of multivariate statistics. EOF analysis can be used for a number of investigations, including identification of relationships among ice core chemical records, which can be associated with climatic variables (e.g. Mayewski \textit{et al.} 1994, O’Brien \textit{et al.} 1995).

Results from EOF analysis on Siple Dome core data (using eight major species) are presented in Table III. The first EOF (EOF1) describes 50% of the total data-set variance, and accounts for >90% of principal seasalt species (Na\textsuperscript{+}, Cl\textsuperscript{-}, Mg\textsuperscript{2+}). Components of the EOF that explain a large proportion of the variance in a multivariate data-set usually have an important physical significance (Peixoto & Oort 1992). This result supports the hypothesis that the dominant control on Siple Dome glaciochemistry is the advection of marine air masses to the site. The second EOF (EOF2) primarily represents two species, nssSO\textsubscript{4}\textsuperscript{2-} and NO\textsubscript{3}, both of which are deposited mainly in late spring/summer based on comparison to stratigraphic and d\textsuperscript{18}O measurements. The input of nssSO\textsubscript{4}\textsuperscript{2-} most likely occurs through the lower troposphere, and is linked to enhanced summer ocean productivity (Whitlow \textit{et al.} 1992). Deposition of NO\textsubscript{3} is thought to be derived from multiple sources (most notably lightning and soil exhalation) and is transported to Antarctica through the upper troposphere/ lower stratosphere (Legrand & Delmas 1986). Therefore, EOF2 may represent the coeval summer influence of lower tropospheric input (ocean biogenic products) and upper atmosphere air masses (NO\textsubscript{3}) at Siple Dome. A significant fraction of NH\textsubscript{4} is represented by EOF3, which may indicate a separate source and/or transport pathway for NH\textsubscript{4}. EOF4 and EOF5 are loaded mainly with Ca\textsuperscript{2+} and K\textsuperscript{+}, most likely reflecting upper atmosphere (long-travelled continental dust) transport since there are no immediate local Ca\textsuperscript{2+} and K\textsuperscript{+} sources.

Although exact transport pathways to Siple Dome are still unknown, large scale atmospheric circulation patterns capable of transporting seasalt to Siple Dome are most likely related to the strength of the Amundsen Sea low pressure system. The Siple Dome EOF1 time-series (Fig. 8) therefore potentially provides a way to investigate changes in lower tropospheric transport strength and associated changes in the Amundsen Sea Low. Because EOF1 represents a large portion of the Na\textsuperscript{+}, Cl\textsuperscript{-}, Mg\textsuperscript{2+}, and K\textsuperscript{+} species, the time series EOF1 record (Fig. 8) closely matches the chemical time series. There is large interannual and decadal-scale variability over the past 110 years in the EOF1 record. The major increase in seasalt concentration during 1933–35 is also present in EOF1. Anomalously high d\textsuperscript{18}O values during 1933–35 were noted in Dolleman Island, James Ross Island, and Siple Station ice

![Fig. 8. EOF1 time-series from the upper 24 m of the 1994 Siple Dome ice core. The dashed line represents the raw EOF1 time-series (8–10 samples year\textsuperscript{-1}), and the dark line is an 11-point moving average.](image-url)
cores (Peel 1992, Mosley-Thompson et al. 1991), which also may be related to increased moisture transport produced by the deepening of the Amundsen Sea low. A factor of 3 increase in South Pole Cl, K, and Ca concentrations also occurred during 1933–35 (Herron 1980, E. Meyerson, personal communication 1997), which may indicate increased transport of long-travelled air masses to the site. Although the exact mechanisms responsible for synchronous atmospheric changes at these three sites are not yet apparent, these findings suggest that unique events in high-resolution Antarctic glaciochemical records can be used both as time-stratigraphic markers and to investigate major shifts in atmospheric circulation.

Assuming that the Siple Dome EOF1 record provides a proxy of marine cyclogenesis, there appears to be no significant trend in marine air mass advection or strength and position of the Amundsen Sea low over the last 110 years. This finding may be consistent with the lack of post-Little Ice Age (LIA) warming (1900 AD–present) noted in West Antarctic (Siple Station and James Ross Island) δ18O records (Mosley-Thompson et al. 1990). To fully investigate atmospheric changes during the LIA, records of at least 1000 years must be obtained to span the entire LIA interval (Kreutz et al. 1997).

Conclusions

Concentrations of seasalt species are strongly dependent on elevation, and to a lesser degree on site distance from the coast. In areas of small topographic relief (i.e. ice shelves) distance inland is the major control on snow seasalt concentrations. MSA concentrations display a similar decrease with increasing elevation. However, the decrease in concentration is not as dramatic as that seen in seasalt species, nor is there a significant relationship between MSA concentrations and distance inland, raising the possibility that there is an additional input of MSA at high elevation sites. It has been suggested that this source may be transport of MSA from low latitudes through the upper troposphere (Legrand & Feniet-Saigne 1991). On the other hand, nssSO42− concentrations are independent of elevation, yet statistically linked to distance inland. While this finding argues for a high-latitude marine source for nssSO42−, it does not preclude long range transport of this species to high elevation sites. NO3− concentrations are independent of distance inland and elevation. More work is clearly needed on the deposition and preservation of NO3− in Antarctic snow and ice records.

Analysis of species concentration and accumulation rate data does not reveal a statistically significant relationship between the two variables for most species, suggesting that there is no appreciable dilution effect. Two species that do demonstrate significant relationships with accumulation rate are NO3− and Ca2+. The relationship noted in NO3− may be due to post-depositional loss at low accumulation rate sites, while the Ca2+ relationship is likely related to sample collection in areas proximal to large Ca2+ sources. Therefore, in general it appears that concentration measurements rather than flux calculations are sufficient to relate changes in chemical timeseries records to changes in source and transport strength.

By placing new West Antarctic glaciochemical data in context with other Antarctic sites, we provide a method for studying major controls on surface snow chemistry in these regions. Snowpit data from three new inland West Antarctic locations are similar in mean concentration to previous work in the region and other locations on the East Antarctic polar plateau. However, there is significant spatial variability in the chemical profiles, and well-preserved annual chemical signals are present in only one pit (IWA C). Field observations indicate the possible presence of an ice divide in the area. If such a divide exists, it may also have affected the atmospheric circulation and glaciochemistry in the area. There is a significant change in accumulation rate in the region, which may correspond to an observed gradient in cloud cover.

Surface snow glaciochemistry at Siple Dome is anomalous in that snowpit seasalt and MSA concentrations are much higher than other sites of a similar distance inland. This suggests that lower tropospheric circulation is enhanced in the Siple Dome area, with stronger advection of marine air masses to the site. Transport of seasalt to Siple Dome is most likely related to the strength and position of the Amundsen Sea low pressure system. Statistical (EOF) analysis of the upper 24 m (last 110 years) of the Siple Dome ice core reveals that seasalt species dominate EOF1, representing almost 60% of the overall glaciochemical time series variance. EOF1 time-series over the past 110 years contain significant interannual and decadal-scale variability, however there is no general trend in the record. This suggests that the strength of the Amundsen Sea low has not changed significantly over the past 110 years.

Sites with surface snow chemistry data in Antarctic are largely confined to the coastal region. Large portions of both the West and East Antarctic polar plateau have received little or no attention. Until more work is done in these regions, it will be difficult to accurately characterize the snow chemical spatial distribution and climatic change on the polar plateau. In particular, West Antarctica, already known to be the most climatologically and glaciologically dynamic area of the continent, is shown here to be a region of significant glaciochemical and accumulation rate variability. Further sampling is needed to discern the dominant modern and pre-observational transport pathways to Siple Dome and inland West Antarctic sites. Choosing an appropriate location for future inland West Antarctic deep ice coring will depend on knowledge of transition regions between maritime and continental climates. Furthermore, accurate interpretation of any deep core data from West Antarctica will benefit from an improved understanding of the controls on glaciochemistry over the entire region.

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References


