2004

A 200-year Sulfate Record from 16 Antarctic Ice Cores and Associations with Southern Ocean Sea Ice Extent

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Recommended Citation

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A 200-YEAR SULFATE RECORD FROM 16 ANTARCTIC ICE CORES AND ASSOCIATIONS WITH SOUTHERN OCEAN SEA ICE EXTENT

By

Daniel A. Dixon

B.Sc. University of Southampton, 2000

A THESIS
Submitted in Partial Fulfillment of the
Requirements for the Degree of
Master of Science
(in Quaternary and Climate Studies)

The Graduate School

The University of Maine

August, 2004

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A 200-YEAR SULFATE RECORD FROM 16 ANTARCTIC ICE CORES AND ASSOCIATIONS WITH SOUTHERN OCEAN SEA ICE EXTENT

By Daniel A. Dixon

Thesis Advisor: Dr. Paul A. Mayewski

An Abstract of the Thesis Presented
in Partial Fulfillment of the Requirements for the
Degree of Master of Science
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Data from sixteen, 50m- to 115m-deep, sub-annually dated ice cores are used to examine the recent spatial and temporal concentration variability of sea salt (ss)SO_4^{2-} and excess (xs)SO_4^{2-} over West Antarctica for the last 200 years. The preservation of seasonal layers throughout the length of each record results in a dating accuracy of better than one year based on known global scale volcanic events. A dual transport source for West Antarctic ssSO_4^{2-} and xsSO_4^{2-} is observed: lower tropospheric for areas below 1000m elevation and mid-upper tropospheric/stratospheric for areas located above 1000m. The xsSO_4^{2-} records with volcanic peaks removed do not display any evidence of an anthropogenic impact on West Antarctic SO_4^{2-} concentrations but do reveal that a major climate transition takes place over West Antarctica ~1940.

Global-scale volcanic eruptions appear as significant peaks in the robust spline residual xsSO_4^{2-} records from sites located above 1000m elevation but do not appear in the residual records from sites located below 1000m. These high-resolution records show

that the controls on ss- and $xsSO_4^{2-}$ deposition vary from site to site and can only be resolved using the type of framework of ice core records available from the International Trans-Antarctic Scientific Expedition (ITASE). Sources of SO_4^{2-} from Ross Sea sea ice and Ross Sea Polyna primary production, combined with transport over the Ross Ice Shelf via frequent cyclogenesis, significantly increases the net transport of $ssSO_4^{2-}$ and $xsSO_4^{2-}$ aerosols to low elevation sites in western West Antarctica.

Based on linear correlation analysis, $ssSO_4^{2-}$ concentrations are higher when sea ice extent (SIE) is greater, and $xsSO_4^{2-}$ concentrations are higher when SIE is lesser. The South Pole receives the majority of its $xsSO_4^{2-}$ from different sources than the rest of West Antarctica, and the Weddell region may be a significant source of aerosol chemistry for eastern West Antarctic sites.

ACKNOWLEDGEMENTS

Thanks to my entire family for being so strong and so supportive. Although you have all been an ocean away, your love and strength have always kept me going and allowed me to fulfill this major goal in my life.

Many, many thanks go out to my advisor, Dr. Paul Mayewski, for providing me with the chance to study in the United States and ultimately Antarctica. The past three years I have spent in the U.S. have been among the best of my life, and recollections of my time in Antarctica will be forever cherished.

Thanks to the Office of Polar Programs, National Science Foundation, 109th Air National Guard, Ice Core Drilling Services, Raytheon Polar Services and Glacier Data for making it all happen and getting us home safely.

Thanks to my committee members, Kirk Maasch, Gordon Hamilton and Karl Kreutz, for providing help and support in all matters.

I would like to thank all the great people who traversed West Antarctica with me during the field seasons of 2001, 2002 and 2003. There are too many names to mention but I thoroughly enjoyed working with all of you. I would also like to thank Ann Zielinski for keeping the daily logs up to date in such a fine fashion.

Thank you to everyone in the Climate Change Institute: Sharon Sneed and Mike Handley for working so hard to get these cores melted and analyzed; Debbie, Nancy and Betty for being my surrogate "Moms"; Andrei Kurbatov, Eric Meyerson and Susan Kaspari for all your helpful comments, our discussions are always enlightening; and

“Mad Props” to Dr. Vandy Blue Spikes, thanks for all my gridding lessons and for being a good friend.

Last, but definitely not least, thanks a million to my lovely new wife, Erika, for proofreading my thesis work, sitting through many practice presentations, and for being generally sesquinormal. Who would have thought our first meeting at the Bear Brew would turn out to be so serendipitous?

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Chapter 1

INTRODUCTION

Since the beginnings of civilization humans have always felt the need to understand their surroundings, not just through natural inquisitiveness, but in order to better control their destiny and enhance chances of survival. Recent discoveries have shown that major changes in Earth's climate system can occur in a matter of decades [Mayewski and others, 1993a; O'Brien and others, 1995]. As a result the scientific community is striving to understand these changes and hopes to be able to predict rapid climate change events in order to lessen their harmful impact on life.

The earth's climate is essentially a dynamic, heat-driven, multi-component, coupled system. The heat driving the climate system comes almost entirely from the Sun. Only ~2/3 of the Sun's total energy reaching the earth is absorbed, the remaining ~1/3 is reflected back into space (albedo) by clouds, ice, atmosphere, water, etc. Antarctica plays a very important role in global climate variability and change, especially in the Southern Hemisphere. The higher latitudes of the Southern Hemisphere, including the ice sheet and the surrounding sea-ice zone, constitute one of the two primary areas on Earth where there is net loss of energy from the atmosphere to space. Studies with global climate models (GCM) have suggested that both Southern Hemisphere and global atmospheric circulations are sensitive to modest changes in the temperature of the Antarctic atmosphere [Bromwich & Parish, 1998].

Ice Core records from Antarctica are becoming increasingly useful as a proxy for climate change due to their virtuous geographical position and their clean atmospheric environment [Jouzel and others, 1983; Mayewski and others, 1995; in press; Cullather and others, 1996; Kreutz and others, 1997; 2000a; Meyerson and others, 2002]. The fragility of the polar atmosphere, accompanied by the snow accumulating beneath, makes it a perfect long-term recorder of atmospheric changes. Ice cores already recovered from Antarctica go back tens to several-hundred-thousand years into Earth's climatic history. However, the spatial distribution of the shallow cores does not allow for objective analysis of spatial variability or decadal-scale variability, especially during the pre-industrial era. The deep cores are an invaluable means of discovering the intimate workings of the earth's atmosphere over millennial to decadal scales, but they are too widely spaced geographically to determine spatial variability.

The International Trans-Antarctic Scientific Expedition (ITASE) is designed to fill in the void that the many shallow and the very few deep ice cores available leave in our understanding of Antarctic climate. ITASE is a coordinated effort by many nations to determine the spatial variability of Antarctic climate and the environmental variability of Antarctica over the last 200+ years.

In the first chapter of this study sixteen sub-annually resolved, 50m- to 115m-deep, continuously sampled, multivariate ice core records (eight from US ITASE) are used to investigate recent spatial and temporal concentration variability of the soluble $ssSO_4^{2-}$ and $xsSO_4^{2-}$ over West Antarctica and the South Pole for the last 200 years. The second chapter utilizes the same cores and focuses on individual site variability and associations between SO_4^{2-} concentrations and Southern Ocean sea ice extent.

Chapter 2

A 200-YEAR WEST ANTARCTIC PALEOCLIMATE RECORD FROM U.S. ITASE ICE CORES

2.1 Introduction

Antarctica's role in the global climate system is both pivotal and complex. West Antarctica in particular is the most dynamic area of the continent both atmospherically and glaciologically [Cullather and others, 1996; Bindschadler, 1998]. It is impacted by several major atmospheric weather systems: the Amundsen Sea Low, and, to a lesser degree, the Weddell Sea Low and the Davis Sea Low. These large atmospheric low-pressure systems are the primary transport mechanisms for moisture and aerosols to the West Antarctic Ice Sheet.

Instrumental climate records are relatively sparse over the Southern Hemisphere and extend back <100 years. Over Antarctica such records extend back only a few decades. Glaciochemical proxy data can extend the paleoclimate record back hundreds to thousands of years and also provide a unique resource for examining changes in the sources, pathways, and distribution of chemical species in the atmosphere through time [Mayewski and others, 1993]. This chapter focuses on the sulfate (SO_4^{2-}) time series available from a series of 16 ice cores collected over West Antarctica.

2.1.1 Atmospheric Sulfate

Sulfate 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]. In addition to anthropogenic emissions, sulfur is released into the atmosphere from a variety of natural sources including sea salt, continental dust, volcanic eruptions, the terrestrial biosphere, and the marine biosphere.

Major volcanic events, such as the eruption of Mount Pinatubo in 1991, can inject large volumes of sulfur gases (H_2S, SO_2), ash, dust, and crustal material directly into the stratosphere. Most large volcanic eruptions (such as Krakatau in 1883 and Agung in 1963) significantly increase stratospheric SO_4^{2-} concentrations for at least 1-2 years after the event. Occasionally, an exceptionally large eruption, such as Tambora in 1815, will increase atmospheric SO_4^{2-} concentrations for 3-4 years [Self and others, 1981]. Large volcanic eruptions significantly affect stratospheric chemistry, inducing a higher catalytic destruction rate of ozone resulting in enhanced levels of UV-B radiation at the Earth's surface [Berresheim and others, 1995].

Antarctica is an ideal place to study natural atmospheric SO_4^{2-} variability due to its isolated location, the fact that Antarctic precipitation is an excellent repository for the deposition of soluble and insoluble chemical species, and its remoteness from major anthropogenic SO_4^{2-} sources that can confound the investigation of natural variability over more populated regions [Shaw, 1982; Legrand and Mayewski, 1997]. The primary types of SO_4^{2-} in Antarctic aerosols are sea salt (ss) SO_4^{2-} and excess (xs) SO_4^{2-}, the latter composed predominantly of marine biogenic emissions, volcanic emissions [Delmas, 1982; Legrand, 1997] and an as yet either non-existent or undetermined contribution from anthropogenic activity. Marine biogenic emissions dominate the overall sulfur budget in the Southern Hemisphere [Bates and others, 1992; Legrand and Mayewski, 1997].

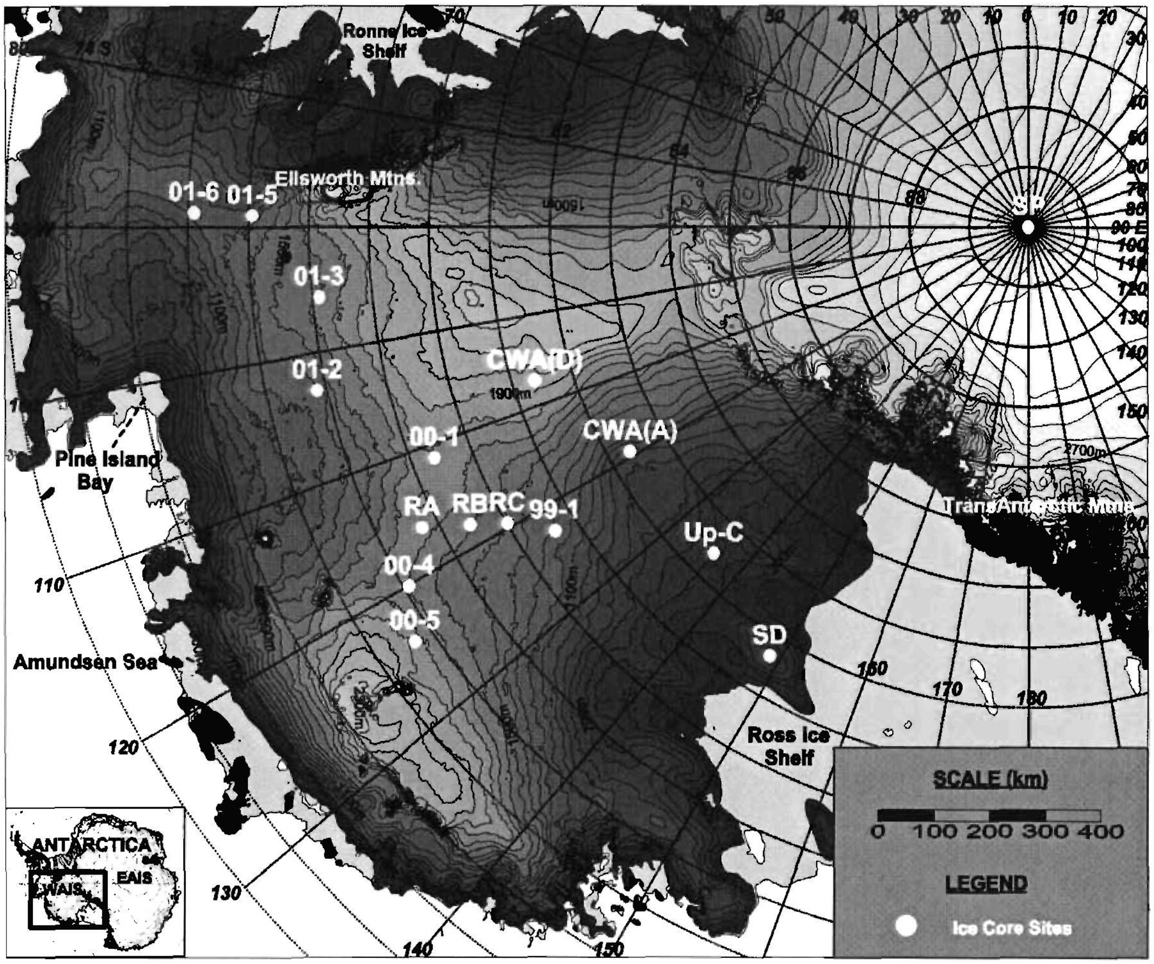


Figure 2.1:
Location map of sites for all ice cores used in this study. RA, RB, and RC represent core sites RIDS-A, RIDS-B, and RIDS-C, respectively. Map created using the RAMP Digital Elevation Model [Liu and others, 2001].

In this study sixteen sub-annually resolved, continuously sampled, multivariate ice core records (fifteen from West Antarctica and one from South Pole – Figure 2.1) are used to investigate ice core SO_4^{2-} concentrations over West Antarctica. The sixteen ice cores capture the sub-annual variability in Antarctic SO_4^{2-} loading over the period 1487-2002 with a ~200-year overlap (1799-1992) for six of the cores, a 101-year overlap (1891-1992) for eleven of the cores and a 50-year overlap (1952-1992) for all cores except 01-6 (Table 2.1).

Location	Lat.	Long.	Elev. (m)	Mean Acc. (cm H2O)	Distance from open water (km)	ssSO4 Conc. (1891-1991 Mean)	xsSO4 Conc. (1891-1991 Mean)	ssSO4:xsSO4 (1891-1991 Mean)	Depth (m)	Time Period (Years AD)	Sampling Res. (cm)	Samples Per Year (High Res. Mean)
ITASE 01-6	76.0968	89.0147	1232	39.7	320	6.6	29.7	0.22	18	2000-1978	2.1 - 3.6	28
ITASE 01-5	77.0593	89.1375	1246	36.5	400	7.4	29.8	0.25	114	2002-1781	1.5 - 3.5	23
ITASE 01-3	78.1202	95.6463	1633	32.7	370	4.0	24.2	0.17	71	2002-1859	1.5 - 3.2	20
ITASE 01-2	77.8436	102.9103	1353	42.5	295	5.9	32.0	0.18	71	2002-1890	1.7 - 4.1	27
ITASE 00-1	79.3831	111.2286	1791	22.3	475	5.4	27.7	0.20	105	2001-1651	1.6 - 3.5	13
ITASE 00-4	78.0829	120.0764	1697	19	460	7.4	32.4	0.23	58	2001-1799	1.4 - 3.1	13
ITASE 00-5	77.6821	123.9914	1828	14.6	400	7.2	50.9	0.14	60	2001-1708	2 - 6.4	8
ITASE 99-1	80.6200	122.6300	1350	13.6	640	10.7	37.2	0.29	58	2000-1713	2 - 4.3	8
RIDS-A	78.7300	116.3300	1740	23.6	440	5.9	26.8	0.22	160	1996-1831	3 & 60	11
RIDS-B	79.4600	118.0500	1603	14.8	535	5.3	37.6	0.14	60	1996-1926	3, 20, & 30	9
RIDS-C	80.0100	119.5600	1530	11.1	580	5.9	43.8	0.13	60	1996-1905	2, 3, & 25	9
Siple Dome-94	81.6481	148.7900	620	11.8	385	29.8	84.3	0.35	150	1995-1891	2 & 25	10
South Pole-95	90.0000	0.0000	2850	8.2	1300	2.7	48.9	0.05	71	1992-1487	2	6
CWA-(A)	82.3671	119.2855	950	14.5	850	12.5	50.5	0.25	93.5	1994-1939	3 & 40	9
CWA-(D)	81.3723	107.2750	1930	21.3	735	5.3	32.1	0.17	50.5	1994-1952	3 & 60	13
Up-C	82.4391	135.9720	525	11.5	640	18.7	78.7	0.24	28	1996-1870	3	7

Table 2.1:
Information for each ice core used in this study (100-year means). Elev. = elevation, Mean Acc.=mean annual accumulation, Conc.=concentration, Sampling Res.=sampling resolution, and Samples Per Year=mean number of samples per year calculated from high entire high-resolution section of each core.

Each ice core SO_4^{2-} time series is separated into its primary constituents, seasalt (ss)SO_4^{2-} and excess (xs)SO_4^{2-}, from which the spatial and temporal variation of these fractions is investigated for the period of the last 200 years. The methods used for separating ss from xs are discussed later. Volcanic peaks are extracted from the xsSO_4^{2-} time series by calculating the residuals from a robust spline smoothing of the raw xsSO_4^{2-} data following the technique used by Zielinski and others [1994].

Several well-documented volcanic events are detected in each $xsSO_4^{2-}$ series and these are used to reinforce the identification of annual layer dating by providing absolute depth-age horizons.

The $xsSO_4^{2-}$ remaining after removal of the volcanic peaks is the robust spline-smoothed $xsSO_4^{2-}$. This remaining $xsSO_4^{2-}$ ($rxsSO_4^{2-}$) is assumed to be a mixture of total marine biogenic SO_4^{2-} and stratospheric background SO_4^{2-}. The stratospheric background SO_4^{2-} is potentially composed of non-explosive volcanic SO_4^{2-}, an admixture of sources that reside in polar stratospheric clouds (PSC), and continental SO_4^{2-} sources such as anthropogenic emissions and dust.

2.1.2 The Antarctic Atmosphere and Sulfate Aerosols

Throughout the year Antarctic coastal and low elevation areas are strongly influenced by lower tropospheric air masses compared to higher elevation interior areas. The influence of mid-upper tropospheric and stratospheric air masses on coastal sites is minor [Minikin and others, 1998; Legrand and Wagenbach, 1999]. The sea salt fraction of the total SO_4^{2-} budget is large at coastal and low elevation sites, contributing over 25% to sites such as Siple Dome (Table 2.1). Several studies have shown that $xsSO_4^{2-}$ concentrations and deposition timing are similar from site to site around the Antarctic coastline (Prospero and others, 1991; Legrand and Pasteur, 1998; Minikin and others, 1998; Legrand and Wagenbach, 1999]. This similarity implies that $xsSO_4^{2-}$ concentrations at coastal Antarctic sites are controlled by large-scale processes related to both the distribution of sulfur sources in the Southern Ocean and the atmospheric mixing and transport patterns [Prospero and others, 1991]. Coastal $xsSO_4^{2-}$ concentrations are influenced throughout the year by long-range transport of marine biogenic emissions from mid-latitude sources located at 50°-60°S. During the summer months these same coastal sites are inundated by $xsSO_4^{2-}$ from marine biogenic sources located south of 60°S [Minikin and others, 1998]. Concentrations of $xsSO_4^{2-}$ at coastal sites exhibit a well-defined peak from November to January. This summer $xsSO_4^{2-}$ peak corresponds to the breakup of the Antarctic sea ice south of 60°S and a subsequent enrichment of chlorophyll concentrations [Minikin and others, 1998]. The marine biogenic $xsSO_4^{2-}$ component accounts for roughly two thirds of the winter and over 90% of the summer coastal $xsSO_4^{2-}$ concentrations [Minikin and others, 1998]. The remaining percentage of winter and summer coastal $xsSO_4^{2-}$ comes from sources such as long-range transport from continental areas and sedimentation from the stratospheric reservoir.

High-elevation areas such as inland West Antarctica, South Pole, and the Polar Plateau also receive SO_4^{2-} from a variety of sources. The $ssSO_4^{2-}$ fraction peaks during the winter/spring transition months when intense cyclonic activity and intrusions of lower tropospheric marine air masses are common [Whitlow and others, 1992; Legrand and others, 1992; Hogan, 1997]. The oceans surrounding Antarctica are ice covered during the winter/spring transition. Therefore, a low/mid latitude source is proposed for the $ssSO_4^{2-}$ [Prospero and others, 1991]. By the time lower tropospheric parcels of air reach the Polar Plateau they are severely depleted of heat, moisture, and aerosols due to the long distances traveled [Hogan and others, 1982; Proposito, 2002]. As a result, $ssSO_4^{2-}$ accounts for <5% of the total SO_4^{2-} budget on the Polar Plateau during the winter/spring and <1% during the summer [Harder and others, 2000; Isaksson and others, 2001].

Mid-upper tropospheric air masses carry $xsSO_4^{2-}$ aerosols emitted primarily from low-mid latitude marine biogenic productivity sources [Shaw, 1982; Legrand and others, 1992; Minikin and others, 1998] as well as episodic $xsSO_4^{2-}$ input from volcanic eruptions [Legrand and Wagenbach, 1999]. The SO_4^{2-} contained in these mid-upper tropospheric air masses dominates the summer SO_4^{2-} budget of high-elevation Antarctic areas, such as inland West Antarctica, South Pole and the interior portions of the Polar Plateau [Delmas and Boutron, 1978; Delmas, 1982; Kreutz and Mayewski, 1999; Harder and others, 2000; Isaksson and others, 2001].

High-elevation Antarctic areas are also impacted by the stratospheric SO_4^{2-} layer. The stratospheric contribution of SO_4^{2-} is generally assumed to be weak [Legrand, 1997; Bergin and others, 1998] except after global scale volcanic eruptions [Legrand and Delmas, 1987; Dibb and Whitlow, 1996]. The SO_4^{2-} aerosols in the stratosphere sink and mix downward into the troposphere. The slow sedimentation of SO_4^{2-} from the stratosphere is periodically enhanced by disruptions to the tropopause that often occur during the spring breakup of the polar vortex [Saxena and others, 1995].

2.2 Methodology

Of the sixteen cores used in this study, eight have been previously reported. The Siple Dome core (SDM94) and the three Ross Ice Drainage System cores (RIDS-A, -B, and –C) were collected by a University of New Hampshire team in 1994 and 1995 respectively [Mayewski and others, 1995; Kreutz and others, 1996; 1999; 2000]. The South Pole core (SP95) was collected in 1995 by the Polar Ice Coring Office (PICO) in the designated clean air sector, ~1.5km upwind from South Pole Station in 1995 [Battle and others, 1996; Meyerson and others, 2002]. The Central West Antarctic cores (CWA-A and –D) were collected during the 1994-95 field season by a University of Wisconsin team, and the results are reported by Reusch and others, [1999]. The Up-C ice core was collected during the 1995-96 field season by PICO for Pennsylvania State University.

The eight new cores used in this study were drilled during the U.S. ITASE West Antarctic traverses of 1999-2001 and analyzed at sub-annual, continuous resolution (Table 2.1). The samples were melted using the University of Maine continuous melter system. For this study the system yielded an average resolution of ~50 samples per meter. This high sampling resolution captures the clear seasonal signal that is present in each ion time series (Figure 2.2). All samples were examined for their soluble major ion content (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, SO_4^{2-}). Each was analyzed using a Dionex® DX-500 ion chromatograph coupled with a Gilson® autosampler. 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 were determined with an accuracy of better than 0.1 ppb.

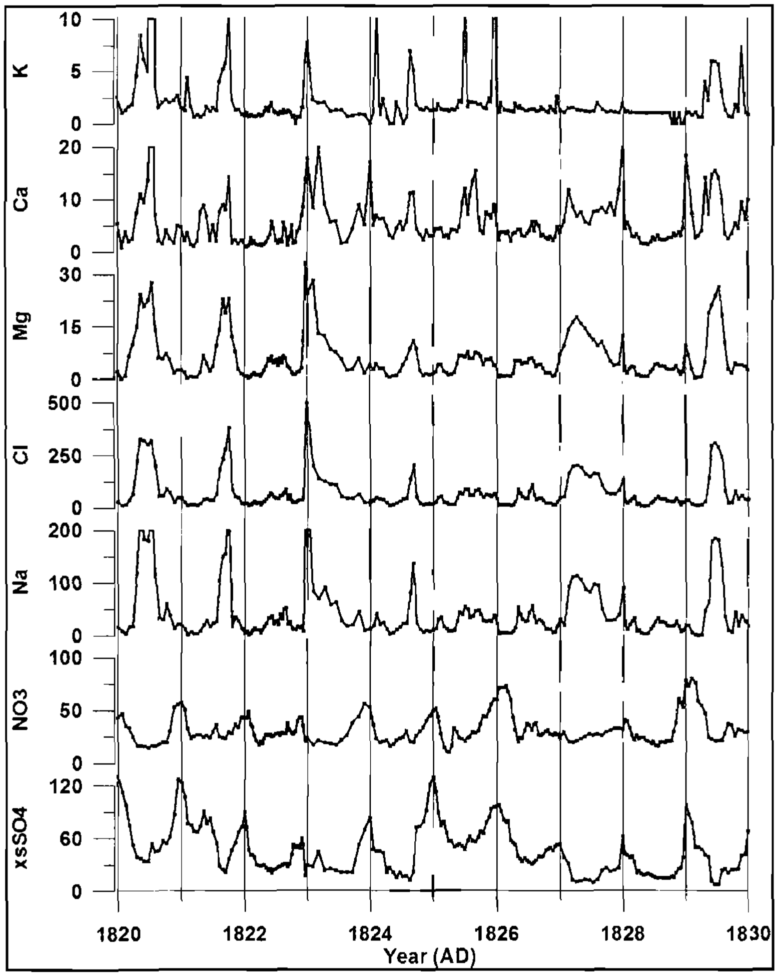


Figure 2.2:
Raw ion data from core 01-5 plotted versus time. Ion concentrations are in parts per billion. This data is from 94-99m depth (1820-1830) in the core. Vertical lines represent 1-year increments.

The 1999-2001 cores are annually dated by matching seasonal peaks from each of the ion time series (Figure 2.2). A 'core-chemistry' year is defined by a winter-spring peak in Na^+, K^+, Mg^{2+}, Ca^{2+}, and Cl^- combined with spring-summer peaks in both NO_3^- and $xsSO_4^{2-}$ in accord with the seasonal timing identified by previous research [e.g. Whitlow and others, 1992; Wagenbach, 1996; Legrand and Mayewski, 1997; Kreutz and Mayewski, 1999]. Counting the seasonal layers down to absolute depth-age horizons (such as the Tambora 1815 volcanic event) demonstrates that each year is preserved in the sub-annual records of each core (Figure 2.3) and that lower resolution records cannot be used to accurately date volcanic events. For this reason, only the high resolution portion of each ice core record is used in this study.

Based on several well-documented global-scale volcanic depth-age horizons, a dating accuracy of better than one year between known volcanic events is achieved for each SO_4^{2-} record. The $ssSO_4^{2-}$ fraction is calculated by applying a standard seawater ratio of 30.61(Na^+), 1.1(K^+), 3.69(Mg^{2+}), 1.16(Ca^{2+}), 55.04(Cl^-), and 7.68(SO_4^{2-}) 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, from O'Brien and others [1995], resulted in Na^+ being the conservative ion for >90% of the samples in each core in this study. Recent studies have noted the effect of frost flowers on the ss fraction of ice core chemistry. Frost flowers are depleted in SO_4^{2-} relative to Na^+ and this produces a $ssSO_4^{2-}$ value which is slightly higher than it should be for sites near the coast [Rankin and others, 2002]. At this time the magnitude of the fractionation effect is not constrained sufficiently for corrections to be made to the cores in this study.

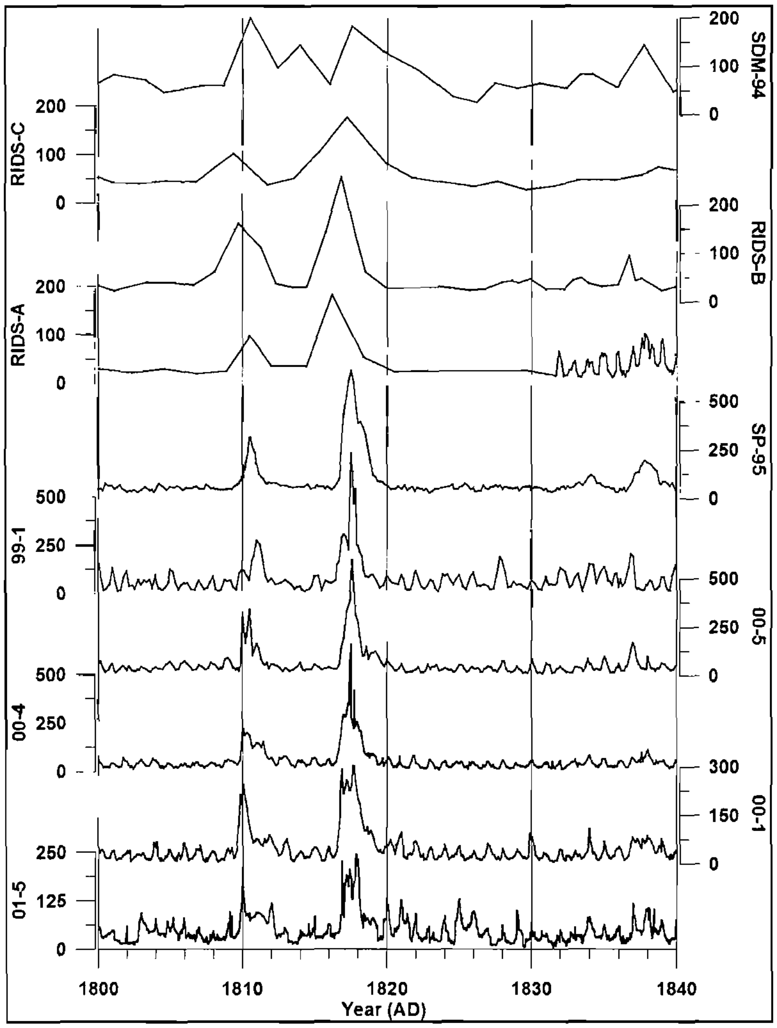


Figure 2.3:
Sub-annual and ~bi-annual raw excess sulfate ion concentration data for the years 1800-1840. Data for ice cores 01-5, 00-1, 00-4, 00-5, 99-1, SP-95, RIDS-A, RIDS-B, RIDS-C, and SDM-94. All concentrations are in parts per billion. Vertical lines represent 2-year increments.

In order to examine the spatial pattern of ss and $xsSO_4^{2-}$, mean concentrations from 1891-1991 (apart from core 01-6, which only has a 23-year record) are plotted vs. site elevation, straight line distance from the nearest open water, and mean annual accumulation rate from 1891-1991 (Figure 2.4). The reason for averaging over this time period is that any variability at lesser timescales will be averaged out. Similar plots were constructed using ss and $xsSO_4^{2-}$ concentrations averaged from 1891-1940 and 1940-1991 to see if mean values from these different time periods affected the results.

The values, although slightly different, retained their same trends with respect to elevation, straight-line distance from the nearest open water, and mean annual accumulation rate. The temporal pattern of $ssSO_4^{2-}$ is examined by plotting the mean annual concentrations vs. time for each core (Figure 2.5). A five-year running average is superimposed over this annual data to highlight any long term trends. EOF analysis is used on the annual $ssSO_4^{2-}$ and $xsSO_4^{2-}$ concentrations for the years 1891-1991 and 1939-1991 to see if any site-to-site associations exist in the ice core records. These two time periods are used for the EOF calculations because the former represents the longest period of overlap between 10 of the ice core records, and the latter represents the longest period of overlap between 13 of the records (the record from 99-1 was not used in the EOF analysis because of data gaps).

Volcanic peaks are first identified from the $xsSO_4^{2-}$ data using a robust spline. A robust spline has the advantage over most smoothing functions because it is not affected by large outliers (such as volcanic peaks). The robust spline tool outputs two separate time series which, when combined, make up the original series. One of these time series is the robust spline-smoothed series and the other is the robust spline residuals (peaks).

The amount of smoothing applied to each $xsSO_4^{2-}$ series is between 80-90% as this value provides the best approximation of the mean non-volcanic background concentrations beneath large volcanic spikes compared to adjacent years without volcanic SO_4^{2-}.

The first step of the robust spline technique is to average the raw $xsSO_4^{2-}$ data to annual resolution. The annual average calculation incorporates the raw background $xsSO_4^{2-}$ concentrations into the annual values. Thus, a large volcanic event that manifests as a significant rise in background $xsSO_4^{2-}$ concentrations will be recognized by the robust spline. The robust spline function is applied to the annually averaged $xsSO_4^{2-}$ time series and the robust spline-smoothed series and associated $xsSO_4^{2-}$ residuals are extracted. The mean residual $xsSO_4^{2-}$ concentration is calculated from the positive post-1825 $xsSO_4^{2-}$ residual values (this prevents the large Tambora volcanic $xsSO_4^{2-}$ signal from causing an anomalously high mean residual $xsSO_4^{2-}$ value). The mean + 1σ and mean + 2σ residual $xsSO_4^{2-}$ values are used to isolate the larger peaks from the $xsSO_4^{2-}$ residuals. Each residual $xsSO_4^{2-}$ peak greater than the mean + 2σ value represents a strong volcanic signal, and each residual $xsSO_4^{2-}$ peak greater than the mean + 1σ value represents a probable volcanic signal (hereafter referred to as 1σ and 2σ peaks). The 1σ and 2σ peaks are plotted on the same time axis for each core (Figure 2.6).

As it is not currently possible to unambiguously separate the total marine biogenic and background stratospheric $rxsSO_4^{2-}$ components, the $rxsSO_4^{2-}$ time series for each core is used to examine the long term trends in these two components over the last 200 years (Figure 2.7). EOF analysis is used to determine if any associations exist between the $rxsSO_4^{2-}$ records from 1891-1991 and from 1939-1991.

2.3 Results and Discussion

2.3.1 Ion Concentrations and Accumulation Rate

Previous research reveals no significant correlations between snow ion concentration and accumulation rate [e.g. Mulvaney and Wolff, 1994; Kreutz and Mayewski, 1999; Kreutz and others, 2000]. This suggests that any dilution effects which do exist are offset by additional inputs such as dry and fog deposition [Bergin and others, 1995; Kreutz and others, 2000]. Varying wet deposition scavenging ratios can further confuse these effects. Empirical Orthogonal Function (EOF) analyses of the mean annual ion concentrations and mean annual accumulations for each U.S. ITASE core resulted in weak correlations for most cores. The mean annual values of accumulation were used because this was the best resolution achievable for accumulation rate. The correlations between annual accumulation rate and SO_4^{2-} are inconsistent and highly variable from site to site. The associations range from almost zero to <50%. These results suggest that although some portion of the SO_4^{2-} is being deposited by wet deposition, another portion not associated with wet precipitation is also deposited. Because the dry deposition velocity and wet scavenging ratio for SO_4^{2-} in West Antarctica are not well constrained and there is no consistent association between ion concentration and accumulation rate, flux corrections for accumulation were not applied.

2.3.2 Sea Salt Sulfate

In Figure 2.4a the mean $ssSO_4^{2-}$ concentrations for sites located above 1000m elevation (Figure 2.1) display a relatively consistent range of values (~4-7 ppb) apart from site 99-1, which has a mean $ssSO_4^{2-}$ concentration of ~11 ppb. The high mean $ssSO_4^{2-}$ value observed at site 99-1 may be due to enhanced lower tropospheric circulation near this site, resulting in stronger advection of marine air masses to the area located over and to the east of the Ross Ice Shelf [Kreutz and Mayewski, 1999]. Sites located below 1000m elevation (SDM-94, Up-C, and CWA-A) have mean $ssSO_4^{2-}$ concentrations of ~12-30 ppb and they are located to the west of site 99-1. The South Pole site has a very low mean $ssSO_4^{2-}$ concentration of ~3 ppb.

Comparison between concentrations of $ssSO_4^{2-}$, annual accumulation and distance from the coast (Figure 2.4b, c) does not immediately reveal any clear trends. However, if the sites below 1000m elevation, site 99-1 and the South Pole site, are ignored, remaining sites display relatively similar $ssSO_4^{2-}$ concentration values (~4-7 ppb).

These results suggest that two distinct depositional regimes occur over West Antarctica. One affects sites above 1000m elevation and the other affects sites below 1000m elevation. This supports previous findings of Kreutz and Mayewski [1999] that lower tropospheric circulation is enhanced in the SDM-94 vicinity because of stronger advection of marine air masses to this area. The most likely aerosol source for the low elevation sites to the east of the Ross Ice Shelf is the Ross Sea.

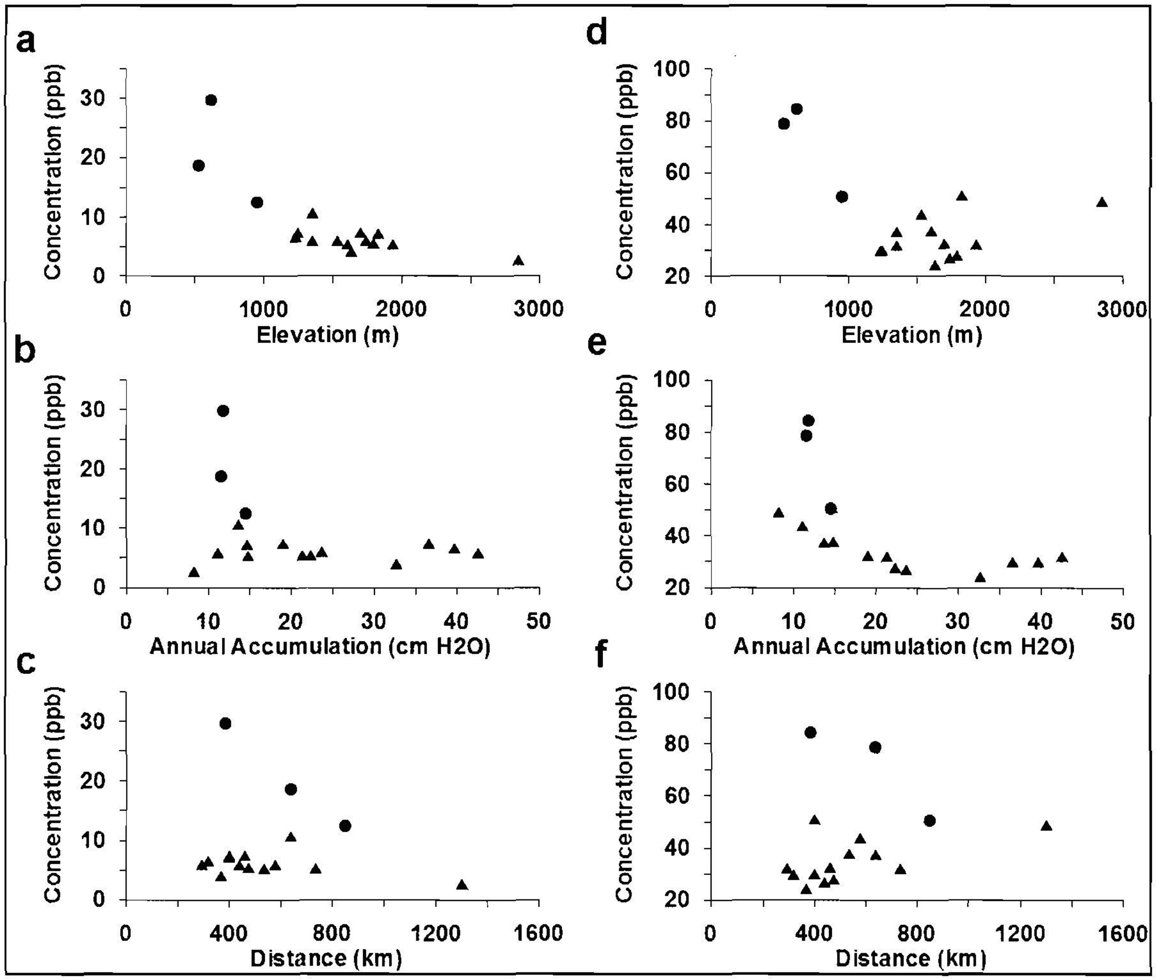


Figure 2.4:
Mean sea salt sulfate ($ssSO_4^{2-}$) and excess sulfate ($xsSO_4^{2-}$) concentrations for the years 1900-1990. (a) $ssSO_4^{2-}$ vs. elevation, (b) $ssSO_4^{2-}$ vs. annual accumulation, (c) $ssSO_4^{2-}$ vs. straight line distance from nearest open water, (d) $xsSO_4^{2-}$ vs. elevation, (e) $xsSO_4^{2-}$ vs. annual accumulation, and (f) $xsSO_4^{2-}$ vs. straight line distance from nearest open water. Distances to open water are ignoring sea ice. Circles represent sites located below 1000m elevation and triangles represent sites located above 1000m elevation. All concentrations in parts per billion.

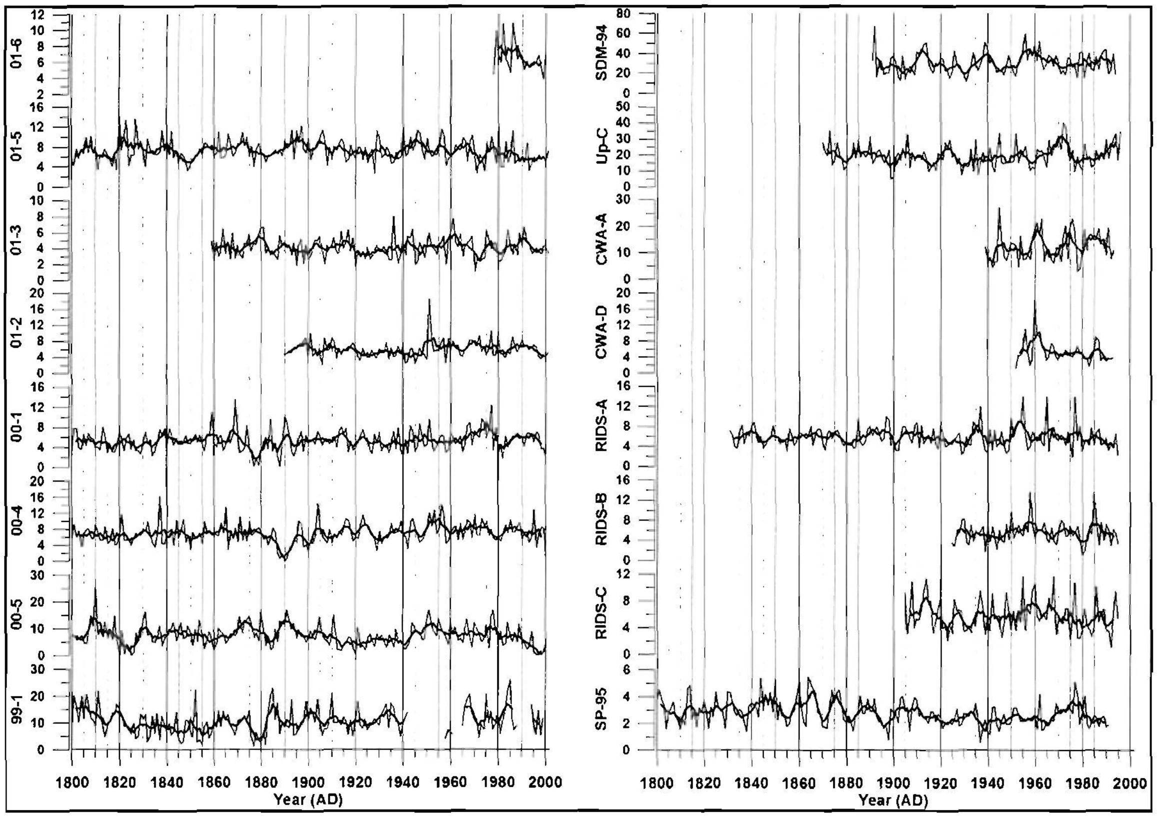
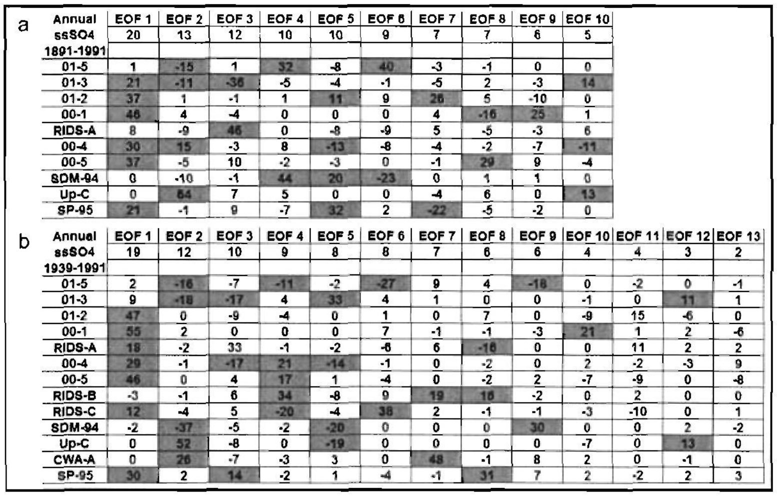


Figure 2.5:
Annual sea salt sulfate concentrations in parts per billion for the years 1800-2002. Data for each ice core used in this study. Lighter lines represent annual concentration values and thick darker lines represent a 5-year running average. Vertical lines represent 5-year increments.

Inspection of the annual $ssSO_4^{2-}$ concentrations reveals no significant long-term trends (Figure 2.5). However, sites with the highest concentrations display the greatest concentration variability. An EOF (Table 2.2a) performed on ten cores with annual $ssSO_4^{2-}$ values spanning the years 1891-1991 reveals a relatively strong association (EOF 1, 20% total variance and 21%-46% variance of each core) of SP-95 with other sites located above 1000m elevation apart from site 01-5 (Table 2.2a). This suggests that South Pole receives a significant fraction of its $ssSO_4^{2-}$ aerosols from the same air masses that supply West Antarctic sites located above 1000m elevation.

Statistical associations also occur between sites 01-5 and SDM-94; for example, in Table 2.2a EOF 4 (10% total variance, 32% and 44% variance of each core) these two sites are positively correlated and in Table 2.2a EOF 6 (9% total variance, 40% and 23% variance of each core) they are negatively correlated. This positive-negative association may be related to findings by Bromwich and others [2003] who noted that the ENSO phenomena causes a pronounced dipole structure over the Ross Ice Shelf-Marie Byrd Land area and over the Weddell Sea-Filchner/Ronne Ice Shelf. The dipole structure is observed in surface temperatures, meridional winds, cloud fraction, and precipitation. An EOF of annual $ssSO_4^{2-}$ concentrations from thirteen cores spanning the years 1939-1991 yielded similar results (Table 2.2b) between SP-95 and other sites located above 1000m elevation (EOF 1, 19% total variance and 12%-55% variance of each core). SDM-94 also displays similar positive-negative associations with site 01-5 (EOF 2, 12% total variance, 37% and 16% variance of each core; EOF 9, 6% total variance, 18% and 30% variance of each core). The similarity between these two EOFs implies that the $ssSO_4^{2-}$ deposition has remained relatively constant over West Antarctica for at least the last century.



a

Annual	EOF 1	EOF 2	EOF 3	EOF 4	EOF 5	EOF 6	EOF 7	EOF 8	EOF 9	EOF 10
ssSO4	20	13	12	10	10	9	7	7	6	5
1891-1991										
01-5	1	-15	1	32	-8	40	-3	-1	0	0
01-3	21	-11	-36	-5	-4	-1	-5	2	-3	14
01-2	37	1	-1	1	11	9	26	5	-10	0
00-1	46	4	-4	0	0	0	4	-16	25	1
RIDS-A	8	-9	46	0	-8	-9	5	-5	-3	6
00-4	30	15	-3	8	-13	-8	-4	-2	-7	-11
00-5	37	-5	10	-2	-3	0	-1	29	9	-4
SDM-94	0	-10	-1	44	20	-23	0	1	1	0
Up-C	0	64	7	5	0	0	-4	6	0	13
SP-95	21	-1	9	-7	32	2	-22	-5	-2	0

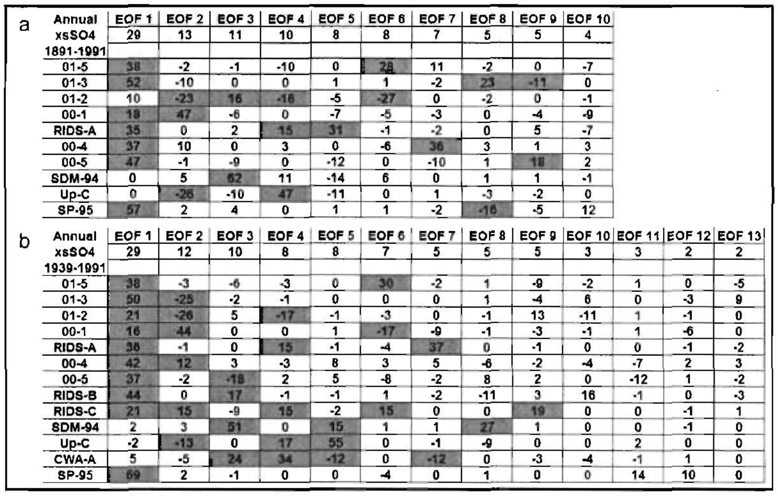
b

Annual	EOF 1	EOF 2	EOF 3	EOF 4	EOF 5	EOF 6	EOF 7	EOF 8	EOF 9	EOF 10	EOF 11	EOF 12	EOF 13
ssSO4	19	12	10	9	8	8	7	6	6	4	4	3	2
1939-1991													
01-5	2	-16	-7	-11	-2	-27	9	4	-18	0	-2	0	-1
01-3	9	-18	-17	4	33	4	1	0	0	-1	0	11	1
01-2	47	0	-9	-4	0	1	0	7	0	-9	15	-6	0
00-1	55	2	0	0	0	7	-1	-1	-3	21	1	2	-6
RIDS-A	18	-2	33	-1	-2	-6	6	-16	0	0	11	2	2
00-4	29	-1	-17	21	-14	-1	0	-2	0	2	-2	-3	9
00-5	46	0	4	17	1	-4	0	-2	2	-7	-9	0	-8
RIDS-B	-3	-1	6	34	-8	9	19	16	-2	0	2	0	0
RIDS-C	12	-4	5	-20	-4	38	2	-1	-1	-3	-10	0	1
SDM-94	-2	-37	-5	-2	-20	0	0	0	30	0	0	2	-2
Up-C	0	52	-8	0	-19	0	0	0	0	-7	0	13	0
CWA-A	0	26	-7	-3	3	0	48	-1	8	2	0	-1	0
SP-95	30	2	14	-2	1	-4	-1	31	7	2	-2	2	3

Table 2.2:
EOF of annual sea salt sulfate concentrations. (a) Results for 1891-1991, and (b) Results for 1939-1991.

2.3.3 Excess Sulfate

The $xsSO_4^{2-}$ signals for the ice core records in this study are more complex than $ssSO_4^{2-}$ signals because the former have multiple sources. The location of a particular site with respect to physical parameters such as elevation and distance inland is critical to deciphering the $xsSO_4^{2-}$ signal. Examination of the data in figure 2.4d reveals that $xsSO_4^{2-}$ concentrations decrease as elevation increases to approximately 1700m above sea level. Above this elevation the decreasing trend in $xsSO_4^{2-}$ concentration switches and as elevation increases $xsSO_4^{2-}$ concentrations rise, although not as sharply as they decrease from sea level. This relationship illustrates the effects of multiple $xsSO_4^{2-}$ sources, local biogenic SO_4^{2-} near the coast, and mid-upper tropospheric/stratospheric SO_4^{2-} input to higher elevation areas.



a

Annual	EOF 1	EOF 2	EOF 3	EOF 4	EOF 5	EOF 6	EOF 7	EOF 8	EOF 9	EOF 10
xsSO4	29	13	11	10	8	8	7	5	5	4
1891-1991										
01-5	38	-2	-1	-10	0	28	11	-2	0	-7
01-3	52	-10	0	0	1	1	-2	23	-11	0
01-2	10	-23	16	-16	-5	-27	0	-2	0	-1
00-1	18	47	-6	0	-7	-5	-3	0	-4	-9
RIDS-A	35	0	2	15	31	-1	-2	0	5	-7
00-4	37	10	0	3	0	-6	36	3	1	3
00-5	47	-1	-9	0	-12	0	-10	1	18	2
SDM-94	0	5	62	11	-14	6	0	1	1	-1
Up-C	0	-26	-10	47	-11	0	1	-3	-2	0
SP-95	57	2	4	0	1	1	-2	-16	-5	12

b

Annual	EOF 1	EOF 2	EOF 3	EOF 4	EOF 5	EOF 6	EOF 7	EOF 8	EOF 9	EOF 10	EOF 11	EOF 12	EOF 13
xsSO4	29	12	10	8	8	7	5	5	5	3	3	2	2
1939-1991													
01-5	38	-3	-6	-3	0	30	-2	1	-9	-2	1	0	-5
01-3	50	-25	-2	-1	0	0	0	1	-4	6	0	-3	9
01-2	21	-26	5	-17	-1	-3	0	-1	13	-11	1	-1	0
00-1	16	44	0	0	1	-17	-9	-1	-3	-1	1	-6	0
RIDS-A	36	-1	0	15	-1	-4	37	0	-1	0	0	-1	-2
00-4	42	12	3	-3	8	3	5	-6	-2	-4	-7	2	3
00-5	37	-2	-18	2	5	-8	-2	8	2	0	-12	1	-2
RIDS-B	44	0	17	-1	-1	1	-2	-11	3	16	-1	0	-3
RIDS-C	21	15	-9	15	-2	15	0	0	19	0	0	-1	1
SDM-94	2	3	51	0	15	1	1	27	1	0	0	-1	0
Up-C	-2	-13	0	17	55	0	-1	-9	0	0	2	0	0
CWA-A	5	-5	24	34	-12	0	-12	0	-3	-4	-1	1	0
SP-95	69	2	-1	0	0	-4	0	1	0	0	14	10	0

Table 2.3:
EOF of annual excess sulfate concentrations. (a) Results for 1891-1991, and (b) Results for 1939-1991.

Two $xsSO_4^{2-}$ EOFs (Table 2.3a, b) demonstrate the separation between sites located above and below 1000m elevation (both EOF 1, 29% total variance and 16%-69% variance of each core located above 1000m, 0%-5% for cores located below 1000m). This is suggestive of two separate source regions, or transport pathways, supplying $xsSO_4^{2-}$ to West Antarctica. All the core sites located above 1000m elevation exhibit a decrease in $xsSO_4^{2-}$ concentrations as accumulation increases (Figure 2.4e). However, this only occurs up to a threshold annual accumulation value of 20-24cm H_2O. Sites with annual accumulation values greater than this threshold do not display any significant trends in $xsSO_4^{2-}$ concentration. Sites located below 1000m elevation (SDM-94, Up-C, and CWA-A) do not show any clear trends associated with annual accumulation, although these sites do exhibit a decreasing trend in $xsSO_4^{2-}$ concentrations vs. distance from the nearest open water (Figure 2.4f). Sites located above 1000m elevation display the opposite trend: increasing $xsSO_4^{2-}$ concentrations vs. distance from the nearest open water (Figure 2.4f). These results suggest that sites located above 1000m elevation receive the majority of their xsSO_4^{2-} from mid-upper tropospheric/stratospheric air masses and that sites located below 1000m elevation do not receive a significant fraction of their xsSO_4^{2-} from this source. Previous work suggests that the xsSO_4^{2-} supplied to sites located below 1000m is deposited from lower tropospheric air masses [Kreutz and Mayewski, 1999].

2.3.4 Volcanic Sulfate Peaks

There are many volcanic events evident in the 16 ice core xsSO_4^{2-} records used in this study (Figure 2.6). The strength of the volcanic signal preserved in polar ice varies according to the size, sulfur content, explosivity, and location of the eruption. The preserved volcanic signal is also highly dependent on the location of the core. Global scale volcanic eruptions, such as Pinatubo in 1991, erupt with sufficient explosive force to inject large amounts of volcanic material directly into the stratosphere. Significant amounts of H_2S and SO_2 gas are emitted during a global scale eruption. The H_2S is quickly converted to SO_2 and this volcanic SO_2 is subsequently oxidized to H_2SO_4 [Junge and others, 1961; Berresheim and others, 1995]. Elevated stratospheric SO_4^{2-} concentrations can take as much as 3-4 years to return to pre-volcanic levels following a global-scale eruption [Self and others, 1981]. As a result, volcanic SO_4^{2-} in the stratosphere can spread over the entire globe before it is removed by mechanisms such as sedimentation.

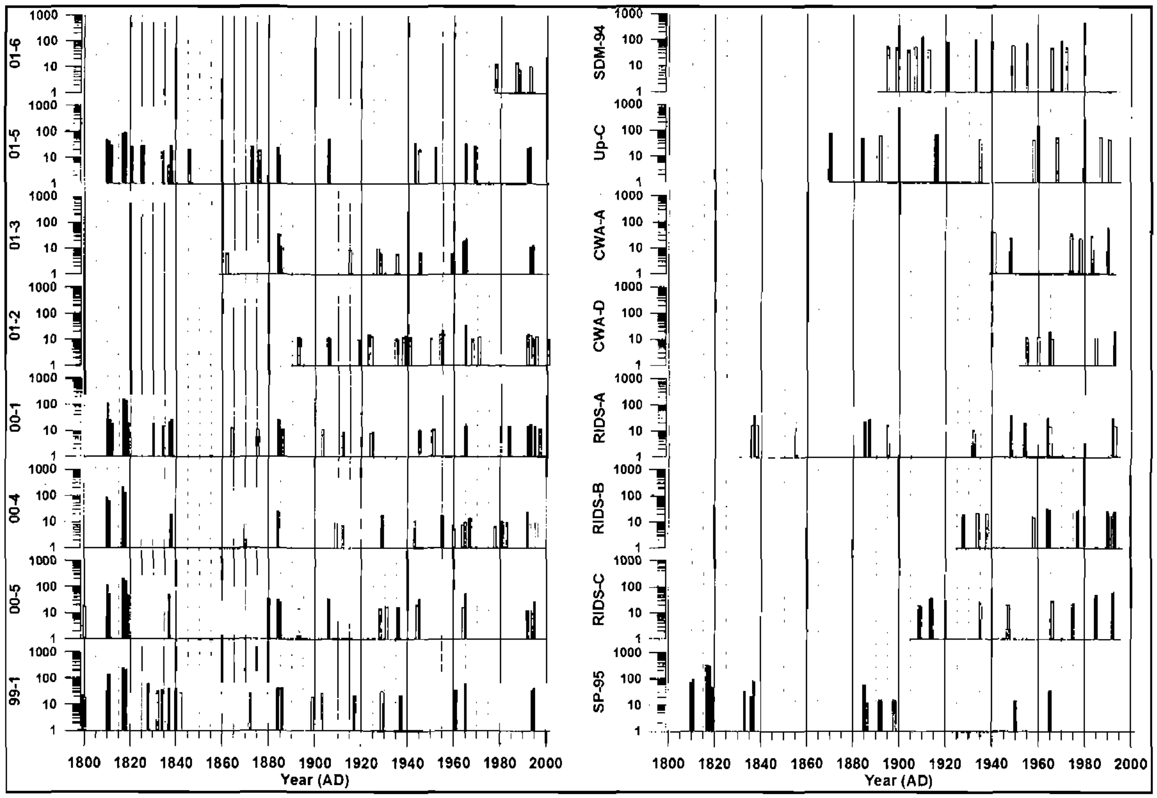


Figure 2.6:
Positive residuals from robust spline smoothed annual excess sulfate concentrations for each ice core for the years 1800-2002. Peaks that are mean + 1σ above the mean are shown in white and peaks that are mean + 2σ above the mean are shown in black. All concentrations are in parts per billion. Vertical lines represent 5-year increments.

In this study global scale eruptions (such as Tambora in 1815, Krakatau in 1883, and Agung in 1963) appear simultaneously as 2σ peaks in all of the robust spline residual $xsSO_4^{2-}$ records from sites located above 1000m elevation, but they are not obvious at sites located below 1000m elevation, such as SDM-94, Up-C, and CWA-A (Figure 2.6). The lack of global scale volcanic eruption signatures in low-elevation records supports the idea that coastal and low elevation sites in Antarctica are not strongly influenced by mid-upper tropospheric/stratospheric air masses.

2.3.5 Remaining Excess Sulfate

Examination of the rxsSO_4^{2-} curves in Figure 2.7 reveals that an overall decreasing trend takes place in all records from 1800 to ~1940. Several of the rxsSO_4^{2-} records exhibit an increasing trend from ~1940 to ~1990 (00-1, 00-4, 00-5, RIDS-A, RIDS-B, RIDS-C, and, to a lesser extent, SP-95). Several sites exhibit a decrease in rxsSO_4^{2-} during this same time period (01-5, 01-3, and 01-2). The remaining records do not show any significant trends or are too short to make an informed determination (site 99-1 is ignored beyond ~1940 because of missing data). The opposing rxsSO_4^{2-} trends observed in our records suggests that the source is not anthropogenic. If an anthropogenic rise in rxsSO_4^{2-} were occurring, it should occur in all rxsSO_4^{2-} records simultaneously. A second argument against an anthropogenically forced rise in rxsSO_4^{2-} is the fact that the rise which does occur from 1939-1991 does not increase rxsSO_4^{2-} levels higher than they were during the early 1800s.

EOF results of rxsSO_4^{2-} for the years 1891-1991 (Table 2.4a) reveal a strong association (EOF 1, 40% total variance and 13%-77% variance of each core) between cores 01-5, 01-3, 00-1, RIDS-A, 00-4, 00-5, Up-C, and SP-95. This 1891-1991 EOF captures the significant structure in the rxsSO_4^{2-} curves. The majority of this structure consists of broad rxsSO_4^{2-} peaks centered around ~1910, ~1947, and 1965 (Figure 2.7). The large 1965 rxsSO_4^{2-} peak indicates that some fraction of volcanic SO_4^{2-} is still present in these records after the robust spline residuals are removed. However, the ~1910 and ~1947 rxsSO_4^{2-} peaks may be a result of local volcanic eruptions or increases from non-volcanic sources such as marine biogenic SO_4^{2-}.

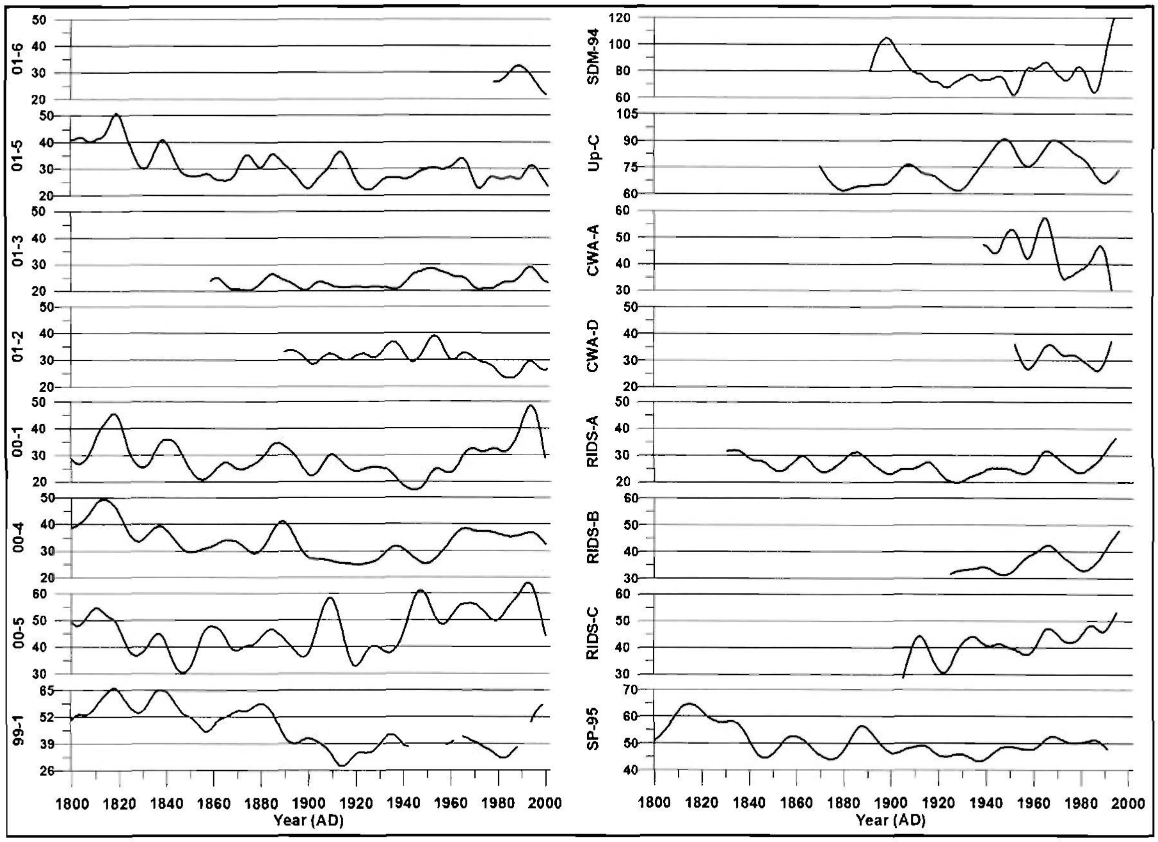


Figure 2.7:
Robust spline smoothed annual excess sulfate (rxsSO_4^{2-}) concentrations for each ice core for the years 1800-2002. All concentrations are in parts per billion. Vertical lines represent 10-year increments.

a

Annual xsSO4	EOF 1	EOF 2	EOF 3	EOF 4	EOF 5	EOF 6	EOF 7	EOF 8	EOF 9	EOF 10
Spline Smoothed	40	24	13	7	6	5	3	2	1	1
1891-1991										
01-5	23	27	32	-9	-3	-2	0	-1	-3	0
01-3	13	54	0	-3	12	16	0	-1	0	-1
01-2	-25	38	11	2	-9	7	0	7	0	0
00-1	41	-40	0	-9	0	2	0	6	0	-1
RIDS-A	75	0	4	0	-1	-1	18	0	2	0
00-4	52	-15	0	14	-1	14	0	-1	-2	1
00-5	60	14	-9	0	8	-2	0	5	0	2
SDM-94	2	-12	62	9	14	-1	-1	0	0	0
Up-C	31	34	-7	19	-1	-5	-1	0	0	-2
SP-95	77	-2	1	0	-5	0	-10	-1	3	0

b

Annual xsSO4	EOF 1	EOF 2	EOF 3	EOF 4	EOF 5	EOF 6	EOF 7	EOF 8	EOF 9	EOF 10
Spline Smoothed	41	23	12	11	6	4	2	1	0	0
1939-1991										
01-5	-13	65	-5	4	-10	-1	2	-1	0	0
01-3	-42	26	0	-25	-1	-3	1	0	0	0
01-2	-68	17	-1	8	0	0	-3	2	0	0
00-1	80	0	-1	-3	-6	-3	-1	6	0	0
RIDS-A	44	42	3	0	5	1	-5	0	0	0
00-4	84	0	-7	6	0	1	0	-1	-1	0
00-5	8	17	51	-8	3	-12	-1	-1	0	0
RIDS-B	28	50	-16	0	-2	0	-3	0	0	0
RIDS-C	76	0	10	-2	1	7	2	0	2	0
SDM-94	20	14	-24	3	26	-7	5	1	0	0
Up-C	-8	1	24	66	1	0	0	0	0	0
CWA-A	-9	62	4	-2	0	20	2	1	-1	0
SP-95	54	2	12	8	-19	-1	3	0	0	0

Table 2.4:
EOF of robust spline-smoothed annual excess sulfate concentrations. (a) Results for 1891-1991, and (b) Results for 1939-1991.

The EOF results of rxsSO_4^{2-} for the years 1939-1991 reveal a strong negative association (EOF 1, 41% total variance and 13%-84% variance of each core) between two groups of cores (Table 2.4b). The first group consists of 01-5, 01-3, and 01-2. The second group is comprised of 00-1, 00-4, RIDS-A, RIDS-B, RIDS-C, SDM-94, and SP-95. This 1939-1991 EOF captures the overall long term trend in rxsSO_4^{2-} that takes place during this time period. The reason for the negative association is that the first group of cores (01-5, 01-3, and 01-2) displays a decreasing trend in rxsSO_4^{2-} concentrations from 1939-1991 and the second group (00-1, 00-4, RIDS-A, RIDS-B, RIDS-C, SDM-94, and SP-95) displays an increasing trend (Figure 2.7). The trends in these rxsSO_4^{2-} records suggest that a climate transition takes place over West Antarctica during ~1940. At this time the atmospheric circulation over West Antarctica changes in such a way as to increase the transport of rxsSO_4^{2-} to central West Antarctica.

Chapter 3

A 200-YEAR SULFATE RECORD FROM 16 ANTARCTIC ICE CORES AND ASSOCIATIONS WITH SOUTHERN OCEAN SEA ICE EXTENT

3.1 Introduction

Reliable instrumental records of Earth's climate have only been collected since the late 1800s; 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.

3.1.1 Antarctica, Ice Cores and Sulfate

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, among others, atmospheric temperature, atmospheric circulation, precipitation, the El Niño-Southern Oscillation, and sea ice extent [Jouzel and others, 1983; Mayewski and others, 1995; in press; Cullather and others, 1996; Kreutz and others, 1997; 2000a; Meyerson and others, 2002]. Furthermore, strong teleconnections link the continent to the mid- and low-latitudes [Carleton, 1992] ensuring that records of Southern Hemisphere climate are captured in the chemistry of its snow and ice layers.

Sulfate (SO_4^{2-}) is one of the major chemical species present in Earth's atmosphere and its aerosols are involved in many important atmospheric processes. 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 resulting in enhanced levels of 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].

3.1.2 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, in press]. 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, in press]. 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 [Whitlow and others, 1992; Legrand 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 $ssSO_4^{2-}$ concentrations to decrease concurrently. 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 they are regions of greatly enhanced primary and secondary production in summer [Arrigo and Van Dijken, 2003a; Kaspari and others, this issue]. 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. 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 - $Na_2SO_4 \cdot 10H_2O$) 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 [Mulvaney and Peel, 1988; Wagenbach and others, 1998], indicating that frost flowers are a dominant source of marine aerosols to coastal sites in winter. However, Kreutz and others [2000a], using the Siple Dome ice core, and Kaspari and others [this issue], using ITASE cores, show that the ice core sea salt record is a proxy for the strength and position of the Amundsen Sea Low. This indicates 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 and consistent association with the methanesulfonate (MS) seasonal cycle of marine productivity [Minikin, 1998]. Peel and others [1996] show that 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 sixteen 50-115m deep, sub-annually dated ice core records (Figure 3.1) 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. Associations between the $xsSO_4^{2-}$ and $ssSO_4^{2-}$ concentration time series from each core and SIE are investigated. The importance of the SIE-SO_4^{2-} correlations in terms of the 1940 background $xsSO_4^{2-}$ rise observed in a previous study [Dixon and others, in press] is discussed.

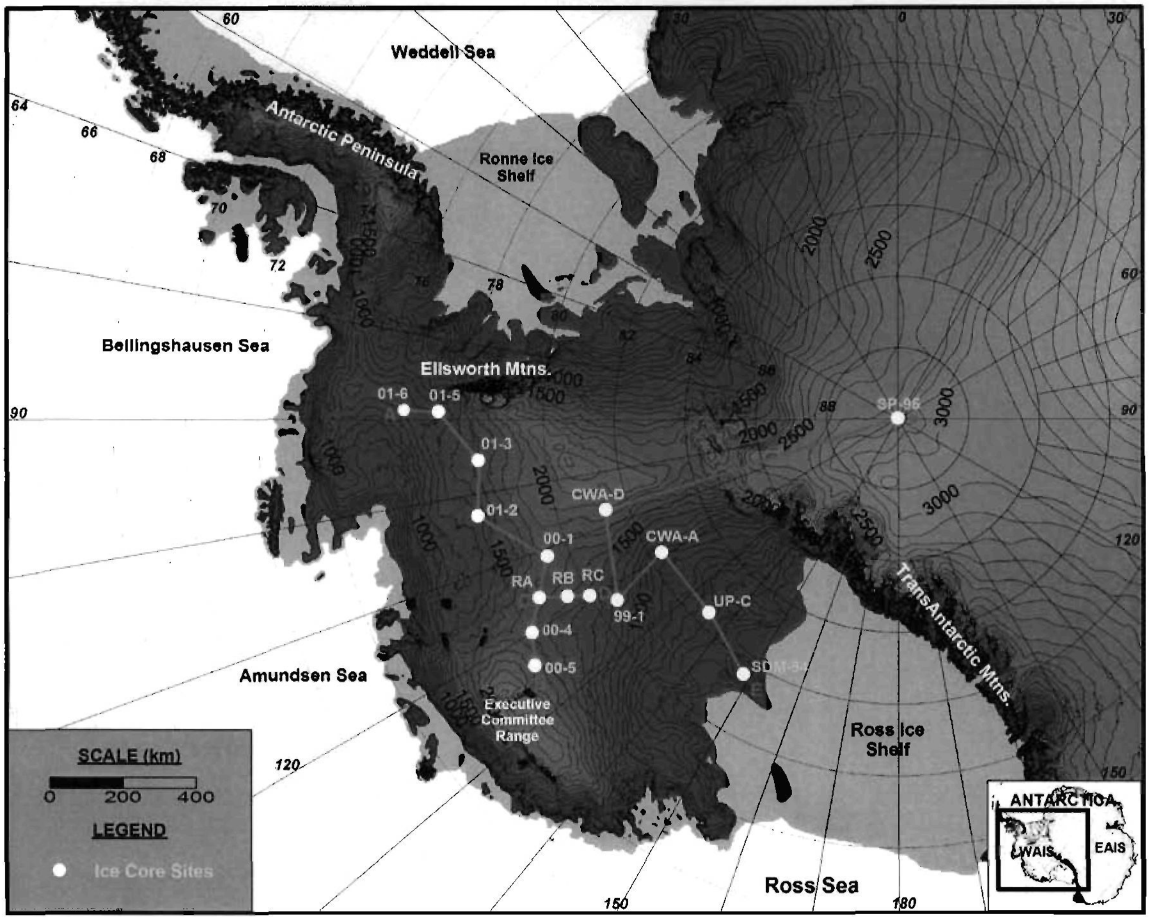


Figure 3.1:
Location map of sites with transects. RA, RB, and RC represent core sites RIDS-A, RIDS-B, and RIDS-C, respectively. Red lines (A-B, C-D and E-F) are transects referred to in figure 3.2. Map created using the RAMP Digital Elevation Model [Liu and others, 2001].

3.2 Methodology

The ice cores used in this study were collected during the Antarctic field seasons of 1994-2001 and sampled at high resolution (up to 50 samples per meter; Table 3.1) to develop sub-annually resolved time series [Dixon and others, in press]. Each sample was analyzed using ion chromatography for its soluble major ion content (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, SO_4^{2-}) and concentrations are reported in micrograms per liter (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, in press]. The counting of annual peaks between known large explosive volcanic events in our ion records, such as the 1815 eruption of Tambora, the 1883 eruption of Krakatau, the 1963 eruption of Agung and the 1991 eruption of Pinatubo, confirms that each year is preserved in each high-resolution ice core record and allows a dating accuracy of better than one year [Dixon and others, in press].

Location	Lat.	Long.	Elev. (m)	Mean Acc. (cm H2O)	Distance from open water (km)	ssSO4 Conc. (1952-1991 Mean)	xsSO4 Conc. (1952-1991 Mean)	ssSO4:xsSO4 (1952-1991 Mean)	Depth (m)	High-Res. Time Period (Years AD)	Sampling Res. (cm)	Samples Per Year (High Res. Mean)
ITASE 01-6	76.0968	89.0147	1232	39.7	320	7.1	29.9	0.24	18	2000-1978	2.1 - 3.6	28
ITASE 01-5	77.0593	89.1375	1246	36.5	400	6.8	29.4	0.23	114	2002-1781	1.5 - 3.5	23
ITASE 01-3	78.1202	95.6463	1633	32.7	370	4.2	24.9	0.17	71	2002-1869	1.5 - 3.2	20
ITASE 01-2	77.8436	102.9103	1353	42.5	295	6.4	30.8	0.21	71	2002-1890	1.7 - 4.1	27
ITASE 00-1	79.3831	111.2286	1791	22.3	475	5.7	30.0	0.19	105	2001-1651	1.6 - 3.5	13
ITASE 00-4	78.0829	120.0764	1697	19	460	7.9	37.2	0.21	58	2001-1799	1.4 - 3.1	13
ITASE 00-5	77.6821	123.9914	1828	14.6	400	8.1	53.7	0.15	60	2001-1708	2 - 6.4	8
RIDS-A	78.7300	116.3300	1740	23.6	440	6.2	28.0	0.22	150	1996-1831	3 & 60	11
RIDS-B	79.4600	118.0500	1603	14.8	535	5.9	39.1	0.15	60	1996-1926	3, 20, & 30	9
RIDS-C	80.0100	119.5600	1530	11.1	580	5.8	45.7	0.13	60	1996-1905	2, 3, & 25	9
Siple Dome-94	81.6481	148.7900	620	11.8	385	32.7	82.4	0.40	150	1995-1891	2 & 25	10
Up-C	82.4391	135.9720	525	11.5	640	21.5	85.7	0.25	28	1996-1870	3	7
CWA-(A)	82.3671	119.2855	950	14.5	860	13.1	46.1	0.28	93.5	1994-1939	3 & 40	9
ITASE 99-1	80.6200	122.6300	1350	13.6	640	11.8	40.3	0.29	58	2000-1713	2 - 4.3	8
CWA-(D)	81.3723	107.2750	1930	21.3	735	5.5	30.3	0.18	50.5	1994-1952	3 & 60	13
South Pole-95	90.0000	0.0000	2850	8.2	1300	2.6	52.6	0.05	71	1992-1487	2	6

Table 3.1:

Information for each ice core used in this study (50-year means). Elev. = elevation, Mean Acc.=mean annual accumulation, Conc.=concentration in ppb, Sampling Res.=sampling resolution, and Samples Per Year=mean number of samples per year calculated from high entire high-resolution section of each core.

Each ice core SO_4^{2-} time series is separated into its primary constituents, $ssSO_4^{2-}$ and $xsSO_4^{2-}$, using the technique described by O'Brien and others [1995]. 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 thereby lessening the likelihood of a possible $ssSO_4^{2-}$ 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, 2000b] or for the glaciochemical series used in this study [Dixon and others, in press], so flux corrections for accumulation were not applied.

In order to characterize and compare the total $ssSO_4^{2-}$ and $xsSO_4^{2-}$ concentration at each ice core site the mean values for the period 1952-1991 (Figure 3.2) are calculated. The 1952-1991 period is used because this is the longest time period covered by a significant number of the cores in this study (mean value for site 01-6 is calculated from 1978-1991 – the full length of the record). Raw $ssSO_4^{2-}$ and $xsSO_4^{2-}$ time series for the last 200 years are plotted to determine the seasonal- and longer-term variance in each of the ice core SO_4^{2-} records (Figure 3.3).

Linear correlations of annually averaged $ssSO_4^{2-}$ and $xsSO_4^{2-}$ concentrations from each core versus SIE data [Jacka, 1983] are performed (the Up-C core is not used because of data gaps) to determine how SIE affects SO_4^{2-} concentrations at the South Pole and across West Antarctica. The annual $xsSO_4^{2-}$ concentration is calculated for each year from June to June (referred to as type A), and the annual $ssSO_4^{2-}$ concentration is calculated from January to January (type B), as these periods best cover the annual concentration peak in each SO_4^{2-} time series. The SIE data were compiled from satellite derived maps (U.S. Navy and National Oceanic and Atmospheric Administration Joint Ice Center) which by definition has the ice edge determined by a sea ice concentration of >15% [Jacka, 1983, and monthly updates]. For each month (January 1973 to 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 is August 1975 for all longitudes. The August average (1973-1996) 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 1974-1996 and 1973-1996 respectively. Correlations are performed between the $xsSO_4^{2-}$ (A) and SIE (A) data and the $ssSO_4^{2-}$ (B) and SIE (B) data. Longitudinal SIE segments that correlate above 95% significance are plotted on polar stereographic maps of Antarctica (see table 3.2 for corresponding r-values).

ssSO4-SIE (B) Correlation	r = 95%	r=99%
01-6-ssSO4	0.456	0.575
01-5-ssSO4	0.405	0.516
01-3-ssSO4	0.405	0.516
01-2-ssSO4	0.405	0.516
00-1-ssSO4	0.405	0.516
00-4-ssSO4	0.405	0.516
00-5-ssSO4	0.405	0.516
RIDS-A-ssSO4	0.414	0.526
RIDS-B-ssSO4	0.414	0.526
RIDS-C-ssSO4	0.414	0.526
SDM-94-ssSO4	0.423	0.537
CWAA-ssSO4	0.433	0.549
99-1-ssSO4	0.497	0.623
CWAD-ssSO4	0.433	0.549
SP-95-ssSO4	0.456	0.575

xsSO4-SIE (A) Correlation	r = 95%	r=99%
01-6-xsSO4	0.456	0.575
01-5-xsSO4	0.414	0.526
01-3-xsSO4	0.414	0.526
01-2-xsSO4	0.414	0.526
00-1-xsSO4	0.414	0.526
00-4-xsSO4	0.414	0.526
00-5-xsSO4	0.414	0.526
RIDS-A-xsSO4	0.423	0.537
RIDS-B-xsSO4	0.423	0.537
RIDS-C-xsSO4	0.423	0.537
SDM-94-xsSO4	0.433	0.549
CWAA-xsSO4	0.444	0.561
99-1-xsSO4	0.514	0.641
CWAD-xsSO4	0.444	0.561
SP-95-xsSO4	0.468	0.59

Table 3.2:
Pearson's r-values for the 95% and 99% significance level in correlations between annually averaged sea ice extent and annually averaged xsSO4 and ssSO4 concentrations.

3.3 Results and Discussion

3.3.1 Fifty-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 (Figure 3.1). From east to west the sites increase in elevation from ~1200m to ~1800m. Mean $xsSO_4^{2-}$ concentrations along this transect display relatively uniform values from eastern to central West Antarctica and an increase from central to western West Antarctica (figure 3.2). The increase in mean $xsSO_4^{2-}$ 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].

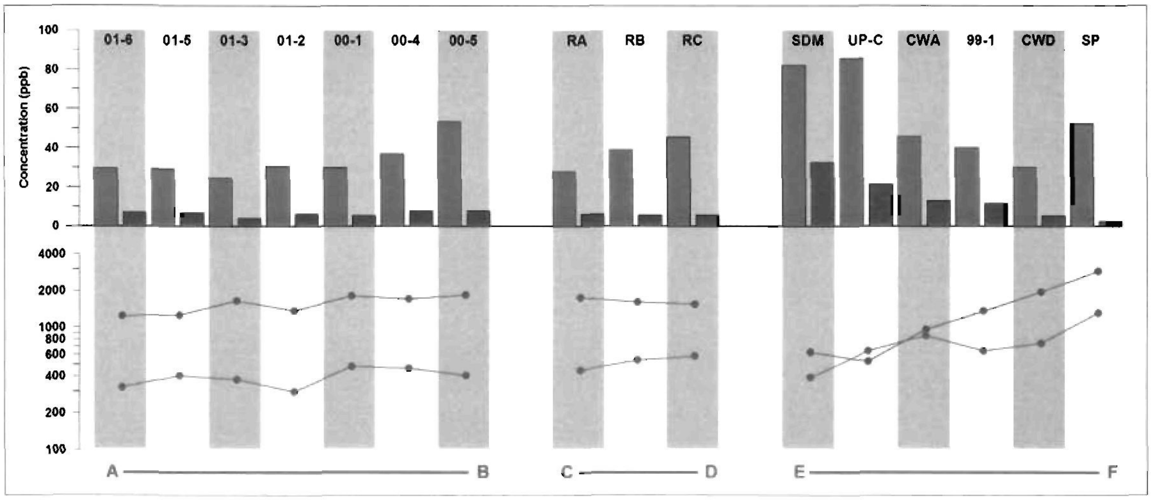


Figure 3.2:
Mean excess (red) and sea salt (blue) sulfate concentrations in ppb from 1952-1991. Data for each ice core used in this study. Green dots represent elevation in meters. Purple dots represent distance from nearest open water in kilometers. Red lines (A-B, C-D and E-F) are transects from Figure 3.1 (not to scale).

Ice core sites RA, RB, and RC are located in a ~300 km NE-SW transect (C-D) descending from the ice divide into the Ross Ice Shelf catchment area (Figure 3.1). Concentrations of $xsSO_4^{2-}$ along this transect exhibit an increasing trend toward site RC (Figure 3.2) 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 $ssSO_4^{2-}$ remain relatively constant over the spread of sites 01-6, 01-5, 01-3, 01-2, 00-1, 00-4, 00-5, 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 620m at the edge of the Ross Ice Shelf to 2850m at South Pole (Figure 3.1). Concentrations of $xsSO_4^{2-}$ decrease with increasing elevation up to site CWA-D, and the trend reverses between CWA-D and SP-95 (Figure 3.2) as a result of multiple input sources (tropospheric and stratospheric) for $xsSO_4^{2-}$ in this area [Proposito and others, 2002; Dixon and others, in press]. Concentrations of $ssSO_4^{2-}$ 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.

3.3.2 Raw Concentrations

Plots of raw (unprocessed) $ssSO_4^{2-}$ and $xsSO_4^{2-}$ concentrations against time (Figure 3.3) illustrate the large (more than an order of magnitude in some cases) increases in $xsSO_4^{2-}$ immediately following several global-scale volcanic eruptions (Tambora 1815, Cosiguina 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.

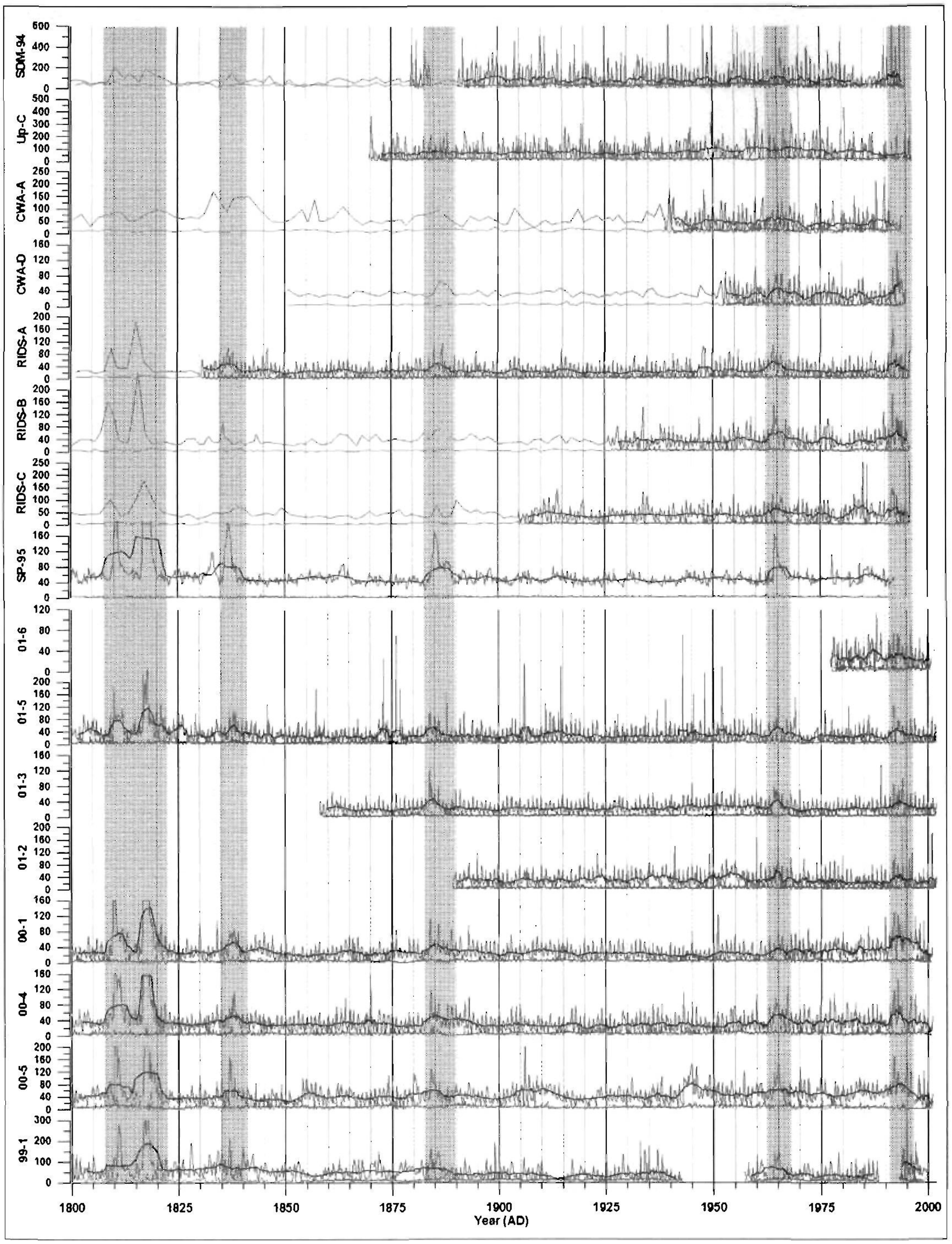


Figure 3.3:
Raw excess (red lines) and sea salt (green lines) sulfate concentrations in ppb for the years 1800-2002. Data for each ice core used in this study. Black lines (excess) and blue lines (sea salt) represent 35-51 point running averages. Vertical lines represent 5-year increments. Shaded areas represent periods of increased $xsSO_4^{2-}$ input from known global-scale volcanic events.

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 $xsSO_4^{2-}$ variance, commonly displaying low winter $xsSO_4^{2-}$ concentrations in the 0-10 ppb range. Site 01-5 (Figure 3.3) has high $xsSO_4^{2-}$ concentration variance and low winter $xsSO_4^{2-}$ concentrations, but it contains numerous large $xsSO_4^{2-}$ 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 $xsSO_4^{2-}$ input from nearby polynyas, or evaporite dust input from the nearby Ellsworth Mountains.

Site SP-95 (Figure 3.3) maintains a relatively high $xsSO_4^{2-}$ baseline (~50ppb) and low (~30-70ppb) variance throughout the year compared to other sites. It also contains unusually large (sometimes more than an order of magnitude above the mean) $xsSO_4^{2-}$ signatures from global-scale volcanic eruptions. The SP-95 $xsSO_4^{2-}$ volcanic signatures are a result of its high elevation (~2850m) and direct access to upper tropospheric/stratospheric air masses [Dixon and others, in press].

Non-volcanic $xsSO_4^{2-}$ concentrations at site 00-5 (Figure 3.3) are similar in structure to those at SP-95 (high background, low variance) during several short periods over the last 200 years (e.g. 1942-1947, 1908-1913) but are similar to the majority of West Antarctic sites for the remainder of the record (low winter values, high variance). The change in $xsSO_4^{2-}$ 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 $xsSO_4^{2-}$ signature at site 00-5 to be more similar to that at SP-95.

The mean $xsSO_4^{2-}$ concentrations at SDM-94 (Figure 3.3) frequently decrease to ~30 ppb; this is comparable to or lower than the mean $ssSO_4^{2-}$ concentration at that site, suggesting a high event frequency of at least one of the major $xsSO_4^{2-}$ sources to the site, probably marine biogenic $xsSO_4^{2-}$. The low elevation and proximity of site SDM-94 to the coast imply that its major SO_4^{2-} sources are sea salt and marine biological productivity from the adjacent ocean area. Therefore, a likely cause for the observed $xsSO_4^{2-}$ fluctuations is reduction of Ross Sea primary production caused by changes in SIE. Arrigo and Van Dijken [2003b] showed that the presence of iceberg C-19 in 2002-2003 restricted the summer loss of sea ice in the southwestern Ross Sea and consequently reduced primary production in the region by over 90%. Interestingly, the $xsSO_4^{2-}$ fluctuations in the SDM-94 record are not observed at Up-C or CWA-A as would be expected from events of this magnitude. An $xsSO_4^{2-}$ record from the SDM-94 site covering the period 2002-2003 would help to confirm whether this iceberg calving event significantly reduced $xsSO_4^{2-}$ concentrations in precipitation.

Almost every core in this study has a mean $ssSO_4^{2-}$ to $xsSO_4^{2-}$ ratio between 0.13 and 0.29 (Table 3.1); 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 $ssSO_4^{2-}$ concentrations resulting from its high elevation and distance from the coast, as well as the fact that $xsSO_4^{2-}$ concentrations at this site maintain a relatively constant baseline (~50ppb) and low (~30-70ppb) variance throughout the year. The high $ssSO_4^{2-}$ to $xsSO_4^{2-}$ 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.

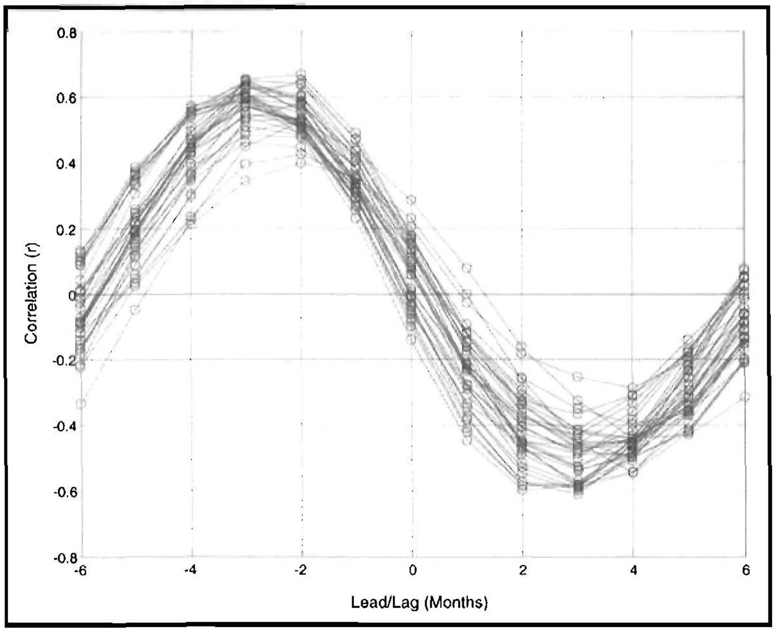


Figure 3.4:
Correlation results for SDM-94 monthly excess sulfate concentrations against every 10-degree monthly sea ice data segment from 0 to 360 degrees longitude.

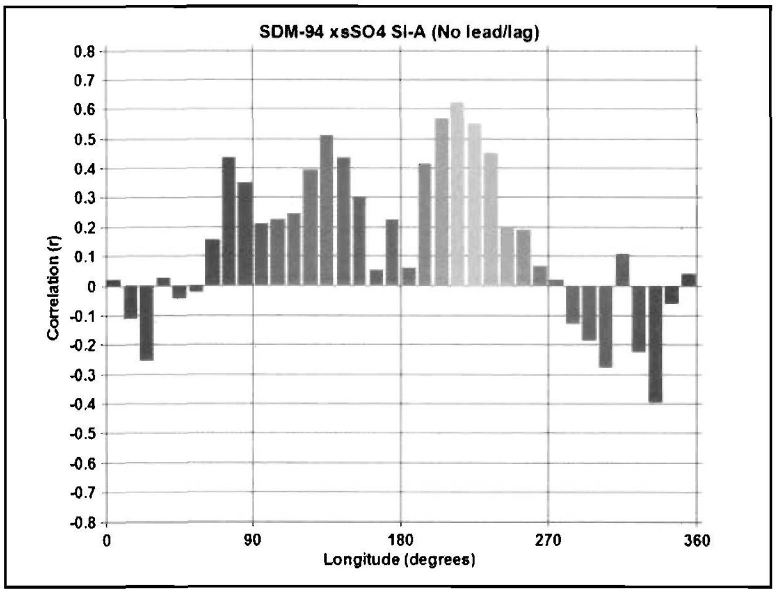


Figure 3.5:
Correlation results for SDM-94 annual excess sulfate concentrations against every 10-degree annual sea ice extent data segment from 0 to 360 degrees longitude. (N=22, r ≥ 0.423 = 95% significant, r ≥ 0.537 = 99% significant).

3.3.3 Sea Ice Correlations

Linear correlation between monthly values of SIE and monthly values of SDM-94 $xsSO_4^{2-}$ was performed to determine if SIE controlled $xsSO_4^{2-}$ concentrations in precipitation (Figure 3.4). SDM-94 was chosen to begin with because it is the nearest to open water of our low elevation sites. 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 auto-correlation problems both time series were re-sampled 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. An expanded view of the zero lead/lag segment (Figure 3.5) shows that the strongest correlation occurs with SIE from longitudes 120°-160° and 190°-240°.

Linear correlations with annually averaged SIE were also performed on the annually averaged $xsSO_4^{2-}$ and $ssSO_4^{2-}$ records from each core (Figure 3.6). The statistically significant results (>95%) show that in general the SIE closest to West Antarctic ice core sites, in the Ross, Amundsen and Bellingshausen Seas, is negatively correlated with $ssSO_4^{2-}$ ($r \geq 0.405$ to 0.537) and positively correlated with $xsSO_4^{2-}$ ($r \geq$ 0.414 to 0.561) concentrations. Since the correlation with SIE is a function of latitude on Figure 3.6, a positive correlation means decreased SIE when SO_4^{2-} concentrations are high. A negative correlation means increased SIE when SO_4^{2-} concentrations are high.

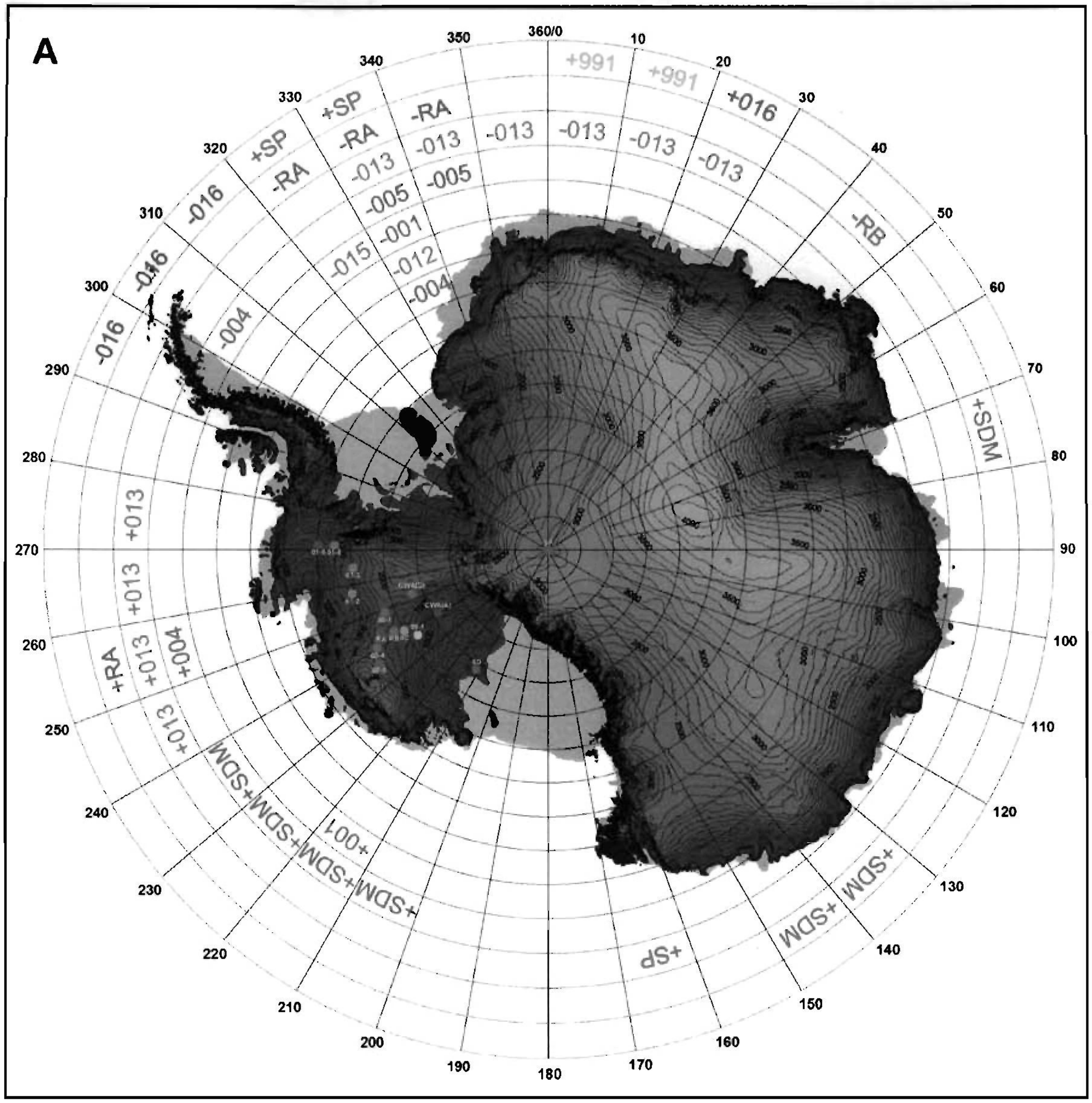


Figure 3.6:
Correlations between a) annually averaged sea ice extent and excess sulfate, and b) annually averaged sea ice extent and sea salt sulfate. All plotted sites represent correlations above 95% significance. A "+" indicates a positive correlation and a "–" indicates a negative correlation for 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. SDM, 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].

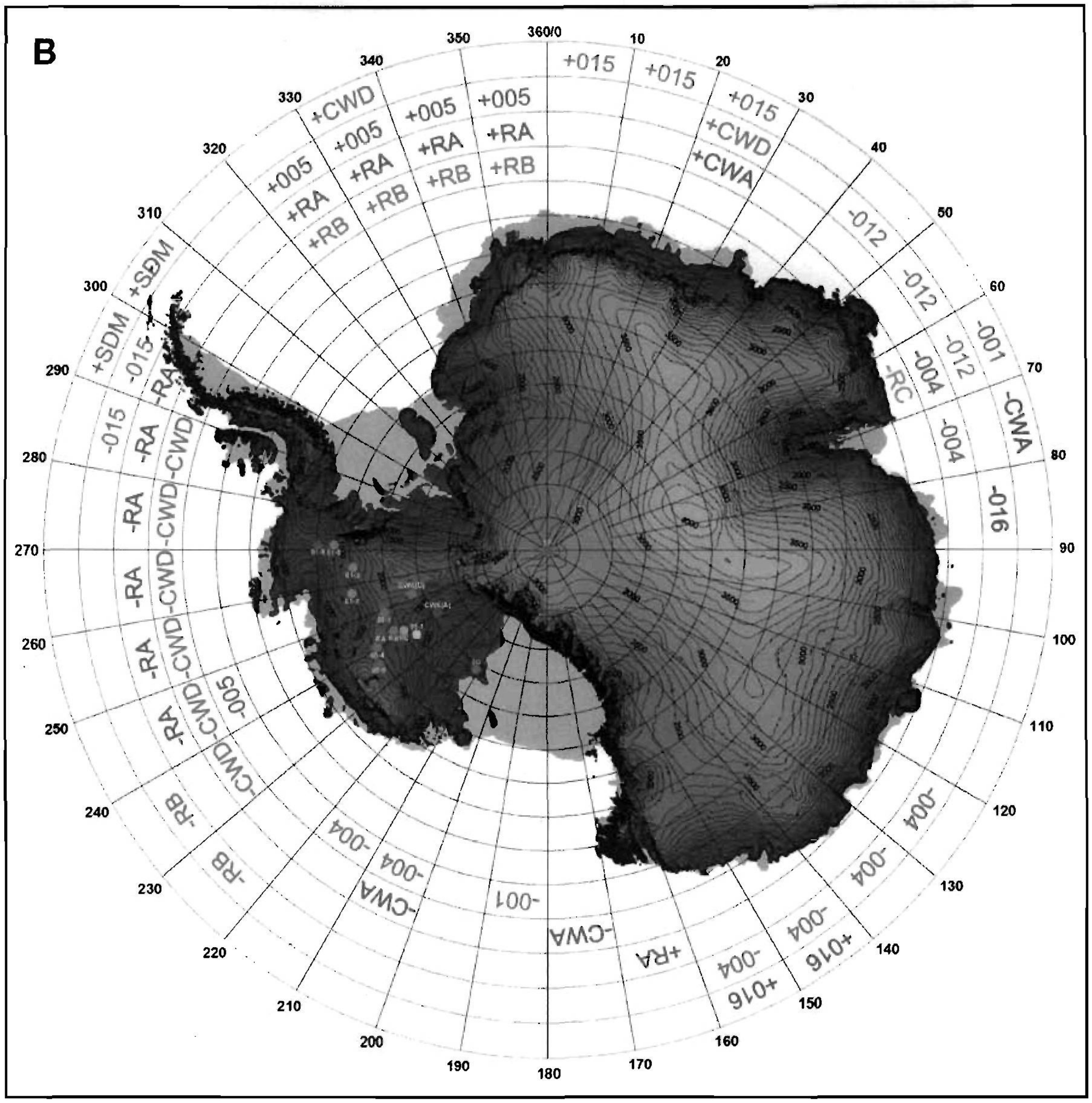


Figure 3.6: (Continued).

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 (Figure 3.6). For example, 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 Atlantic region then this result is in agreement with several previous studies [Welch and others, 1993; Meyerson and others, 2002; Curran and others, 2003]. However, if, as is more likely, the primary $xsSO_4^{2-}$ source for site 01-3 is the Bellingshausen-Amundsen-Ross region, then the results in this study suggest that the SIE-$xsSO_4^{2-}$ relationship is opposite to that of SIE-MS and 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]. The differences between the results of this study and those of previous studies [Welch and others, 1993; Curran and others, 2003] may be due to the fact that none of the sites in this study are truly coastal (although SDM-94 has some coastal characteristics). Also, this study examines $xsSO_4^{2-}$ 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 (Figure 3.6) 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 resulting in greater volumes of highly saline aerosols [Rankin and others, 2002; Kaspari and others, this issue]. 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, 2000a]. 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.

This study of $xsSO_4^{2-}$ does not reveal strong associations between longitudinal bands of SIE in the Amundsen-Ross region and SP-95 $xsSO_4^{2-}$ concentrations, but it does show a positive association between increased SP-95 $xsSO_4^{2-}$ concentrations and reduced SIE in the Weddell Sea region. The SP-95 SIE correlation of Meyerson and others [2002] is based upon smoothed (7-point running mean) monthly MS and SIE values and an average SIE calculated from 185° to 245° longitude, which probably explains why similar patterns are not observed in this study. The positive association observed between increased SP-95 $xsSO_4^{2-}$ concentrations and reduced SIE in the Weddell Sea region suggests that the source region for SP-95 $xsSO_4^{2-}$ is probably different to that of the high-elevation West Antarctic cores in this study.

With the exception of site 01-3 and 01-5 (both eastern West Antarctic sites), the location of the majority of these SIE-$ssSO_4^{2-}$ and SIE-$xsSO_4^{2-}$ associations in the Bellingshausen-Amundsen-Ross region (above 95% significance) is central and western West Antarctica. One reason for this grouping of SIE associations may be that the SIE in the Weddell region affects sites in eastern West Antarctica, potentially canceling out the signal from the Bellingshausen-Amundsen-Ross region.

Another important consideration is the effect of coastal polynyas on the sulfur budget of West Antarctica. Three of the four most productive Antarctic polynyas surround West Antarctica, and the dominant polynya with respect to total area-weighted production is in the Ross Sea, accounting for half of the total polynya production on the entire Antarctic continental shelf [Arrigo and Van Dijken, 2003a]. 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, 2003a]. As a result, polynyas may be a significant source of both $ssSO_4^{2-}$ (in winter) and $xsSO_4^{2-}$ (in summer) to West Antarctic sites.

3.3.4 Background Sulfate Concentrations

A previous study [Dixon and others, in press] has shown that a significant rise in background $xsSO_4^{2-}$ concentrations occurs from 1940-present in central West Antarctic ice core sites (00-1, 00-4, 00-5, RIDS-A, RIDS-B and RIDS-C; Figure 3.7). The rise could not be attributed to anthropogenic activities because it does not show up in all high-elevation $xsSO_4^{2-}$ concentration records. This study suggests that the 1940 $xsSO_4^{2-}$ rise cannot be attributed to changes in sea ice extent because $xsSO_4^{2-}$ concentrations at sites 00-5, RIDS-B and RIDS-C are not statistically related to SIE above 95% significance, and sites 00-1, 00-4 and RIDS-A are not related to SIE above 99% significance. The robust spline-smoothed $ssSO_4^{2-}$ curves for sites 00-1, 00-4, 00-5, RIDS-A, RIDS-B and RIDS-C do not exhibit any downward trends around 1940 (Figure 3.7) as would be expected if the trends were SIE related.

A study by Kaspari and others [in press] 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 either a change in production in the mid-low latitudes and/or increased transport from the mid-low latitudes to central West Antarctica.

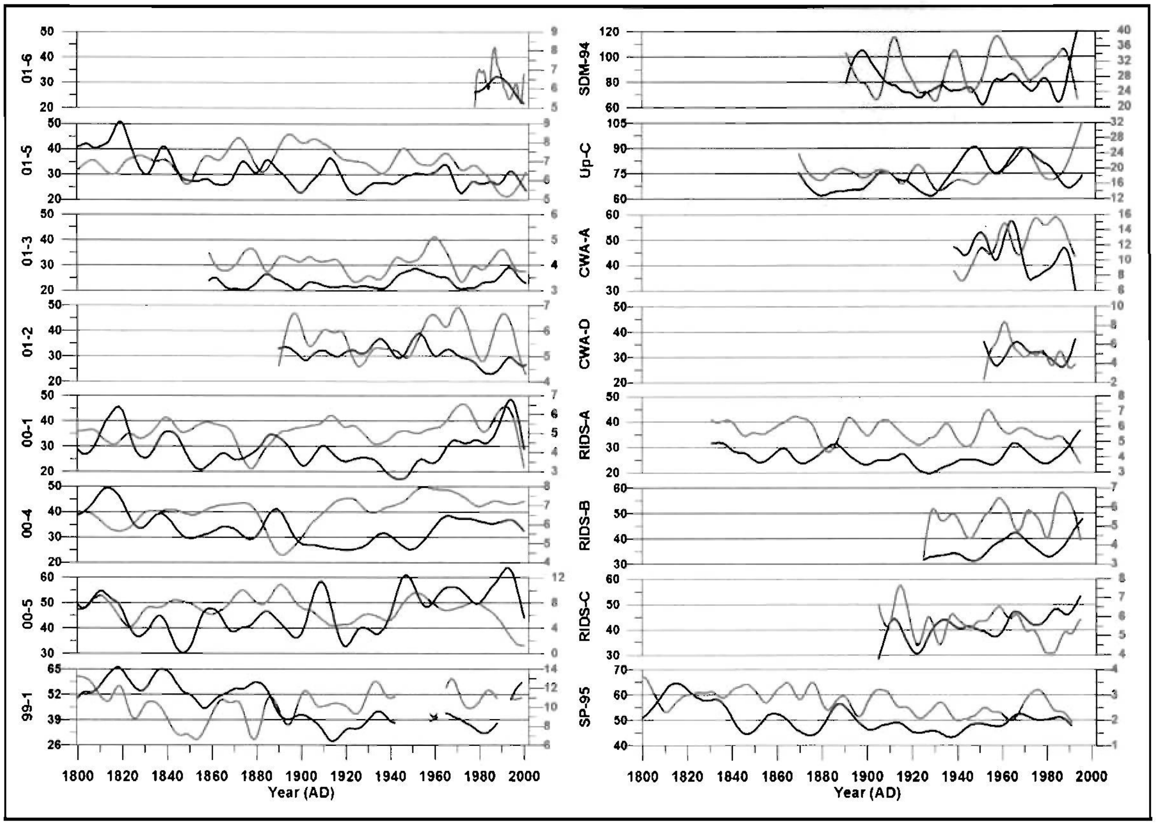


Figure 3.7:
Robust spline-smoothed annual excess sulfate (black) and sea salt sulfate (red) concentrations for each ice core for the years 1800-2002. All concentrations are in ppb. Note scale change from site to site.

Chapter 4

CONCLUSIONS

The 16 high-resolution sub-annual records presented in this study preserve every year of chemical deposition in detail for the full length of each record. The dating accuracy of these records is estimated to be better than 1 year. Each record is calibrated using several known global-scale volcanic horizons. The detailed preservation of annual layers in the ice cores provides a remarkable opportunity for the investigation of major contributions to the Antarctic SO_4^{2-} budget, notably: $ssSO_4^{2-}$, volcanic event $xsSO_4^{2-}$, and $rxsSO_4^{2-}$.

These data show that sites located below 1000m elevation (SDM-94, Up-C, and CWA-A) receive higher concentrations of $ssSO_4^{2-}$ than sites located above 1000m elevation. EOF results suggest that the sites located above 1000m elevation receive a large percentage of $ssSO_4^{2-}$ from common air masses/sources. Sites located below 1000m elevation receive $ssSO_4^{2-}$ from common air masses/sources that are separate from the air masses/sources supplying sites located above 1000m elevation.

Concentration trends imply a dual source for West Antarctic $xsSO_4^{2-}$: lower tropospheric near the coast and mid-upper tropospheric/stratospheric for higher elevation areas. These results highlight the relative importance of different $xsSO_4^{2-}$ sources and pathways for sites at different elevations. The $rxsSO_4^{2-}$ records reveal an overall concentration decrease at all sites over the period 1800 to ~1940. Several of the $rxsSO_4^{2-}$ records also exhibit an increasing trend from ~1940 to ~1990 and several exhibit a decrease during this same time period. These $rxsSO_4^{2-}$ trends suggest that a significant shift in the spatial distribution of SO_4^{2-} took place over West Antarctica at ~1940. The atmospheric circulation changed in such a way as to increase the transport of $rxsSO_4^{2-}$ to inland West Antarctica and decrease it to other West Antarctic sites. This implies a major change in atmospheric circulation at this time which could not have been inferred from a single ice core, highlighting the importance and value of having an array of accurately dated spatially distributed records. The records used in this study do not imply an anthropogenic source for any of the observed trends in $rxsSO_4^{2-}$.

In these records all global-scale volcanic eruptions appear as 2σ peaks, as determined using residuals from a robust spline of the $xsSO_4^{2-}$ records. Global scale volcanic eruptions cannot be consistently resolved in the $xsSO_4^{2-}$ records for sites located below 1000m elevation because the majority of volcanic SO_4^{2-} from global-scale eruptions is transported to Antarctica through the mid-upper troposphere/stratosphere, and sites located below 1000m elevation do not receive a significant fraction of $xsSO_4^{2-}$ from this source. High $ssSO_4^{2-}$ and local marine biogenic SO_4^{2-} further obscure much of the volcanic SO_4^{2-} present at these lower elevation sites. The $xsSO_4^{2-}$ signals from global-scale volcanic eruptions can be used as reliable depth/age markers in West Antarctic cores located above 1000m elevation, but they cannot be used definitively at sites located below 1000m elevation.

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. For example, the proximity of the Ellsworth Mountains affects the $xsSO_4^{2-}$ record at site 01-5, chemical concentrations at sites SDM-94 and Up-C are significantly affected by their proximity to the Ross Ice Shelf and the Ross Sea Polynya. The high elevation of site SP-

95 causes its baseline $xsSO_4^{2-}$ concentration to remain high with low variability because the South Pole site is dominated by upper tropospheric/stratospheric air masses. Ice core sites in the northwest corner of West Antarctica, such as site 00-5, exhibit extended periods of elevated $xsSO_4^{2-}$ baseline that are similar in structure to the SP-95 $xsSO_4^{2-}$ record. These periods of elevated baseline are probably due to extended outbreaks of downwelling upper atmosphere air masses over the Executive Committee Mountains.

Linear correlations between SIE and the $ssSO_4^{2-}$ and $xsSO_4^{2-}$ records from 15 of the cores in this study reveal that $ssSO_4^{2-}$ concentrations are higher with increased SIE and $xsSO_4^{2-}$ concentrations are higher when SIE is decreased. 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 [this issue]. Conversely, our SIE-$xsSO_4^{2-}$ association suggests that open ocean areas favor production of $xsSO_4^{2-}$. 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 $xsSO_4^{2-}$ from the Weddell region, a different source than the other West Antarctic sites in this study that receive $xsSO_4^{2-}$ from the Bellingshausen-Amundsen-Ross region.

The out-of-phase behavior between SIE in the Weddell region and the rest of Antarctica is a common pattern for SIE and is evident in the SIE - SO_4^{2-} associations in this study. 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.

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Since arriving in Maine in October 2000, Dan has been involved in the U.S. ITASE traverses in West Antarctica. He spent three field seasons in Antarctica from 2001-2004 and helped to drill many hundreds of meters of ice core during that time.

After receiving his degree, Dan will pursue a Ph.D. in Earth Sciences at the University of Maine. Dan is a candidate for the Master of Science degree in Quaternary and Climate Studies from The University of Maine in August 2004.