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Ice core glaciochemical records of late holocene climatic variability in West Antarctica

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ICE CORE GLACIOCHEMICAL RECORDS OF LATE HOLOCENE CLIMATIC VARIABILITY IN WEST ANTARCTICA

BY

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ABSTRACT

ICE CORE GLACIOCHEMICAL RECORDS OF LATE HOLOCENE CLIMATIC VARIABILITY IN WEST ANTARCTICA

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The complex atmospheric and glaciological dynamics of West Antarctica make this region of particular interest in addressing the continent's cause and effect relationship in the global climate system, and for evaluating future global change scenarios. Ice core records from this region provide the resolution necessary to both improve our understanding of modern regional climate variability, and to reconstruct past changes in a number of climate components.

High-resolution (subannual to biannual) snow and ice core samples collected from two regions of West Antarctica, Siple Dome and Marie Byrd Land, were analyzed for water soluble major ion content. Examination of detailed surface snow data is used to determine seasonal chemical input timing, spatial variability, depositional and post-depositional processes, chemical sources, and transport pathways.

To develop quantitative relationships between temporal changes in ice core records and regional climatic conditions, Siple Dome glaciochemical data are correlated with meteorological observations, satellite sea ice data, and numerical modeling output. Results indicate that seasalt glaciochemistry at Siple Dome is a reliable proxy for changes in the Amundsen Sea Low pressure system. Multivariate time-series statistical investigation using high-resolution (subannual) chemical data suggests no significant trend in sea level pressure and atmospheric circulation strength over the past 110 years in the high-latitude South Pacific.

West Antarctic ice core glaciochemical records are correlated with other high-resolution climate proxy records to investigate climatic change over the last millennia. Comparison of Siple Dome and Central Greenland (GISP2) glaciochemical records reveals the synchronous onset of the Little Ice Age (LIA) in the polar South Pacific and North Atlantic. In these records, the LIA is recorded as a period of increased meridional wind strength beginning at ~1400 AD., and continuing to present in these two regions.

The research presented in this dissertation provides necessary baseline information for interpreting additional shallow and deep ice core records eventually recovered from West Antarctica. Such records will greatly advance our understanding of the high-latitude Southern Hemisphere climate system, as well as evaluate the past global extent, timing, and phasing of rapid climate change events.

I. INTRODUCTION

I. INTRODUCTION

Knowledge of sources and patterns of climatic variability over the complete range of time scales is essential to understanding how the climate system operates and will react to both internal and external forcings in the future. Most work on natural climatic variability has focused on Milankovitch (10,000-100,000 year) time scales, and has led to an understanding of the external orbital forcing mechanism. Far less, however, is known about natural climatic variability on shorter time scales (10-1,000 year), which are the time scales most relevant to mankind's concerns for global environmental change. Paleoclimatic records contain numerous examples of both short-term and abrupt climatic change. Century-scale events (e.g., the Little Ice Age and Medieval Warm Period), the Younger Dryas, and other millennial-scale (Dansgaard-Oeschger) events during the Last Glacial Maximum and subsequent deglaciation provide evidence that climatic change can be both large in magnitude and abrupt. Recent climatic events (last 2,000 years) are the best preserved, and hence provide the best opportunity for understanding the complex interaction of components of the Earth's climate system. Additional information on the magnitude, frequency, and nature of these short-term climatic events is essential to understanding and predicting current and future climatic trends.

Ice core records have proven to be important indicators of paleoclimatic change due to the decadal or higher resolution, continuous, and multivariate records which can be obtained. While ice cores can potentially be collected from many areas, the best preserved records are generally available from polar ice sheets. Recently recovered ice cores from Greenland document both anthropogenic and natural forcings on the climate system. In particular, glaciochemical records provide a valuable resource for examining climatic change through atmospheric chemistry. Continuous, high-resolution, multivariate glaciochemical records from the Greenland Ice Sheet Project 2 (GISP2) core have provided greater understanding of the following: 1) rapid climate change events; 2) change in chemical composition of the troposphere and stratosphere; 3) regional trends in atmospheric chemistry; 4) transport pathways, sources and input timing of chemical species found in snow; 5) atmospheric circulation (advection of marine air masses, circulation intensity, dustiness, wind strength, and precipitation rate); 6) volcanic events; 7) biogeochemical cycling (e.g., nitrogen and sulfur); and 8) marine biogenic production. Such records provide information to interpret past environments and aid in predictive modeling.

Ice core glaciochemical records have been used to determine paleoclimatic conditions in various Antarctic locations. None of these records, however, are comparable in dating or resolution to the GISP2 core, and very little is known about the Holocene (last 10,000 years). Drilling at Vostok Station recently reached a depth of ~4000 meters (m), providing the oldest ice core record available (~400,000 years). However, low accumulation at the site precludes yearly dating via layer counting available at GISP2, and multivariate chemical analyses have not been performed. Compared to other regions of Antarctica, very little is known about the snow and ice chemistry of West Antarctica. Only one deep core (Byrd Station) has been drilled, and major ion chemistry has been analyzed at very low resolution (1 sample every 50 m). Stable isotope records from West Antarctica provide a complex view of climate change for the last 2,000 years. Additional information is needed to determine the Holocene climate history of West Antarctica, and place this glaciologically and meteorologically dynamic area in a regional and global context.

The focus of the research presented in this dissertation research is the collection and development of new continuous, high-resolution, intermediate (1-2,000 year) ice core glaciochemical records from West Antarctica with similar sampling resolution and quality to that of GISP2. Such records provide important climatic information for the time period (last 2,000 years) deemed critical by the International Geosphere-Biosphere Program (IGBP), as well as address the geographic imbalance in information that exists between the northern and southern hemispheres. Correlation of these new records with those already existing in East Antarctica provides a well-spaced sampling of one of the most climatologically significant areas of Antarctica. The sites used in this study have been chosen by the U.S. ice core community as future deep drilling locations. Therefore, in addition to solving a number of scientific objectives, these records will provide reconnaissance for future drilling efforts in West Antarctica.

The body of this dissertation consists of six sections (II through VII), each of which represents a paper that has already been published (Kreutz et al., 1997a), is in press (Kreutz et al., in press), has been submitted for publication (Kreutz and Mayewski, in review), or is intended for submission for publication. Other papers dealing with West Antarctic snow chemistry that have been published but are not presented here include Kreutz et al. (1996) and Kreutz et al. (1997b). Each section of the dissertation contains its own abstract, introduction, review of methods, presentation and discussion of results, conclusions and acknowledgments. A complete reference list is given at the end of the dissertation. All of these papers deal with a different aspect of our glaciochemical research in West Antarctica. Together, these papers provide an improved understanding of glaciochemical sources, transport and spatial variability, as well as addressing the overall

objective of reconstructing atmospheric circulation conditions over the last 1000 years in West Antarctica.

Section II (Spatial Survey of Antarctic Surface Snow Glaciochemistry) provides a review of all published surface snow glaciochemical data developed from snow and firn samples collected prior to 1997. This compilation emphasizes the paucity of data available from the East and West Antarctic polar plateaus, and highlights the need for an improved spatial and temporal understanding of glaciochemical records from these regions. Existing data is used to study the effects of distance from the coast, elevation, and accumulation rate on glaciochemical concentrations in Antarctica, and to place glaciochemical concentrations from study sites used in this dissertation in a broader context.

Section III (Seasonal Variations of Glaciochemical, Isotopic, and Stratigraphic Properties in Siple Dome Surface Snow) presents a multiparameter technique for dating annual layers in Siple Dome surface snow. Limitations in several individual measurements are noted (due to lack of identifiable seasonal signals, or post-depositional processes), and the most accurate species signals are identified. Results of this study are used in other regions of West Antarctica, which demonstrate similar seasonal glaciochemical signals.

Section IV (Spatial Variability and Relationships Between Glaciochemistry and Accumulation Rate at Siple Dome and Marie Byrd Land, West Antarctica) assesses several critical issues relating to glaciochemical time-series interpretation. Dating techniques are tested and are found to be accurate in records longer than those presented in Section III. Glaciochemical spatial variability in both study regions is examined to determine if annual layer variability is significant. Investigation of the glaciochemical/accumulation rate relationship suggests that each parameter contains independent information on climate processes. Finally, spatial and temporal gradients in accumulation rates are examined, and linked to dominant moisture transport pathways.

Section V (Post-Depositional Processes in West Antarctic Glaciochemical Records) documents post-depositional migration of MSA, NO_3^-, and Mg^{2+} in a Siple Dome ice core. While the migration of these species is shown to be limited to within one annual layer, interpretation of past atmospheric dynamics and chemistry must take these phenomena into account. Potential mechanisms responsible for the observed chemical migration are discussed, which are likely related to the distinct character of summer (more acidic) and winter (more basic) snow at Siple Dome.

Section VI (Sea-Level Pressure Variability in the Amundsen Sea over the Past Century Inferred From a West Antarctic Glaciochemical Record) describes the development of an ice core glaciochemical proxy record of atmospheric circulation conditions in the West Antarctic region over the past 110 years. Using operational numerical analyses, sea-ice

extent data, and station pressure data, a record of seasalt aerosol transport and deposition at Siple Dome is calibrated to sea-level pressure (SLP) conditions in the Amundsen Sea region (the Amundsen Sea Low). This calibrated ice core proxy record is then used to examine interannual SLP variability in the region over the past 110 years.

Section VII (Comparison of West Antarctic and Greenland Climate over the Last Millennium) represents the overall objective of this dissertation, namely to reconstruct atmospheric circulation conditions in West Antarctica over the past 1000 years and correlate observed changes with other proxy records. This paper presents the first calibrated proxy record of atmospheric circulation in West Antarctica over the past 100 years, and documents the onset of Little Ice Age (LIA) conditions in the region (intensified meridional atmospheric circulation related to the Amundsen Sea Low). Onset of LIA conditions in the polar South Pacific is found to be synchronous with changes observed in the polar North Atlantic (based in the Greenland Ice Sheet Project Two [GISP2] ice core) at ~1400 A.D. Atmospheric circulation conditions common during the LIA in both regions appear to have persisted into the 20th century.

The final section (VII; Concluding Remarks) provides an overall interpretation of the dissertation results, as well as outlining the significance and contribution of the research presented here to other programs.

II. SPATIAL SURVEY OF ANTARCTIC SURFACE SNOW GLACIOCHEMISTRY

Section II has been submitted to Antarctic Science for publication (full citation appears in the Complete List of References)

II. SPATIAL SURVEY OF ANTARCTIC SURFACE SNOW GLACIOCHEMISTRY

ABSTRACT

Ice core glaciochemical records provide detailed information on past changes in atmospheric chemical composition and circulation, which is essential for understanding 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 seasalt and methanesulfonic 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.

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, 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). Knowledge of the spatial and temporal variations in chemical species has added to our understanding of atmospheric circulation (Mayewski and Lyons, 1982; Legrand et al., 1988), biogeochemical cycling (Mayewski et al., 1986;

Mayewski et al., 1990), sea-ice extent (Welch et al., 1993), and volcanic activity (Delmas et al., 1985).

Due to its isolation both geographically and meteorologically, Antarctica is an ideal place to study modern background levels of atmospheric chemicals, as well as collect long records of changes in atmospheric composition. Several ice cores have been recovered and analyzed for soluble ionic chemistry in Antarctica (Fig. II.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 and Legrand 1985; Mayewski et al., 1996), and document significant decadal scale variability in chemical composition during the last few centuries (Mayewski and Lyons 1982; Mosley-Thompson, 1992; Welch et al., 1993). In addition, new ice core glaciochemical evidence suggests that climate variability during the last glacial/interglacial transition was similar in both the northern and southern hemispheres (Mayewski et al., 1996). Two sites in West Antarctica (Siple Dome and inland West Antarctica) have been identified as locations for new U.S. 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., in press) (Fig. II.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 and 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, accumulation rate). In this way, an individual site or region can be compared to overall trends to indicate dominant glaciochemical controls. Recently, Mulvaney and Wolff (1994; and references therein; hereafter refered to as MW) compiled selected Antarctic surface snow chemistry data to examine spatial variability on a continent-wide scale. Relationships in seasalt (ss) (i.e. Na^+, Cl^-), nonseasalt (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 and Langway, 1979; Herron, 1982; Legrand and Delmas, 1985), were found to be the same on a continental scale. The effect of accumulation rate on nssSO_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 methanesulfonate (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 seasalt, 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), dimethylsulfide (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 Nino-Southern Oscillation (ENSO) (Legrand and 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. seasalt, volcanoes, biogenic activity, nitrogen fixation) has been demonstrated by Legrand and Delmas (1984). Statistical analysis of the full glaciochemical ion suite has been used to develop air mass reconstructions for the last 110,000 years in Greenland (Mayewski et al., 1997).

To examine the major atmospheric controls (chemical sources, transport pathways and strength) 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 glaciochemical data from these sites.

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 sulfur, nitrogen, halogen and carbon cycles (Barrie and Delmas, 1994). Under present climatic conditions, soluble species dominate the impurity content of Antarctic snow (e.g. Legrand and Delmas, 1984; Legrand, 1987). The soluble ionic balance of recently deposited Antarctic snow is found to be comprised mainly of sea-salt aerosols, crustal aerosols, and gas-derived secondary aerosols (H_2SO_4, HNO_3, and HCl). An equation describing the ionic balance in Antarctic precipitation can be written as follows (Legrand and Delmas, 1985):

$$[H^+] + [Na^+] + [NH_4^+] + [K^+] + [Ca^{2+}] + [Mg^{2+}] =$$
$$[SO_4^{2-}] + [NO_3^-] + [Cl^-] \text{ (in equivalence units)}$$

Seasalt aerosols, created by bursting air bubbles at the ocean surface during vigorous stirring (Toba, 1966), are responsible for the majority of certain species (Na^+, Cl^-, and Mg^{2+}) and a smaller percentage of other species (K, Ca^{2+}, and SO_4^{2-}) in the Antarctic atmosphere. Aerosol measurements at Antarctic coastal (Neumayer [Wagenbach, 1996] and Mawson [Savoie et al., 1992]) and inland (South Pole [Tuncel et al., 1989]) stations reveal a seasonal cycle in seasalt which peaks in the winter season. However, short-term seasalt peaks have also been observed throughout the year at Mawson and Neumayer Stations, and have been linked to local storm activity (Wagenbach, 1996). Because the seasalt cycle is out of phase with seasonal sea ice fluctuations, transport of seasalt aerosols during the winter season is most likely by rapid long-range advection from large open water areas as well as from local polynias opened by heavy storm winds (Wagenbach, 1996). Surface snow concentrations of seasalt-derived species also have a seasonal cycle which peaks in winter at South Pole (Whitlow et al., 1992) and in Dronning Maud Land (Osada, 1994).

A second source of aerosols in the Antarctic atmosphere are terrestrially-derived salts. Because the vast majority of the Antarctic continent is ice-covered, crustal aerosols are most

likely long-traveled and present in relatively low levels in modern Antarctic surface snow (Legrand, 1987). Areas of exposed bedrock in Antarctica (ice-free valleys) can have an impact on the chemistry of local surface snow (Welch, 1993).

Sulfur species (SO_4^{2-} and MSA) dominate the summer Antarctic aerosol, and are probably primarily of marine origin (oxidation of DMS) (Wagenbach, 1996). Additional SO_4^{2-} sources in Antarctic air and snow are volcanic emissions and seasalt aerosols. The amount of seasalt SO_4^{2-} in polar snow is relatively small, especially at high-altitude sites in Antarctica (Delmas et al., 1982). Major volcanic eruptions occur at random intervals, and therefore can produce large spikes in snow and ice nssSO_4^{2-} concentrations. The effect of SO_2 emission from Mt. Erebus on the SO_4^{2-} budget of Antarctic snow is still unclear (Delmas, 1982), but may affect the background SO_4^{2-} level in Antarctica (Zreda-Gostynska et al., 1993). Summer peaks in nssSO_4^{2-} and MSA aerosols at Neumayer Station are well correlated with the annual DMS cycle measured at the sub-Antarctic Macquairie Island (Gillett et al., 1993), suggesting that the three are directly related (Wagenbach, 1996). Additionally, the temporal pattern of the seasonal MSA and nssSO_4^{2-} aerosol cycles in coastal aerosols exhibits a high degree of regularity (Wagenbach, 1996). Likewise, MSA and nssSO_4^{2-} concentrations in surface snow from coastal locations (Filchner-Ronne Ice Shelf [Minikin et al., 1994]) and inland (South Pole [Whitlow et al., 1992]; Dronning Maud Land [Osada, 1994]) demonstrate strong seasonal signals that peak in the summer.

Sources and transport of nitrogen species (NO_3^- and NH_4^+) to Antarctica are still not well understood. Several potential sources of NO_3^- have been proposed: 1) terrestrial sources (biomass burning, and soil release of NO; 2) production of NO by lightning in the troposphere; 3) production in the stratosphere (solar modulation and supernovae influence) (Legrand and Delmas, 1986). Recent analyses and modeling efforts suggest that the main atmospheric and snow source of NO_3^- in Antarctica is via lightning, producing NO at low to mid latitudes with subsequent poleward transport (Legrand and Delmas, 1986; Legrand and Kirchner, 1990; Wolff, 1995). The annual cycle of NO_3^- in Antarctic surface snow and air has been shown to peak in the spring/early summer (Mayewski and Legrand, 1990; Savoie et al., 1992; Whitlow et al., 1992; Mulvaney and Wolff, 1993; Minikin et al., 1994; Osada, 1994; Wagenbach, 1996). Evidence for a stratospheric origin of the summer NO_3^- peak comes from the annual tritium cycle, which also has a late spring/summer maximum, and the $^{15}N/^{14}N$ ratio which is depleted at Neumayer during the summer NO_3^- peak (Pichlmayer and Wagenbach, 1995).

Atmospheric NH_4^+ is commonly derived from continental biogenic sources. In remote marine regions, oceanic biogenic activity may also be a tropospheric NH_4^+ source (Quinn

et al., 1987). Atmospheric NH_4^+ records from Antarctic coastal stations (Mawson and Palmer [Savoie et al., 1992], Neumayer [Wagenbach, 1996], and Dumont D'Urville [Legrand, unpublished data]) all contain a clear annual cycle which peaks in the summer and closely follows the temporal pattern of the biogenic sulfur species. Based on these findings, Wagenbach (1995) suggests that marine biota in the Southern Ocean (and/or in rotting sea ice) are the dominant source of NH_4^+ in Antarctic air and snow. A local NH_4^+ source from coastal penguin colonies has also been obeserved (E. Wolff, pers. commun., 1998). NH_4^+ concentrations in Antarctic snow are very low, and are therefore easily contaminated and difficult to measure. Whitlow et al. (1992) noted that NH_4^+ concentrations in South Pole snow peaked in the summer, however a strong annual cycle in surface snow has not been demonstrated elsewhere in Antarctica.

METHODS

Surface Snow Chemistry Data

Surface snow chemistry data collected since the International Geophysical Year (IGY; 1957-1958) in Antarctica was compiled into a database that includes: site location (latitude and longitude), elevation, site distance from the coast, accumulation rate, mean annual temperature, time interval represented by surface snow sample, concentration of eight major anions and cations (Na^+, Ca^{2+}, K^+, Mg^{2+}, NH_4^+, Cl^-, NO_3^-, SO_4^-) plus methanesulfonic acid (MSA), and analytical technique (see references for a complete list of all publications used).

Because published positional (latitude and longitude) and elevation information was not provided for all sampling sites, estimates were made using the National Science Foundation Gazetteer of the Antarctic (1989) and the United States Geological Survey Satellite Image Map of Antarctica (1996). Sea ice is highly variable in extent and timing, and often contains thin areas and shore leads (MW). For this reason, we have ignored sea ice extent in our calculations of site distance to the coast, and leave this topic to future work. Accumulation rates published with chemistry data were used when available. Otherwise, accumulation rate contours from Giovenetti and Bull (1987) provided estimates for sites where direct measurements were not reported.

To examine the relative contribution of seasalt aerosols to the chemical balance of Antarctic surface snow, ss and nss fractions of chemical species with marine origins were calculated. The assumptions made when examining the ss and nss components are: 1) there is only one dominant source for the reference element; and 2) there is no fractionation of ss during formation, transport or deposition of the aerosol (Keene et al. 1986). To

determine which species should be used as the reference element, all time-series and mean value chemistry data were tested for the most conservative species (e.g. O'Brien et al., 1995). At most sites (>90%), Na^+ was found to be the most conservative element, which agrees with the previous findings of Legrand (1987) and MW.

Surface Snow Chemistry Sites

Fig. II.2 shows all sites in Antarctica where surface snow chemistry (major anions and cations) data has been collected. Six major over-snow traverse routes have resulted in the collection of major chemistry data in Antarctica: Dumont d'Urville-Dome C (Legrand and Delmas, 1985), Filchner-Ronne Ice Shelf (Minikin et al., 1994), Mizuho Station and Plateau (Kamiyama et al., 1989; Osada, 1994), the Antarctic Walk Expedition (Patriot Hills-South Pole; Watanabe et al., 1995; Osada et al., 1995), Dronning Maud Land (Gjessing, 1989), and the 1994 International Trans-Antarctic Expedition (ITAE) (Dahe et al., 1992). Snow samples collected on certain traverses (Mizuho Plateau, Antarctic Walk Expedition) and at some sample locations did not cover complete years, and therefore have not been used in this study. As stated by MW, some species have significant seasonal variations, and therefore only surface snow data that covers complete years or that is averaged over several years are applicable to this study.

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 $nssSO_4^{2-}$) were similar. However, in this study we examine an additional 6 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.

Time Intervals

Different sampling methods (snowpits, shallow cores, 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:

1970-1975 and 1980-1985, and the full database, which covers ~1960-1995 . Sites with surface snow chemistry data covering those time periods are shown in Fig. II.2. The two 5 year time intervals were chosen due to the abundance of sampling during those years, and the predominance of 3 to 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 dataset, which covers ~1960-1995.

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 snow 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 analyses (Table II.1). 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 II.1).

Species with seasalt and crustal fractions (Na^+, Ca^{2+}, K^+, Mg^{2+}, and Cl^-), because of their large aerosol size, are expected to demonstrate a dilution effect at high accumulation rate sites (Herron, 1982). Analysis by Legrand (1987) indicated that there was a dilution effect on seasalt concentrations in Adelie Land. However, our compilation for these species (Na^+, Ca^{2+}, K^+, Mg^{2+}, and Cl^-) does not indicate any statistically significant relationship with accumulation rate for any species except Ca^{2+} (Table II.1 and Fig. II.3). The relationship noted between Ca and accumulation rate can be partially explained by the 4 samples from East Antarctica with high Ca^{2+} concentrations. These samples were collected in low accumulation rate regions of the Transantarctic Mountains, close to ice free areas and hence large crustal material sources (Welch, 1993). Therefore, 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 II.1 and Figs. II.4 and II.5). Of those species, Na^+ and Cl^- display the strongest association with elevation (Table II.1). Several authors have previously noted this trend in surface snow samples collected along coast to inland traverses (Herron, 1982; Warburton and Linkletter, 1978; Delmas and Boutron, 1980; Minikin et al., 1994; MW). As suggested by Legrand and Delmas (1985), fall-out of coarse seasalt aerosols as an air mass moves inland appears to be the main deposition 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 quadradic effect is apparent and has been evaluated (Table II.1). In all cases, results suggest that beyond a threshold distance inland (~500 km), concentrations essentially remain nearly constant. This effect creates the quadradic effect noted, which is opposite to the negative relationship noted between concentration and distance inland in the first 500 km inland. 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 and direction.

Of the sulfur 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. II.3), with no significant statistical relationship between $nssSO_4^{2-}$ concentration and accumulation rate (Table II.1). These findings suggest that either there is inefficient scavenging of $nssSO_4^{2-}$ aerosols as they move inland, or an upper tropospheric source of $nssSO_4^{2-}$ at high elevation sites exists. Likewise, MSA concentrations have no significant statistical relationship with accumulation rate (Table II.1).

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. II.4 and II.5). However, the decrease is not exponential in nature as it is for seasalt (Na^+ and 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 and Feneit-Saigne (1991) have noted a correlation between time-series firn core MSA concentrations at South Pole and El Nino-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 and Boutron, 1978; Herron, 1982; MW) suggests $nssSO_4^{2-}$ concentrations are independent of distance inland and elevation (Figs. II.4 and II.5). Statistical analysis, however, indicates a significant negative relationship between $nssSO_4^{2-}$ concentrations and distance inland (Table II.1). As with seasalt species, a quadradic effect is noted in the $nssSO_4^{2-}$/distance inland analysis, suggesting that transport from marine regions is a major $nssSO_4^{2-}$ source. There is no significant statistical relationship between $nssSO_4^{2-}$ and elevation. If an upper tropospheric source is delivering MSA to high elevation sites, transport of $nssSO_4^{2-}$ from lower latitude sources may also occur, and hence high elevation sites display roughly comparable $nssSO_4^{2-}$ concentrations.

Previous studies in Antarctica have focused on the relationship between NO_3^- and accumulation rate, with different results. Herron (1982) and MW concluded that NO_3^- concentration decreased with increasing accumulation rate, while Legrand and Delmas (1986), Legrand (1987), and Legrand and Kirchner (1990) found NO_3^- concentrations to be independent of accumulation rate. Our analysis indicates a statistically significant inverse relationship between NO_3^- concentrations and accumulation rate (Table II.1). The high variability of NO_3^- concentrations at low accumulation sites (Fig. II.3) may suggest either post-depositional loss of NO_3^- (Mayewski and Legrand, 1990; Dibb and Whitlow, 1996), or a high proportion of dry deposition at these sites (MW).

NO_3^- concentrations have been shown to be independent of distance inland and elevation in previous work (Herron, 1982; Legrand and Delmas, 1985; Minikin et al., 1994). However, these studies were either regional in nature (i.e. Adelie Land and the Filchner-Ronne Ice Shelf), or contained few data points. In their continental-scale compilation, MW found that NO_3^- concentrations increased with elevation. Our analysis indicates no relationship between distance inland or elevation and NO_3^- concentration (Table II.1, Figs. II.4 and II.5). The lack of relationship with distance inland and elevation suggests that there is not a significant marine NO_3^- source. Instead, upper atmosphere (stratosphere and tropical lightning [Legrand and Kirchner, 1990]) sources are more likely. As noted by MW, our understanding of deposition and subsequent re-emission of NO_3^-, especially at high elevation Antarctic sites, is limited and needs to be improved.

There is no significant statistical relationship between NH_4^+ concentrations and any of the three physical parameters studied (Table II.1). This result makes distinguishing upper tropospheric from marine sources difficult with the present dataset. We again note that NH_4^+ measurement in Antarctic snow is difficult due to low concentration and ease of contamination. A more thorough investigation of NH_4^+ sources in Antarctic snow will need to be made when additional NH_4^+ data are available.

DISTRIBUTION OF EXISTING SAMPLE SITES

Historically, the logistical complications involved in operating on the polar plateau have precluded extensive sampling of the Antarctic interior region. Accordingly, the distribution of existing surface snow sample sites compiled in this study reveals that ~80% of the sites are within 100 km of the coast (Fig. II.2). Analysis of surface snow chemistry data by others (MW) and this study suggests that trends identified for each chemical species are similar over different geographical regions of Antarctica. However, virtually nothing is known about time-series surface snow chemistry changes on the East and West Antarctic polar plateau, other than work done at manned bases. Large areas of the interior of the ice sheet are influenced by the continental temperature inversion (Bromwich 1990) while other portions of the interior and the coastal regions are influenced by cyclonic systems circulating around the continent. As a consequence, the peripheral areas are mainly connected with lower tropospheric transport whereas high altitude areas in the interior are more likely influenced by vertical transport from the upper troposphere and stratosphere. The lack of sampling on the Antarctic polar plateau precludes a definitive statement about the exact spatial distribution, depositional and post-depositional processes of surface snow chemistry in those regions.

Modeling results (Bromwich et al., 1995) suggest that the synoptic-scale meteorology of the West Antarctic polar plateau is particularly complex, with large regional variations in accumulation rate, temperature, and atmospheric circulation patterns. About 40% of the water vapor falling as snow in Antarctica enters the continent through West Antarctica (Bromwich et al., 1995). In addition, this sector is subject to the largest interannual variability observed in Antarctica, which is thought to be connected to ENSO (Cullather et al., 1996). The recent discovery of periodic variations in surface pressure, wind strength, temperature, and sea-ice extent around Antarctica (White and Peterson, 1996) furthur indicate the complexity of the ocean/atmosphere interaction and its control on continental climate. Therefore, the distribution of surface snow chemistry in West Antarctica is expected to be similarly complex, underscoring the need to understand the relationship

between chemical source areas, transport pathways, and surface snow chemistry distribution. Accurately reconstructing past climatic fluctuations based on long time-series ice core records now proposed for Siple Dome and the West Antarctic polar plateau will depend on a greater knowledge of these parameters.

INTERPRETATION OF NEW 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 1995/1996 field season, ice cores and 2 meter snowpits were collected at three sites along a 160km traverse from Byrd Surface Camp (575-625km inland; 1500-1800m elevation; Fig. II.1; Kreutz et al. in press). Average chemical values from the inland West Antarctic (IWA) snowpits are presented in Table II.2. Mean ion concentrations in the three pits are similar, and consistent with values obtained by other studies in the Byrd Station area (Murozumi et al., 1969; Boutron et al., 1972; Herron, 1982; Langway et al., 1994) and areas on the East Antarctic polar plateau (e.g. Legrand and Delmas, 1985). IWA snowpits group together with other sample sites of similar distance inland (Fig. II.4) and elevation (Fig. II.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). NO_3^- and $nssSO_4^{2-}$ values from IWA snowpits are also consistent with other interior areas of Antarctica. A major portion of the $nssSO_4^{2-}$ on the West Antarctic polar plateau is most likely of marine biogenic origin (Langway et al., 1994), even though concentrations are much lower than at coastal sites. Transport of

$nssSO_4^{2-}$ through the upper troposphere also occurs, usually associated with volcanic eruptions (Langway et al., 1995). Likewise, transport of NO_3^- most likely occurs through the upper troposphere/stratosphere (Legrand and Kirchner, 1990).

Time-series changes in snowpit ion concentrations are significantly different at the three inland West Antarctic sites (Fig. II.6). Only one site (RIDSC) contains well-defined annual signals in $nssSO_4^{2-}$ and MSA concentrations. In contrast, a 1360-year $nssSO_4^{2-}$ record from Byrd Station beginning in 1989 contains well-defined annual peaks throughout (Langway et al., 1994). It has been shown that during the time interval covered by the IWA snowpits (~1991-1995), the longest recorded El Nino-Southern Oscillation (ENSO) event occurred (Trenberth and Hoar, 1996). The connection between ENSO, West Antarctic precipitation and atmospheric circulation, and polar plateau glaciochemistry is now being revealed (Legrand and Feniet-Saigne, 1991; Smith and Stearns, 1993; Chen et al., 1996; Cullather et al., 1996). It is possible that the variability displayed in these snowpits is in part due to anomalous atmospheric circulation and moisture input to West Antarctica created by the prolonged 1990-1995 ENSO event.

Changes in several physical characteristics (topography, wind speed, and sastrugi direction) were noted between RIDSA and RIDSB, which raises the possibility of an ice divide in the area. Such a divide may have the effect of altering atmospheric circulation patterns sufficiently to cause the observed glaciochemical variability between sites. A sharp gradient in cloud coverage has been noted in satellite images 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 $g/cm^2/yr$ at Byrd Station, based on a peak in beta radioactivity at 8.4m. A beta profile from RIDSA contains a peak at 14.5m, suggesting an accumulation rate of 23 $g/cm^2/yr$ (Kreutz et al., in press). 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; 600m elevation; 600km inland; Fig. II.1) included the recovery of four 2m snowpits at the corners of a 10kmx10km grid centered on the geographic dome summit, and a four meter snowpit at the shallow core (150m) drillsite (Mayewski et al., 1995b). Snowpit glaciochemical results are presented in Table II.2. No

statistical diffrence exists between snowpit mean species values, suggesting that on timescales of 5-10 years there is a relatively homogeneous spatial distribution of surface snow chemistry on Siple Dome. Annual signals in all chemical species (most notably $nssSO_4^{2-}$ and MSA) are preserved in Siple Dome snowpits (Fig. II.6). Maxima in $nssSO_4^{2-}$ and MSA concentration profiles are interpreted as summer peaks, consistent with Antarctic aerosol records (Wagenbach, 1996).

A notable feature of Siple Dome surface glaciochemistry is the high concentration of seasalt species (especially Na^+ and Cl^- [Table II]), $nssSO_4^{2-}$, and MSA. Placing Siple Dome seasalt and MSA values in context with other Antarctic sites compiled in this study reveals that Siple Dome values are consistent with sites of similar elevation (Fig. II.5), but significantly higher than sites of similar distance inland (Fig. II.4). Based on Na^+ and Cl^- concentrations, Siple Dome would need to be ~250-300km closer to the coast to have comparable Na^+ and Cl^- concentrations (Fig. II.4). MSA concentrations suggest that Siple Dome should be located directly on the coast to be comparable with other sites (Fig. II.4). Geophysical observations (GPS topography and radar profiling) indicate that the present configuration of Siple Dome has been stable for at least the last 1000 years (Raymond et al., 1995). Therefore, it is unlikely that either the elevation or distance from the coast of Siple Dome has changed appreciably in recent times.

These findings suggest that transport of marine air masses to Siple Dome is somehow enhanced relative to other inland sites. Seasalt input at Siple Dome occurs mainly in the winter, based on comparison of snowpit $\delta^{18}O$ and seasalt concentrations. In a study of Southern Hemisphere synoptic meteorology, Taljaard (1967) suggested that the winter cyclonic frequency maximum passes near or directly over Siple Dome. However, it was unclear whether the dominant cyclonic path was traveling across the Ross Ice Shelf to Siple Dome or arriving from inland West Antarctica. Comparing Siple Dome and Ross Ice Shelf data reveals that Ross Ice Shelf seasalt values are comparable to or higher than Siple Dome values. This suggests, but does not prove, that the cyclonic path travels from the Amundsen Sea over the Ross Ice Shelf to Siple Dome. Accumulation rate variations in West Antarctica have been shown to depend on their spatial relation to the Amundsen Low, a major source of moisture for West Antarctica (Trenberth and Hoar, 1996). Therefore, marine air masses reaching Siple Dome may be advected across Marie Byrd Land from the Amundsen Sea. Meteorological investigations in West Antarctica proposed in the International Trans-Antarctic Scientific Expedition program are designed to furthur our understanding of the synoptic meteorology in the area.

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 24m 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. II.7). The core was dated using annual chemical signals ($nssSO_4^{2-}$, NO_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 1933-34. This event is comprised of 5 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 1933-34 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 which reflect the various ionic modes of production and transport. One tool commonly used to accomplish this is empirical orthogonal function (EOF) analysis (Peixoto and Oort, 1992; Meeker et al., 1995), which is based on principle 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. The technique identifies common behavior in the glaciochemical dataset, and has been used to reconstruct atmospheric circulation in Greenland during the Holocene (O'Brien et al., 1995) and the last 41,000 years (Mayewski et al., 1994).

Results from EOF analysis on Siple Dome core data (using 8 major species) are presented in Table II.3. The first EOF (EOF1) describes 50% of the total dataset variance, and accounts for >90% of principal seasalt species (Na^+, Cl^-, Mg^{2+}). Components of the EOF which explain a large proportion of the variance in a multivariate dataset usually have an important physical significance (Peixoto and 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,

$nssSO_4^{2-}$ and NO_3^-, both of which are deposited mainly in late spring/summer based on comparison to stratigraphic and $\delta^{18}O$ measurements. The input of $nssSO_4^{2-}$ most likely occurs through the lower troposphere, and is linked to enhanced summer ocean productivity (Whitlow et al., 1992). Deposition of NO_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 and Delmas, 1986). A significant fraction of NH_4^+ is represented by EOF2, suggesting that summer marine biogenic activity may be a partial source of NH_4^+ at Siple Dome. Therefore, EOF2 may represent the coeval summer influence of lower tropospheric input (ocean biogenic products) and upper atmosphere air masses (NO_3^-) at Siple Dome. The third EOF (EOF3) is loaded mainly with Ca^{2+}, most likely reflecting upper atmosphere (long-traveled continental dust) transport since there are no immediate local Ca^{2+} sources. EOF4 and EOF5 represent the residual portions of NO_3^- and $nssSO_4^{2-}$ not explained by EOF2.

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. II.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^+, Cl^-, Mg^{2+}, and K^+ species, the time series EOF1 record (Fig. II.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 $\delta^{18}O$ values during 1933-35 were noted in Dolleman Island, James Ross Island, and Siple Station ice cores (Peel, 1992; Mosely-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^{2+} concentrations also occurred during 1933-35 (Herron, 1980; E. Meyerson, personal communication, 1997), which may indicate increased transport of long-traveled 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) $\delta^{18}O$ records (Mosely-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 (~1400-1900 AD).

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 and Feniet-Saigne, 1991). On the other hand, $nssSO_4^{2-}$ concentrations are independent of elevation, yet statistically linked to distance inland. While this finding argues for a high-latitude marine source for $nssSO_4^{2-}$, it does not preclude long range transport of this species to high elevation sites. NO_3^- concentrations are independent of distance inland and elevation. More work is clearly needed on the deposition and preservation of NO_3^- 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 NO_3^- and Ca^{2+}. The relationship noted in NO3- may be due to post-depositional loss at low accumulation rate sites, while the Ca^{2+} relationship is likely related to sample collection in areas proximal to large Ca^{2+} sources. Therefore, in general it appears that concentration measurements rather than flux calculations are sufficient to relate changes in chemical time-series 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 (RIDSC). 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 formation.

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 24m (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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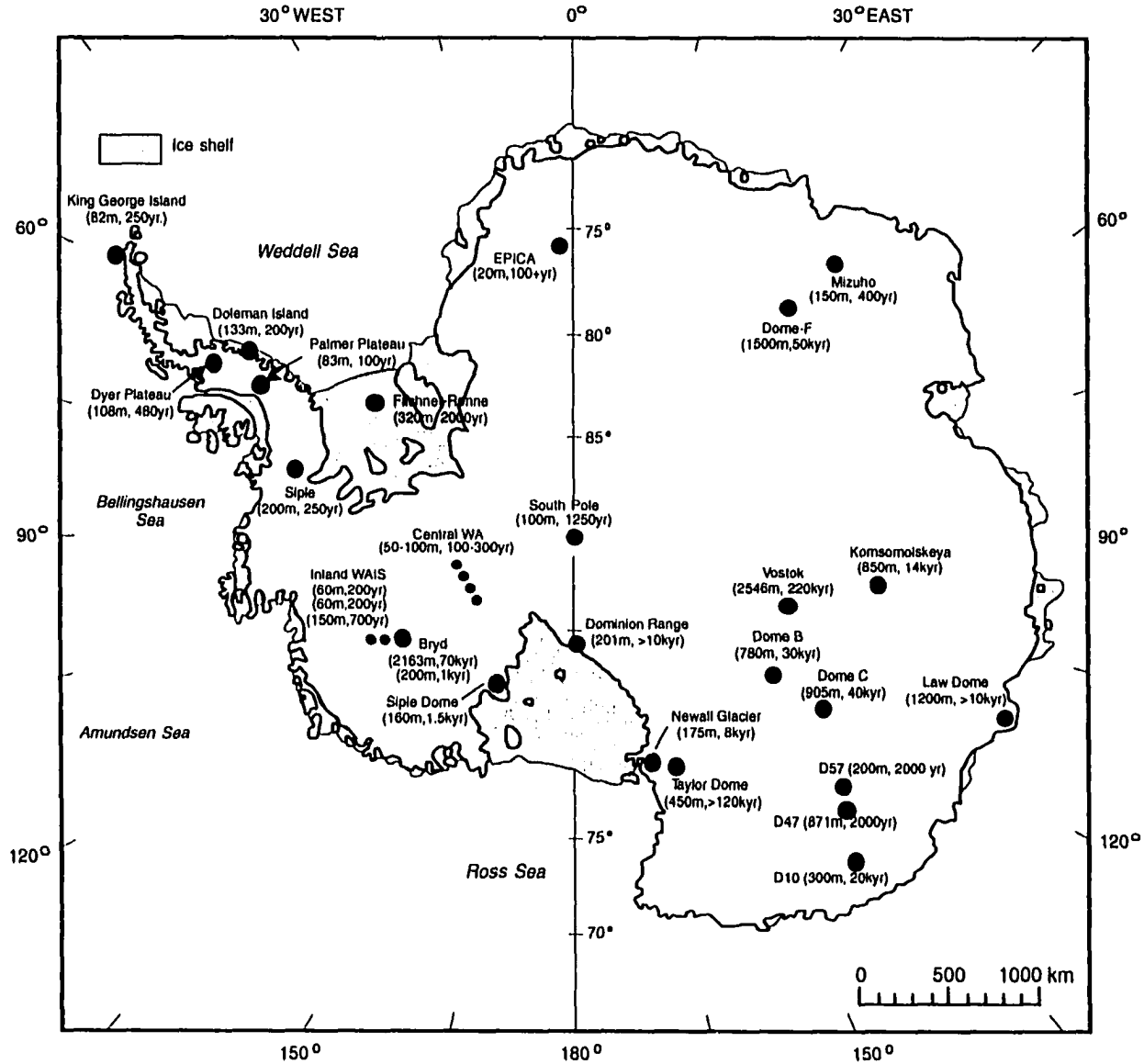

Figure II.1. Core sites in Antarctica with glaciochemical records longer than 100 years.

Figure II.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 1970-1975, d) sites with glaciochemical data covering the time period 1980-1985.

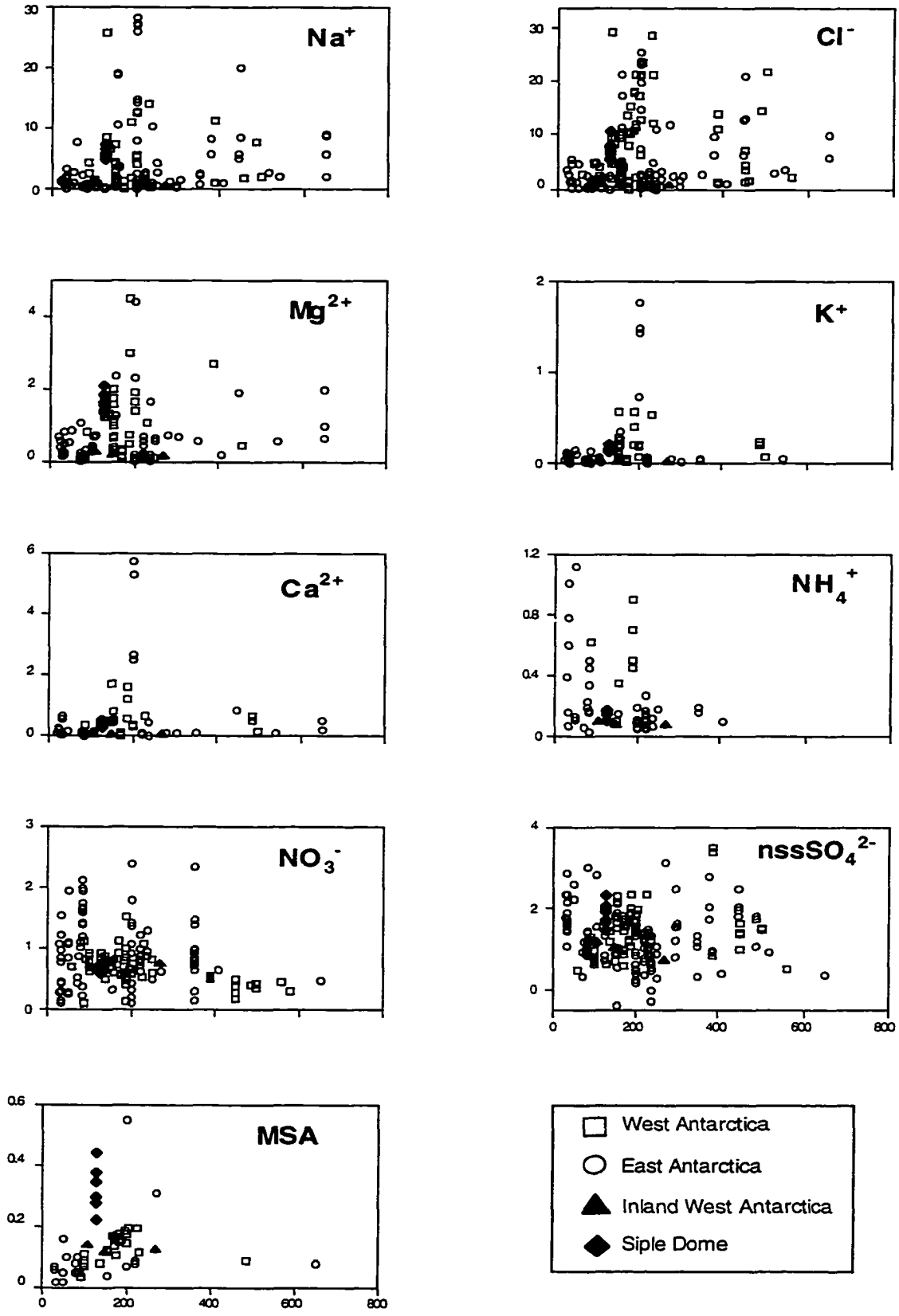

Figure II.3. Major ion concentrations in Antarctic surface snow vs. accumulation rate. Concentrations are in μeq/L, and accumulation rates are in mm/yr.

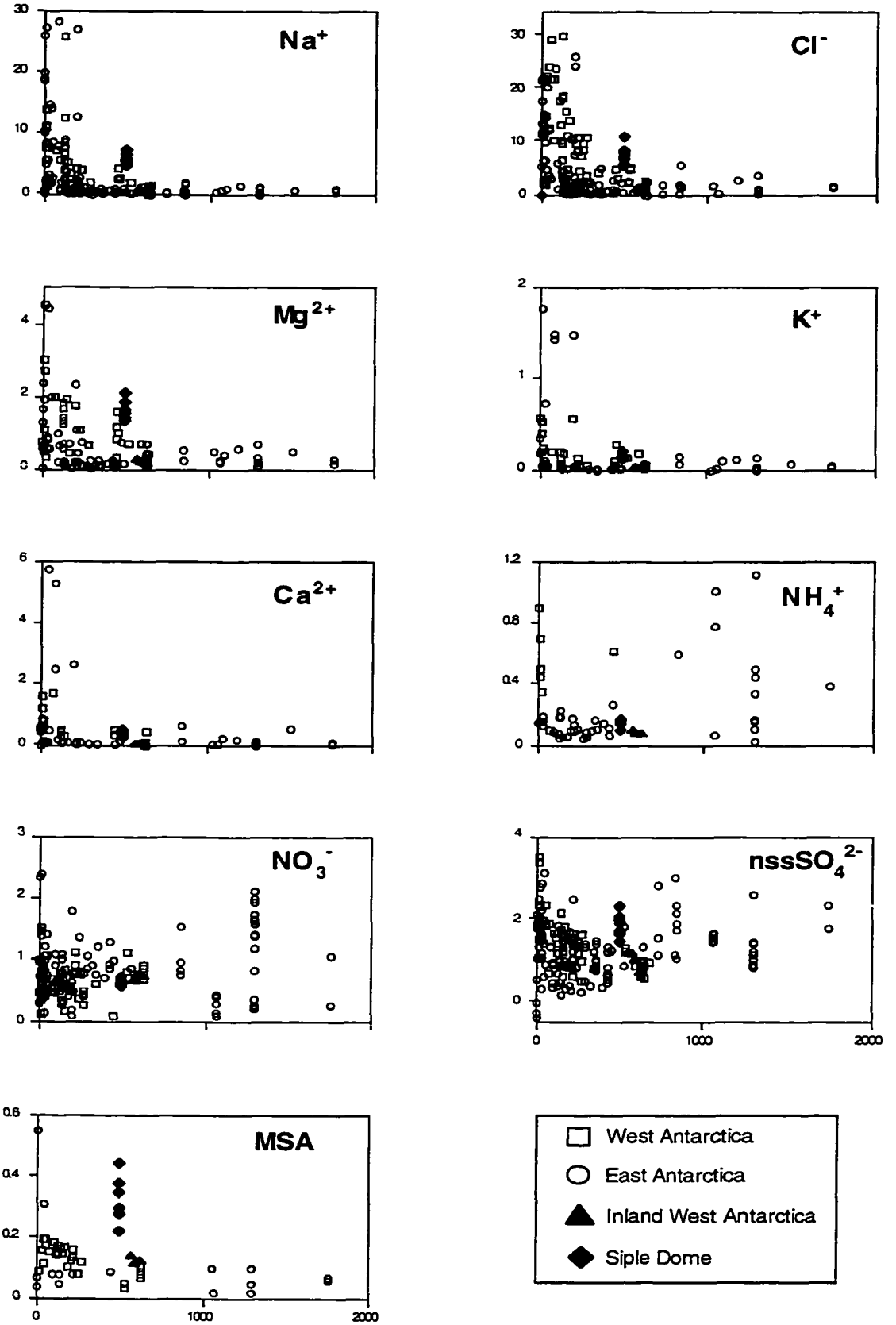

Figure II.4. Major ion concentrations in Antarctic surface snow vs. distance inland. Concentrations are in μeq/L, and distance in km.

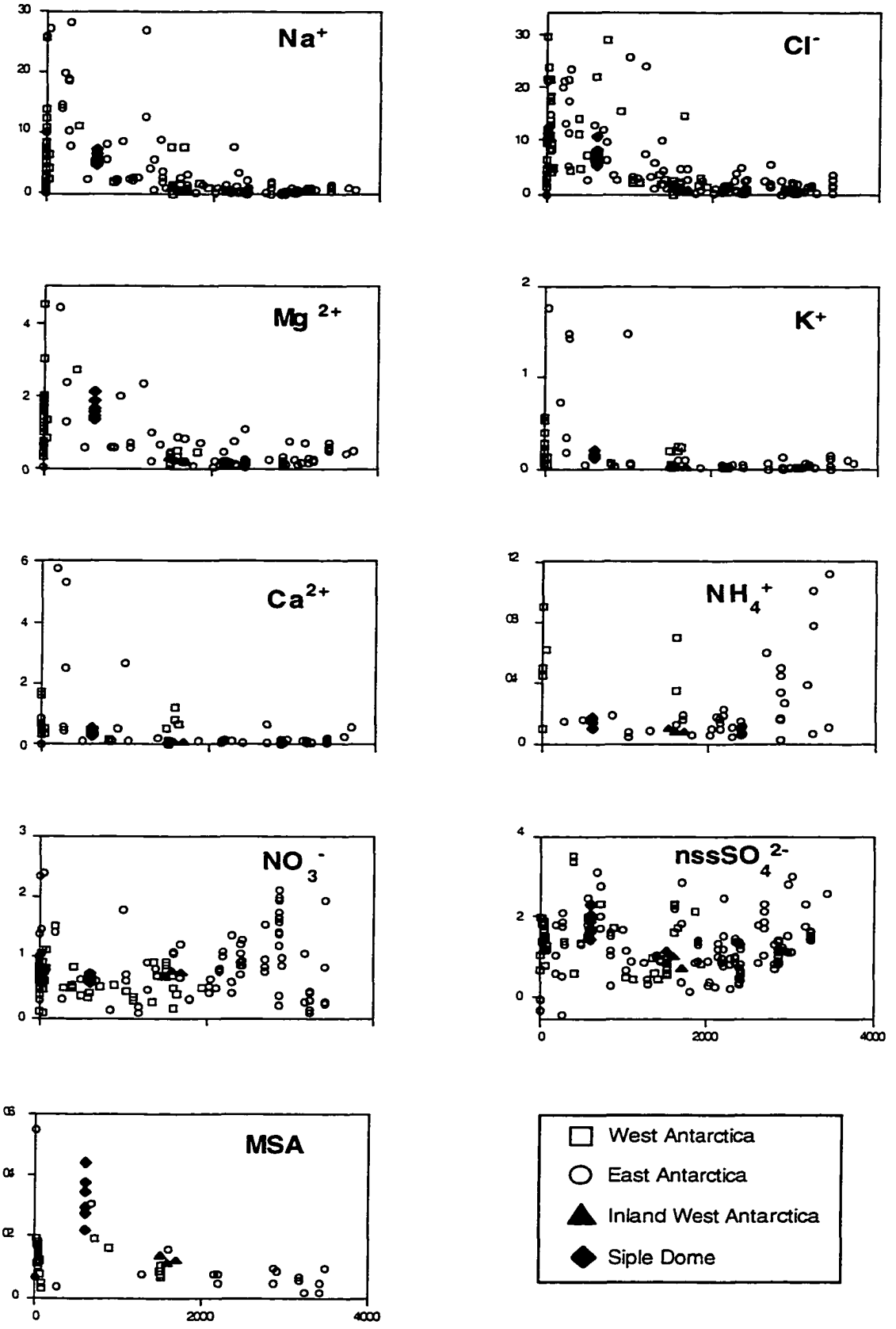

Figure II.5. Major ion concentrations in Antarctic surface snow vs. elevation. Concentrations are in μeq/L, and elevation in meters.

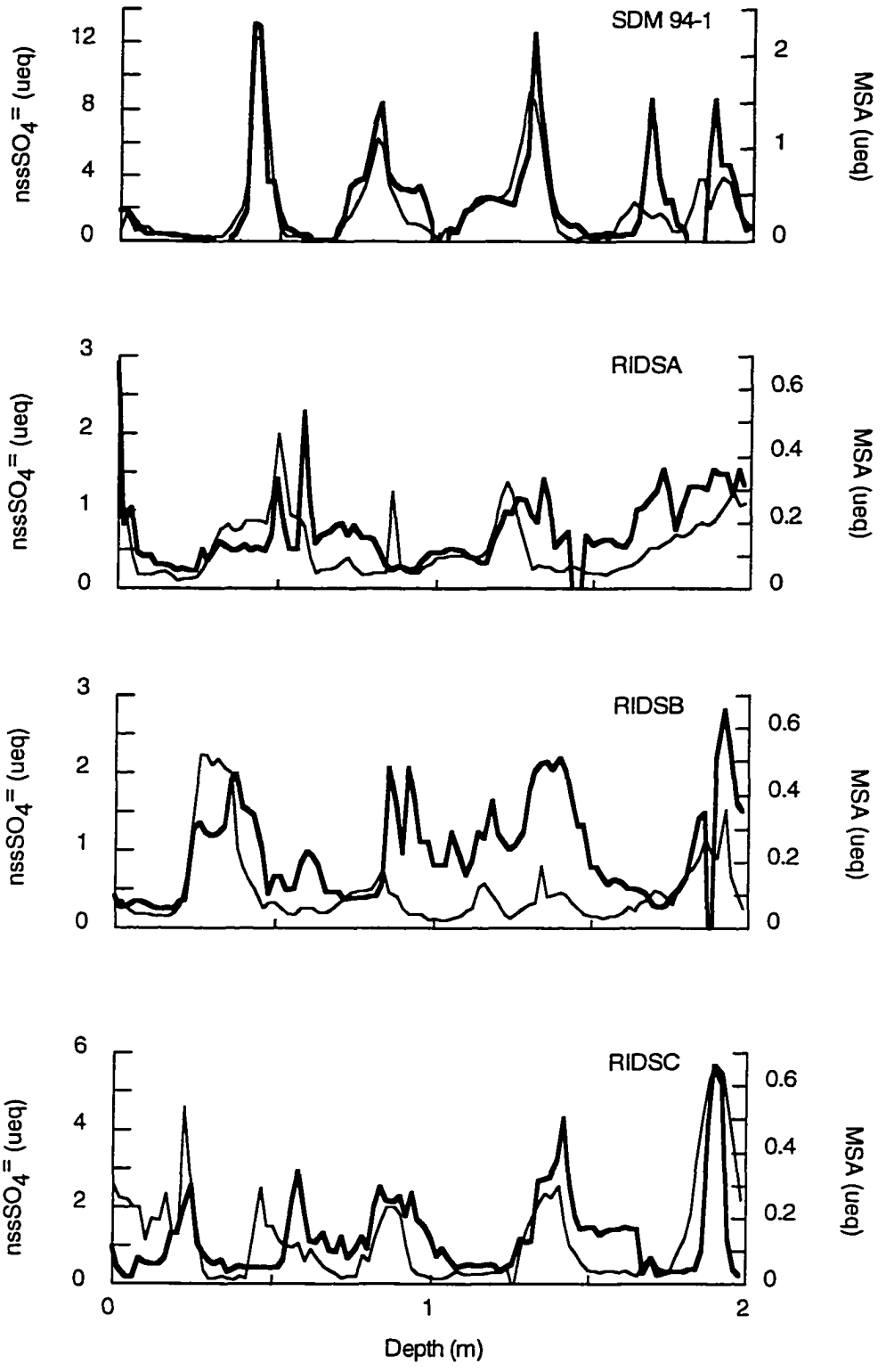

Figure II.6. $nssSO_4^{2-}$ (thick line) and MSA (thin line) concentrations in snowpits from Siple Dome (pit 94-1) and Inland West Antarctic sites (RIDSA-C). Concentrations are in μeq/L.

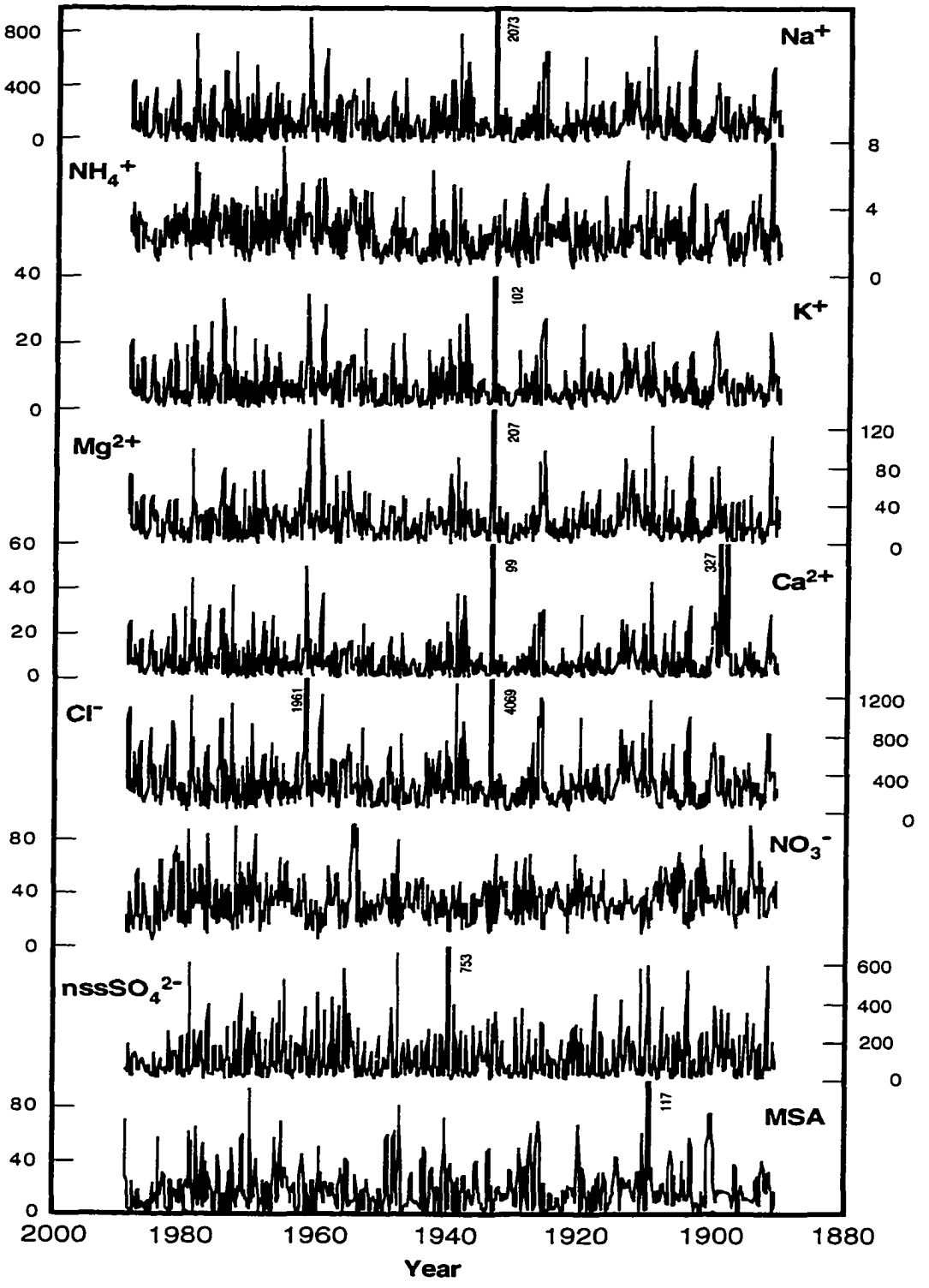

Figure II.7. Major ion time-series from the upper 24 meters of the 1994 Siple Dome ice core.

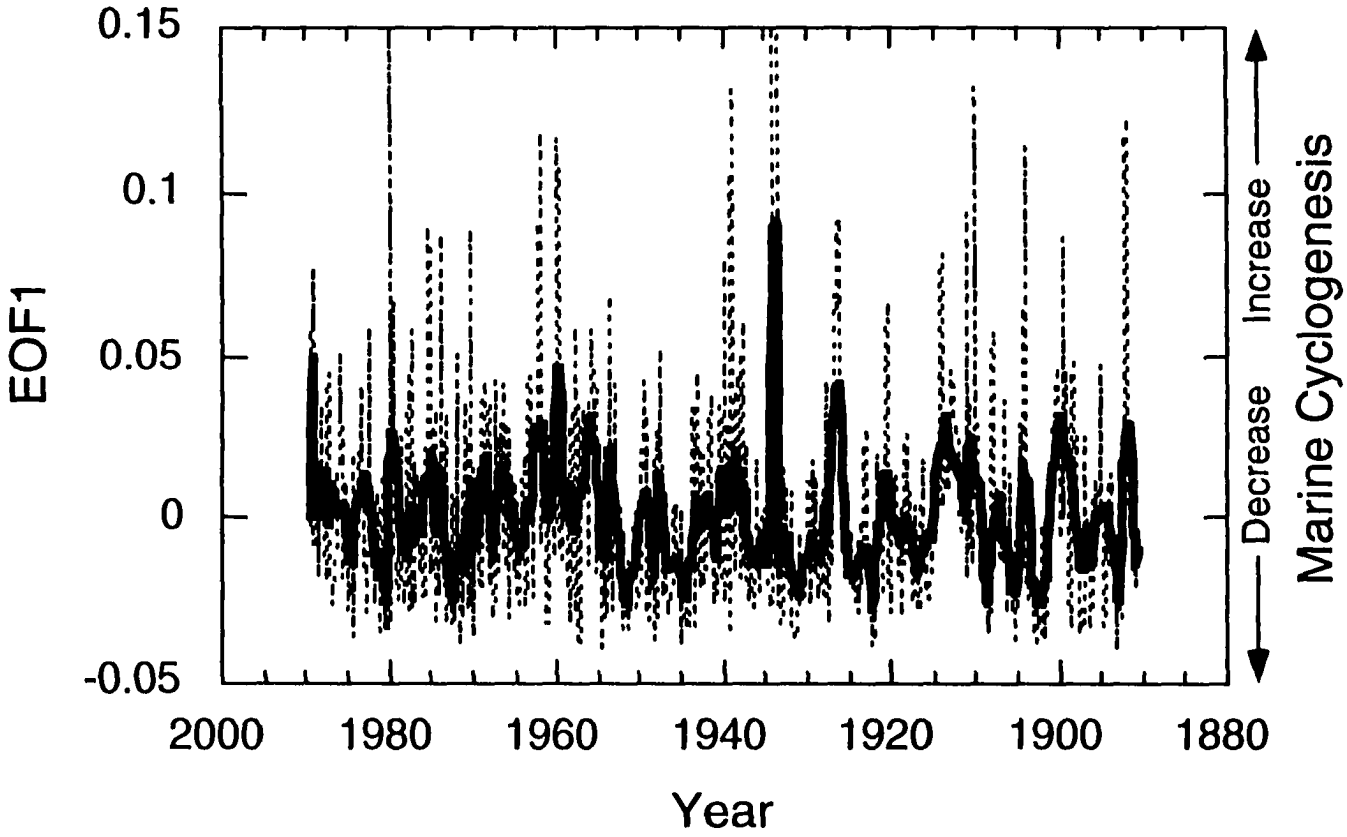

Figure II.8. EOF1 time-series from the upper 24 meters of the 1994 Siple Dome ice core. The dashed line represents the raw EOF1 time-series, and the dark line is an 11-point moving average.

Species	*Distance*	*Distance* ^{2}	*Elevation*	*Acc. Rate*	R^2	*n*
Na (log)	-4.14	4.01	-10.01	0.27	0.54	178
Cl (log)	-4.21	4.39	-10.24	-0.07	0.51	189
Mg (log)	-1.74	1.87	-6.76	-0.54	0.37	120
K (log)	-3.36	3.05	-5.54	-1.06	0.42	98
Ca (log)	-4.25	3.20	-2.47	-2.53	0.35	84
NH_4 (log)	0.82	-	-1.00	-1.92	0.12	62
NO_3 (log)	0.23	-	-0.41	-2.36	0.05	167
$nssSO_4$	-2.60	3.27	-1.69	-0.83	0.02	187
MSA (log)	0.02	-	-2.65	0.44	0.28	55

Table II.1. Multiple regression analysis of Antarctic surface snow glaciochemical data. Data reported are t-values, hence values >|2| are significant at $p<0.05$. Distance^2 values represent the quadradic effect noted in distance vs. concentration analysis.

	Na	NH_4	K	Mg	Ca	Cl	NO_3	$nssSO_4$	MSA
Siple Dome									
				Pit 94-1 (4 meters; at drillsite)					
mean	5.59	0.16	0.16	19.68	0.20	8.18	0.64	2.02	0.27
std. dev.	5.67	0.14	0.16	16.65	0.20	7.04	0.40	2.80	0.33
median	4.23	0.14	0.12	16.54	0.16	6.73	0.52	0.96	0.16
				Pit 94-2 (2 meters; NW corner of grid)					
mean	7.10	0.14	0.20	2.05	0.23	10.98	0.58	1.71	0.35
std. dev.	7.27	0.08	0.21	1.95	0.23	10.89	0.35	3.35	0.60
median	4.69	0.13	0.14	1.57	0.17	7.80	0.51	0.52	0.13
				Pit 94-3 (2 meters; SW corner of grid)					
mean	5.80	2.89	0.15	1.60	0.34	8.95	0.72	2.35	0.37
std. dev.	4.91	1.14	0.12	1.34	0.28	6.85	0.40	3.43	0.40
median	4.25	2.80	0.11	1.14	0.24	6.82	0.63	1.36	0.25
				Pit 94-4 (2 meters; NE corner of grid)					
mean	5.65	0.14	0.13	1.62	0.17	7.93	0.67	2.07	0.30
std. dev.	5.56	0.07	0.15	1.57	0.21	6.77	0.41	3.12	0.46
median	4.27	0.13	0.08	1.18	0.12	6.26	0.57	0.63	0.12
				Pit 94-5 (2 meters; SE corner of grid)					
mean	4.93	0.16	0.14	1.36	0.28	6.70	0.66	1.91	0.22
std. dev.	3.82	0.05	0.10	0.93	0.22	4.46	0.33	2.09	0.23
median	4.16	0.16	0.12	1.16	0.22	5.88	0.61	1.29	0.16
Inland West Antarctica									
				RIDSA (2 meters; 78°44'S 116°20'W; 150 km NE of Byrd Station)					
mean	0.57	0.09	0.03	0.16	0.05	0.86	0.75	0.74	0.13
std. dev.	0.54	0.03	0.03	0.15	0.04	0.68	0.56	0.46	0.09
median	0.39	0.08	0.02	0.12	0.04	0.63	0.66	0.63	0.10
				RIDSB (2 meters; 79°27.66'S 118°02.68'W; 70 km NE of Byrd Station)					
mean	0.68	0.08	0.02	0.20	0.06	1.01	0.76	0.98	0.12
std. dev.	0.52	0.04	0.02	0.16	0.04	0.63	0.30	0.62	0.12
median	0.52	0.07	0.02	0.14	0.05	0.85	0.72	0.84	0.07
				RIDSC (2 meters; 80°S 120°W; 3km NE of Byrd Station)					
mean	0.97	0.11	0.04	0.29	0.07	1.36	0.69	1.21	0.14
std. dev.	0.94	0.04	0.03	0.28	0.06	1.17	0.30	1.05	0.15
median	0.61	0.10	0.03	0.18	0.04	0.96	0.66	0.93	0.09

Table II.2. Summary of soluble ionic components in snowpits from Siple Dome and inland West Antarctica. All concentrations are in μeq/L.

Variance explained by each mode (%)						
	EOF1	**EOF2**	**EOF3**	**EOF4**	**EOF5**	**Total**
	50.60	17.00	10.60	8.60	7.80	94.60
Variance decomposition (%)						
Species						
Na	92.80	0.90	0.00	1.90	0.00	
Cl	92.40	1.30	0.00	2.22	0.00	
Mg	90.90	0.80	0.00	3.10	0.20	
K	46.80	0.00	10.30	1.20	34.60	
Ca	36.50	0.70	10.80	39.40	12.60	
$nssSO_4$	20.40	50.30	0.00	10.10	8.30	
NO_3	6.80	71.30	5.70	0.00	4.50	
NH_4	18.40	10.50	58.23	10.53	2.30	

Table II.3. Empirical orthogonal function analysis of the upper 24 meters (110 years) of the Siple Dome ice core.

III. SEASONAL VARIATIONS OF GLACIOCHEMICAL, ISOTOPIC, AND STRATIGRAPHIC PROPERTIES IN SIPLE DOME, WEST ANTARCTICA SURFACE SNOW

Section III will be submitted to Annals of Glaciology for publication (full citation appears in the Complete List of References)

III. SEASONAL VARIATIONS OF GLACIOCHEMICAL, ISOTOPIC, AND STRATIGRAPHIC PROPERTIES IN SIPLE DOME, WEST ANTARCTICA, SURFACE SNOW

ABSTRACT

Identifying annual layering is a basic and essential component of producing high-resolution snow, firn, and ice core records. Six snowpit records recovered from Siple Dome, West Antarctica during 1994 are used to study seasonal variations in chemical (major ion and H_2O_2), isotopic (deuterium) and physical stratigraphic properties. Comparison of δD measurements and satellite-derived brightness temperature for the Siple Dome area suggests that most seasonal δD maxima occur within ± 2 weeks of each January 1. Several other chemical species (H_2O_2, nonseasalt (nss) SO_4, methanesulfonic acid, and NO_3^-) show coeval peaks with δD, together providing an accurate method for identifying summer layers. Seasalt-derived species generally peak during winter, but episodic input is noted throughout some years. No reliable seasonal signal is identified in species with continental sources, NH_4, or $nssCl^-$. Large depth hoar layers (>5 cm) are associated with summer layers, however smaller hoar layers, hoar complexes and crusts are more difficult to interpret. A multiparameter approach is found to provide the most accurate dating of these snowpit records.

INTRODUCTION

Interpreting past environmental change from snow, firn, and ice core records depends in large part upon accurate construction of depth/age relationships. Several different physical and chemical techniques (visible stratigraphy, stable isotopes, ion chemistry, H_2O_2, electrical conductivity, laser light scattering from dust) have been developed to identify seasonal layering in polar ice sheets (e.g., Mayewski et al., 1987; Beer et al., 1991; Alley et al., 1997; Ram et al., 1997; Taylor et al., 1997; White et al., 1997). Each of these techniques, used independently, has an associated error (identifying a year where one does not exist, or omitting a year where one does exist), which increases with depth or age (Alley et al., 1993). Therefore, combining several of these techniques in a multiparameter dating approach provides the most accurate means for reconstructing accumulation histories and interpreting chemical variability through time. The advantage of such an approach has

been demonstrated in the Greenland Ice Sheet Two (GISP2) ice core record, which currently provides the longest, most continuously dated record of annual layer accumulation available (Meese et al., 1994).

A new deep ice coring project at Siple Dome, West Antarctica (81.65°S, 148.81°W; Figure III.1) aims to produce the first Southern Hemisphere paleoclimatic record of similar resolution as the GISP2 record. As with the GISP2 record, a full suite of chemical and physical parameters will be measured on the Siple Dome core which can be used for core dating, assuming seasonal signals can be identified. Several of these parameters were measured in snowpit samples collected at Siple Dome during the 1994/95 reconnaissance field season (Mayewski et al., 1995; Raymond et al., 1995). Here we present chemical, isotopic, and stratigraphic results from the upper 2 m of the 1994 snowpits, and estimate snowpit annual layer thicknesses based on seasonal fluctuations in chemical and stratigraphic markers.

METHODS

A total of 6 snowpits were sampled at Siple Dome during the 1994/95 field season (Figure III.1). Four 2 m deep pits (pits 94-2, 94-3, 94-4, and 94-5) are located on the corners of a 10km x 10km grid centered on the Siple Dome summit (Raymond et al., 1995), one 4 m deep pit (94-1) was located at the site of a 150 m ice core (Kreutz et al., 1997), and one 1 m pit (94-6) ~300 m NE of the 1994 drillsite (Mayewski et al., 1995). The sampling interval for all pits is 2 cm, except pit 94-6 which is 1 cm. Snowpit sampling was performed by workers wearing non-particulating suits, polyethylene gloves, and particle masks. Samples were collected into precleaned polyethylene containers for frozen shipment and stored below -15°C until melting, immediately prior to chemical analysis. Analysis of major cations (Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}), anions (Cl^-, NO_3^-, SO_4^{2-}), and methanesulfonic (MSA) in all samples was performed at the University of New Hampshire using Dionex 4000 series instruments. Cations were analyzed via suppressed chromatography with a Dionex CS12 column, 0.125 mL loop, and 20m*M* MSA eluent. Anions were analyzed with a Dionex AS11 column, 0.75 mL loop, and 6.0 mM NaOH eluent. MSA measurements were made with an AS11 column, 1.5 ml loop, and 0.5 mM NaOH eluent. Mean ion concentrations for the 1994 pits are given in Kreutz and Mayewski (in review). Partitioning of seasalt (ss) and nonseasalt (nss) fractions is based upon the model described in O'Brien et al. (1995) and Kreutz et al. (in press). Snowpit samples were analyzed for isotopic (δD) composition at the University of Colorado with uncertainties of $\pm 0.5‰$, and are reported in per mil relative to standard mean

ocean water (SMOW). H_2O_2 concentration was determined using the peroxidase-based fluorescence method (Sigg et al., 1992) at the University of Arizona. Physical properties measured in the 1994 pits include density, texture, strength, and temperature (Raymond et al., 1995).

PHYSICAL STRATIGRAPHY

The use of visible strata in the analysis and dating of snowpits, firn, and ice cores is a common glaciological tool, and has been documented on the Siple Coast of West Antarctica (Alley, 1988; Alley and Bentley, 1988). Low density layers are formed when intense insolation warms snow a centimeter below the surface by as much as 5°C above the ambient air temperature (Alley et al., 1993). Vapor diffusion down this steep temperature gradient causes near-surface mass loss accompanied by rapid grain growth, yielding a depth-hoar layer. Some of the vapor lost from the depth hoar apparently condenses on the snow surface to form a low-density, coarse-grained surface hoar layer. Subsequent snowfalls that bury a depth hoar/surface hoar complex typically are finer-grained, denser, and have a smoother upper surface than the hoar. This phenomenon is rare or absent in winter snow, and therefore provides a method for identifying buried summer layers (Alley, 1988).

Stratigraphic layers identified in the Siple Dome snowpits are presented in Figure III.2. The principal feature of the stratigraphy is the pervasive presence of faceted crystals in the snow and firn (Raymond et al., 1995). In each pit, there are approximately 8-10 prominent soft layers (per 2 m) of very strongly-faceted, coarse grained, poorly bonded grains spread over the 2 m sampling. Certain low density layers (identified in Figure III.2) possess a distinctive 'hens-teeth' appearance, with large, symmetrical grains extending from underlying and overlying strata. One possible explanation for this phenomenon is vapor gradient reversal during formation, causing transport both to the surface and down to the snowpack. As noted by Alley (1988) at a nearby location (Ridge BC), such low density layers are generally indicative of summer processes, and therefore allows a first approximation of time-depth relationships in the 1994 snowpits. Variability in hoar layer thickness and number in each pit, however, makes unambiguous identification of annual layers difficult. Unfortunately, surface observations of the timing, extent, preservation, and frequency of hoar formation at Siple Dome are not yet available, and therefore a detailed understanding of hoar formation and preservation is currently lacking. Although the counting of hoar complexes has been shown to be accurate to 1% at century-length time

scales in Greenland (Alley et al., 1993), we may assume that some years in West Antarctica lack an identifiable hoar event and that other years have two or more events.

In addition to low-density layers, a small number (3-5 per 2m pit) of thin (1-2 mm), hard crusts, some of which appear to be produced by melting and re-freezing into ice layers, were identified in all pits. The majority of these crusts are not associated with significant depth hoar layers, suggesting that their formation is not related to summer temperatures. Release of latent heat from katabatic winds descending from the West Antarctic polar plateau may provide sufficiently warm temperatures to produce these crusts. Occasional melt layers (2-5 mm) were also noted, however stratigraphy and temperature profiles (Raymond et al., 1995) indicate that melting is not an important metamorphic and transfer process in comparison to vapor diffusion caused by strong temperature gradients. As discussed below, these apparent melt layers produce no noticeable re-distribution of water soluble constituents in the snowpack.

STABLE ISOTOPES

Like visual stratigraphy, the use of seasonal variations in snow, firn, and ice stable isotope ratios to identify annual layering is a common technique (e.g., van Ommen and Morgan, 1997). Although several factors affect isotopic ratios, numerous studies in polar regions have demonstrated the relationship between increased summer surface temperatures and more positive isotopic ratios (e.g., Dansgaard, 1964). δD profiles in 1994 Siple Dome snowpits (Figure III.2) display significant (~100 ‰) amplitude oscillations, which are assumed to represent winter/summer temperature variability. To investigate δD timing, high-resolution (1 cm sampling) measurements from pit 94-6 were compared to satellite-derived passive microwave brightness temperatures (Figure III.3). This technique (Shuman et al., 1993) is based on the theory that surface density and roughness variations related to hoar formation can influence passive microwave signals through variations in the ratio of vertical to horizontal radiation reflection. The relationship between brightness temperature and physical temperature is assumed to be a function of the physical temperature of the near-snow surface multiplied by its emissivity (Shuman et al., 1995).

The brightness temperature record at Siple Dome contains distinct maxima during the austral summers of 1992/93, 1993/94 and 1994/95, and also shows peaks of lesser amplitude during corresponding winter periods (Figure III.3; Table III.1). Such winter peaks may be related to intrusion of warm, moisture-laden marine air during periods of intense cyclonic activity, causing increased surface temperatures and reduced emissivity (due to fresh snow deposition). The upper-most isotope peak (~0.75-0.25 m) corresponds

to the onset of summer 1994/95 conditions, based on the sampling date for this snowpit 94-6 (12/02/94). Decreased δD in the upper 10 cm is likely related to fresh surface snow present during sampling (pit 94-6 was the last one sampled during the 1994/95 field season, hence the ~10 cm of fresh snow at the surface is not present in other pit profiles). We match the next obvious δD peak and hoar event (~0.25-0.45 cm) with summer 1993/94. Timing of δD peaks is likely within ±2 weeks of January 1, based on this comparison and results of other Antarctic studies (e.g., van Ommen and Morgan, 1997). A broad peak in isotope values occurs between 0.6 and 0.85 m, corresponding to summer 1994/95 deposition. Two hoar events are identified in this depth interval, and it therefore appears that grouping these two hoar events together as a summer complex is necessary for correct identification of a specific single summer season. These results from pit 94-6 do, however, suggest that hoar formation and the δD signal are recording summer intervals.

Using the relationships observed between hoar formation and isotopic composition in pit 94-6, we examine the remaining 1994 snowpits for hoar formation timing (Figure III.2). In all pits, substantial (> 5 cm) hoar layers correspond to summer δD maxima. Hoar events thinner than 5 cm are not always associated with summer layers based on comparison with δD profiles. No relation is noted between δD peak amplitude and hoar thickness. Indeed, predicting a δD profile based on hoar layers alone proves to be difficult, at least in this set of snowpits. Melt layers and thin crusts do not appear to have any definite relationship with δD, as these stratigraphic features occur during both δD maxima and minima.

HYDROGEN PEROXIDE

H_2O_2 is produced in the atmosphere by photochemical reactions involving hydroxyl radicals, hence its atmospheric concentration reflects local atmospheric chemistry and u.v. intensity (Beer et al., 1991). H_2O_2 is a so-called "reversibly deposited species" in snow, and therefore exhibits strong gas-phase exchange and post-depositional signal modification. Surface concentrations in Central Greenland and South Pole snowpits exceed those in previously buried summer layers, with losses being greater at the lower accumulation rate site (South Pole; Sigg and Neftel, 1988; Whitlow et al., 1992; McConnell et al., 1998). Nevertheless, peak H_2O_2 concentrations in surface snow can provide an important indication of summer layers in the snowpack.

H_2O_2 concentrations in 1994 Siple Dome snowpits are presented in Figures 2 and 4. Comparison of H_2O_2 and δD profiles suggests that H_2O_2 peaks during or slightly after δD maxima. This finding is consistent with modeling results using physical parameters

(temperature, accumulation rate) at Siple Dome, which also suggest a late summer peak for H_2O_2 (McConnell, 1997). Further examination identifies a δD peak in the upper 40 cm of pits 94-1 and 94-2 which does not have an associated H_2O_2 maxima. As noted below, this apparently anomalous δD maxima also occurs in pit 94-4, based on comparison with major ion profiles. A possible explanation for this event may be related to two positive excursions in the brightness temperature record seen during winter (April-October) 1994 (Figure III.3). Such events may indicate intrusion of warm, marine air during intense cyclonic activity, accounting for deposition of isotopically heavy snow. This anomalous δD event appears to be confined to pits on the north side of the Siple Dome ice divide.

MAJOR IONS

On seasonal timescales, a correlation is found between aerosol and snow ion concentrations at various Antarctic stations (Whitlow et al., 1992), enabling ion concentration profiles to be used as a dating tool (Herron and Langway, 1979; Warburton and Young, 1981; Mayewski and Legrand, 1990; Mosely-Thompson et al., 1991; Whitlow et al., 1992). Sulfur species (SO_4^{2-} and MSA) dominate the ion content of summer Antarctic aerosol and snowpack, and are primarily of marine origin (oxidation of dimethylsulfide; Wagenbach, 1996). Although the sources of nitrogen species (NO_3^- and NH_4^+) in the Antarctic atmosphere are not well understood, NO_3^- has been shown to peak during the late spring/summer season in aerosol measurements (Savoie et al., 1992; Wagenbach et al., 1988) and in snow (Mayewski and Legrand, 1990; Whitlow et al., 1992; Dibb and Whitlow, 1996). Seasalt-derived species (Na^+, Cl^-, and Mg^{2+}), which dominate the total ion burden of Siple Dome surface snow (Kreutz et al., manuscript in preparation), generally peak during the winter and spring (July to November) months in coastal and polar plateau aerosols and snow (Wagenbach, 1996; Savoie et al., 1992; Tuncel et al., 1989). Because this peak occurs when sea ice extent is at a maximum, increased meridional transport during winter is most likely responsible for the seasalt maxima (Kreutz et al., 1997).

Comparison of Siple Dome surface snow major ion concentrations with isotopic, H_2O_2, and stratigraphic measurements reveals seasonal signals in several species (Figures 2 and 4). Nonseasalt SO_4 and MSA profiles display maxima generally coincident with δD and H_2O_2 peaks. Timing of both nssSO_4 and MSA peaks appears consistent with observations of a peak in Southern Ocean productivity in early/mid-summer (Gibson et al., 1990). A recent comparison of continuous aerosol measurements and firn core nssSO_4 concentrations at South Pole (Bergin et al., in press) demonstrates a consistent summer peak in sulfate

aerosol and firn concentration. Therefore, based on observed $nssSO_4$ profiles at Siple Dome and elsewhere, it appears that $nssSO_4$ concentrations provide a consistent and accurate method for annual layer dating, particularly at coastal sites such as Siple Dome. NO_3 concentrations at Siple Dome peak generally in phase with $nssSO_4$, δD and H_2O_2. The timing of the summer NO_3 peak may be related to increased stratosphere/troposphere exchange as the polar stratospheric vortex breaks down with the onset of sunlit conditions (Mayewski and Legrand, 1990; Mulvaney and Wolff, 1993).

Seasalt concentrations (represented in Figure III.2 by Na) generally peak during the winter ($nssSO_4$, δD and H_2O_2 minima). Unlike South Pole, where snowpit profiles usually show one Na peak per year (Whitlow et al., 1992), Siple Dome Na profiles contain more than one per year. This is likely due to the more coastal location of Siple Dome and its lower elevation (621m). Thus, seasalt input is episodic, and depends on synoptic-scale marine cyclogenesis, which occurs throughout the year in the high southern latitudes (Hogan, 1997). The majority of seasalt input, however, likely occurs during winter (August-November) based on atmospheric aerosol composition data from South Pole (Bodhaine et al., 1986). Frequent intrusions of marine air were also identified as the cause of significant seasalt peaks in Ross Ice Shelf snowpits (Warburton and Young, 1981). Using seasalt species as a primary dating tool at Siple Dome is not viable, however, ss profiles can be used to verify winter troughs in other species.

Peaks in the Cl/Na ratio (Figure III.5), which are thought to reflect input of HCl in the summer from the interaction of H_2SO_4 and long-traveled sea salt aerosols (Legrand and Delmas, 1988; Whitlow et al., 1992), peak prior to $nssSO_4$. Unlike South Pole, the high seasalt concentrations at Siple Dome cause the Cl/Na ratio to be close to seawater values (1.5) for the majority of samples, and therefore Cl/Na ratios do not appear to be an accurate dating tool.

Although NH_4 shows a weak summer maximum in three out of five snowpit years (Figure III.5), low NH_4 concentrations and potential for contamination precludes using NH_4 as a reliable seasonal indicator at Siple Dome. Nonseasalt fractions of Ca, K, and Mg, which are likely related to long traveled, continentally-derived crustal salts (Whitlow et al., 1992), consistently peak during winter (Figure III.5). Peak concentrations, however, may be due to high seasalt concentrations and subsequent partitioning artifacts. Therefore, nssCa, nssK, and nssMg concentration profiles are not likely to be an accurate means of identifying annual layers.

INPUT TIMING SUMMARY AND CONCLUSIONS

Figure III.6 provides a schematic summary of chemical input timing relative to an idealized isotopic profile at Siple Dome. In general, results from these Siple Dome snowpits are consistent with those reported from other Antarctic locations (e.g., South Pole, G.V. Neumayer, Mawson). The most reliable summer indicators in the 1994 Siple Dome snowpits appear to be $nssSO_4^{2-}$, δD, H_2O_2, MSA, and NO_3^-. Where large hoar layers can be identified, they are also useful, but thin layers do not provide unique annual associations. Seasalt species peaks can be used to estimate winter deposition, but caution must be used since seasalt peaks are shown to occur throughout the year on a event basis. Thus, a multiparameter approach is necessary for accurately dating Siple Dome snowpit, firn and ice core samples.

Applying this dating scheme to the 1994 Siple Dome snowpits results in annual layer thicknesses and accumulation rates presented in Table III.2. The mean accumulation rate estimate from pit 94-1 is slightly higher than the 1150-year mean obtained from the 1994 Siple Dome ice core (13.42 vs. 11.30 $gcm^{-2}yr^{-1}$). Given that pit 94-1 was sampled at the drillsite, these results suggest a potential recent accumulation rate increase at Siple Dome. In addition, a gradient in accumulation rate appears to exist, increasing towards the north side of Siple Dome. The main moisture source for Siple Dome would therefore be either the Ross or Amundsen Seas.

Modeling results from Siple Dome suggest that annual layer thicknesses will reach sub-centimeter thickness at about 600-700 m depth, which is below the predicted depth of the Wisconsin/Holocene transition (~550-650 m; Nereson et al., 1996). In their study, Nereson et al. (1996) suggest that if annual stratigraphic or chemical signals exist and have been preserved in the ice, they may be resolved throughout the Holocene. Our results, while only in the top 2 m of the Siple Dome snowpack, suggest that seasonal signals in several parameters do exist and will enable depth/age construction. Continuous chemical measurements made on a 150 m core drilled at Siple Dome verify that seasonal ion signals are preserved at least to 15% of the Siple Dome ice thickness (Kreutz et al., 1997).

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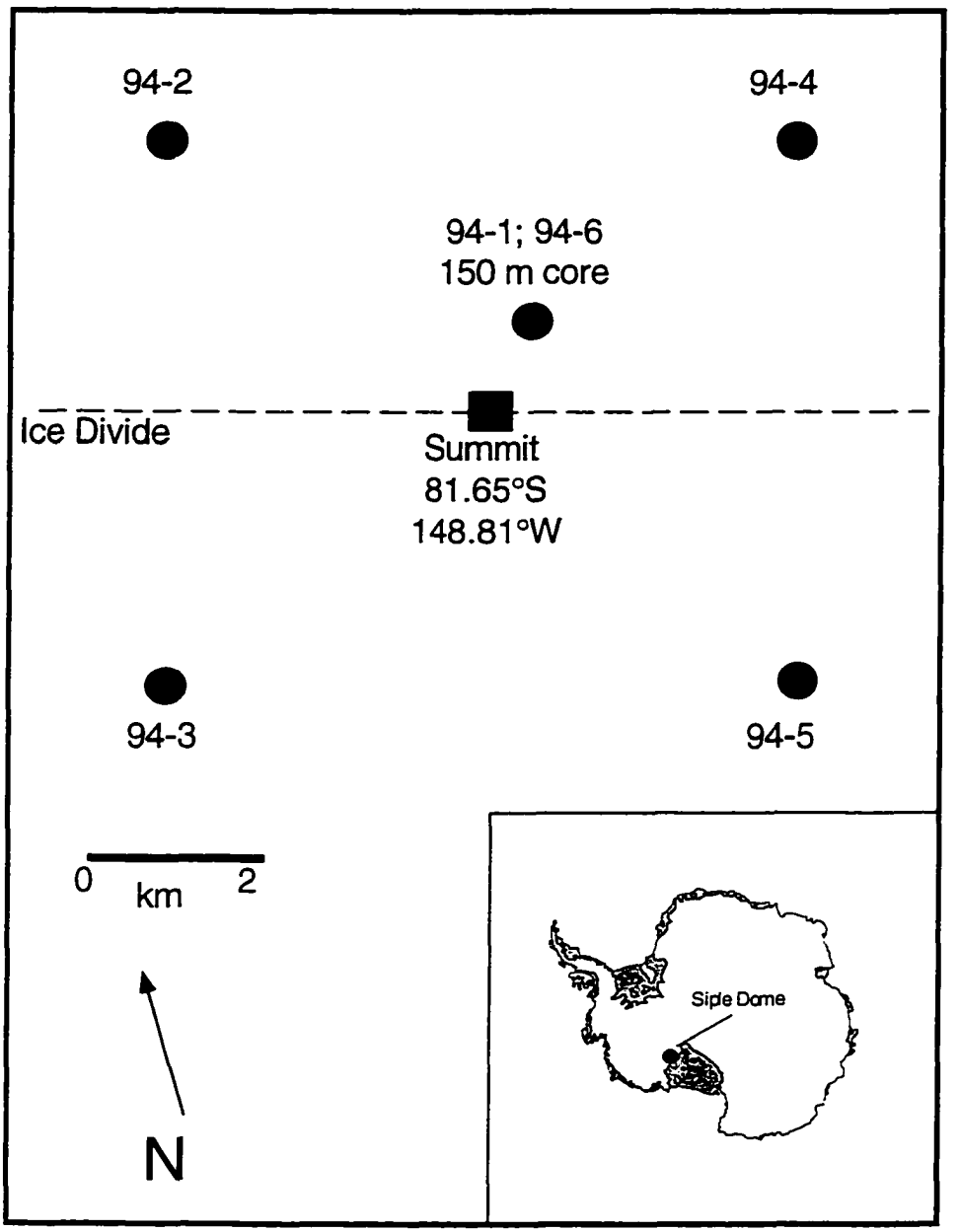

Figure III.1. Location map of 1994 sampling sites on Siple Dome, Antarctica. Pit 94-6 is located ~300 m NE of Pit 94-1, and hence is not represented as a seperate point at this scale.

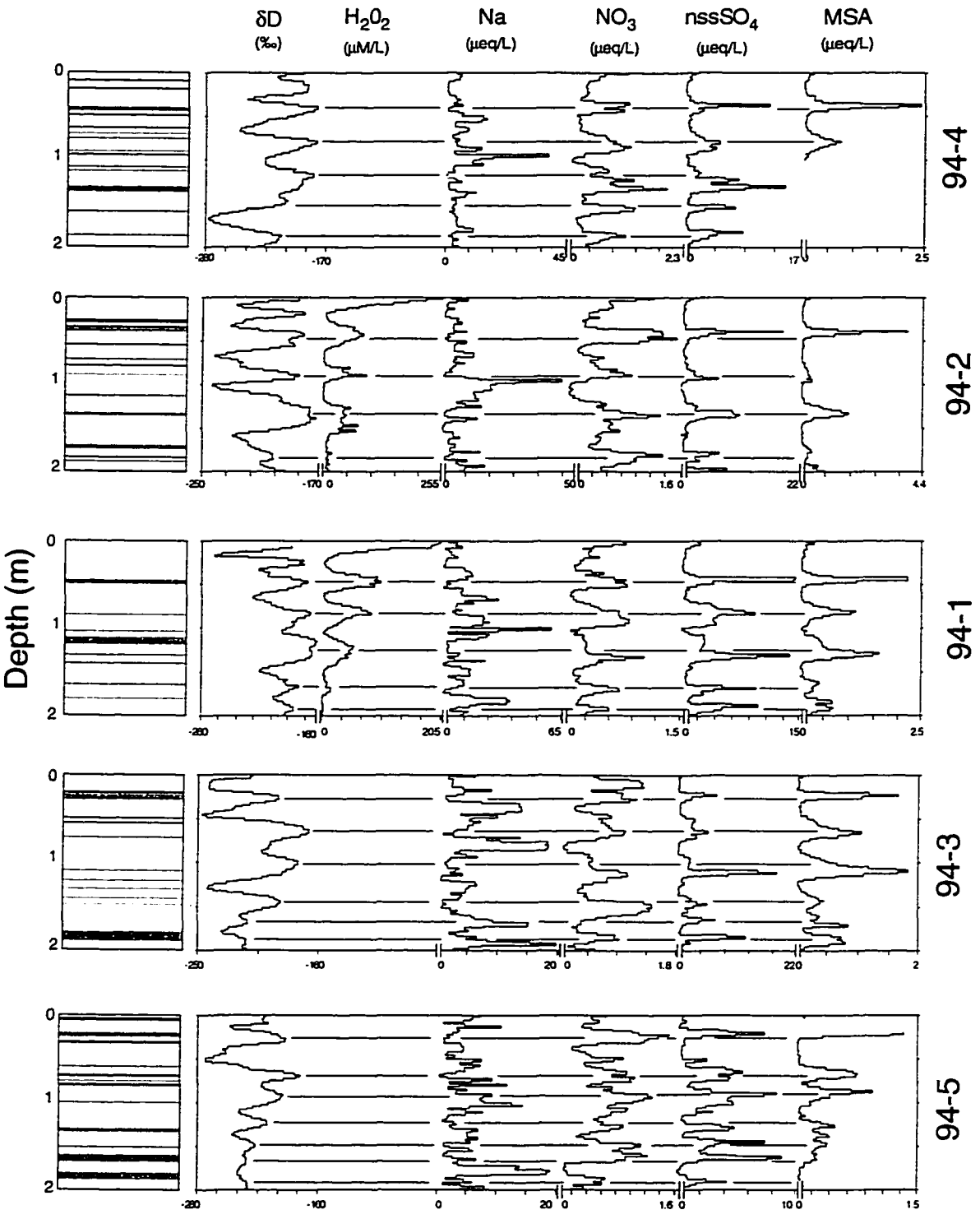

Figure III.2. Stratigraphic, isotopic, and glaciochemical measurements in 2 m Siple Dome snowpits. Snowpits are arranged according to geographical position: pits 94-4 and 94-2 are located 5 km north of the ice divide, pit 94-1 is ~0.7 km north of the ice divide, and pits 94-3 and 94-5 are 5 km south of the ice divide. H2O2 was not measured in pits 94-4, 94-3, and 94-5, and sample volume did not permit MSA measurement in pit 94-4 and the upper 15 cm of pit 94-5. Depth-hoar layers in stratigraphic profiles are represented by grey shading, melt layers (2-5 mm thick) by thick lines, and crusts (1-2 mm thick) by thin lines.

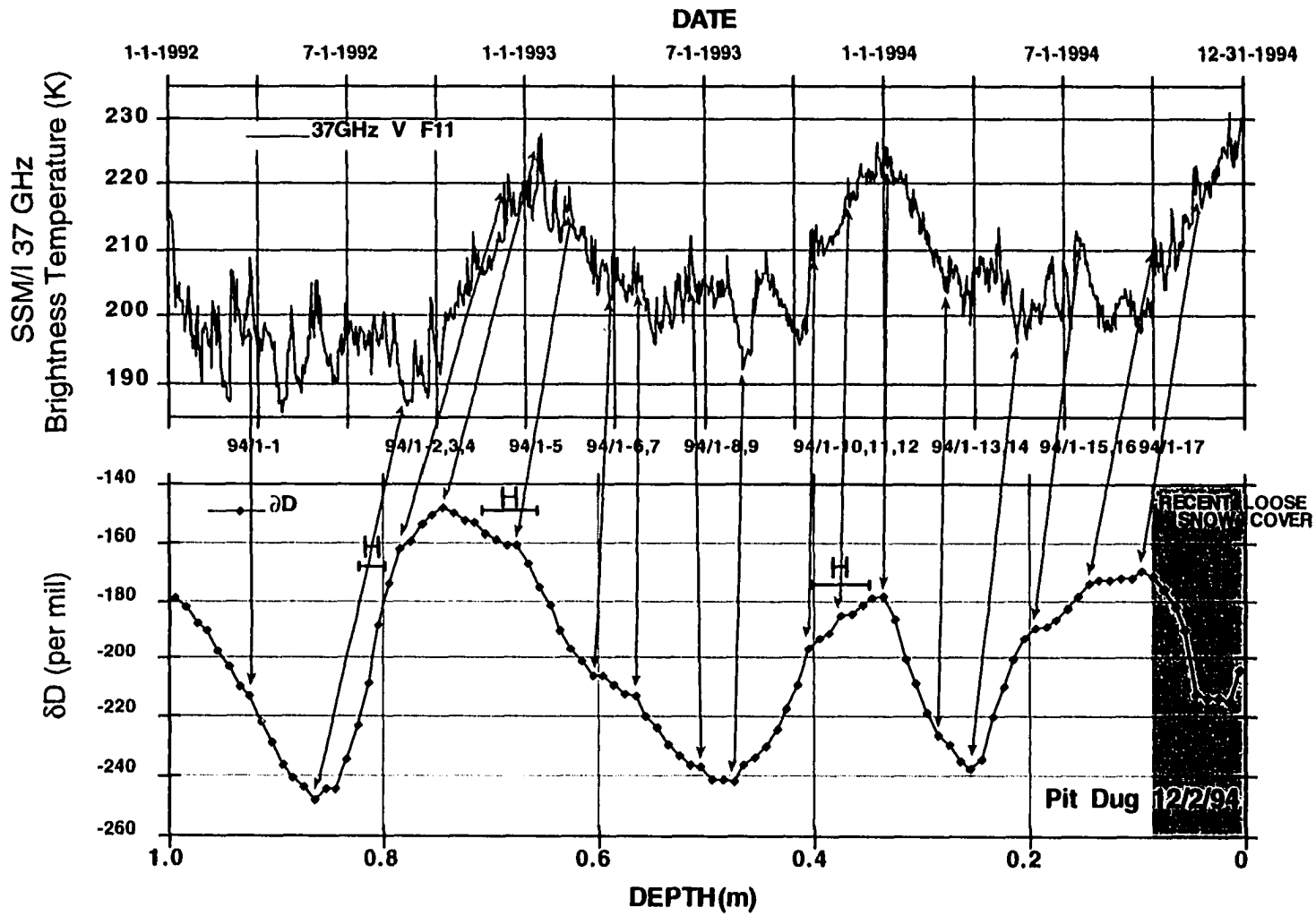

Figure III.3. Comparison of deuterium (dD) ratios in pit 94-6 and brightness temperature derived from SSM/I data. The satellite data used is from daily averaged, 37-GHz, vertical polarization (V), brightness tempeartures (TB) from the scanning multichannel microwave/imager (SSM/I) for the 25 x 25 km grid covering pit 94-6. Depth hoar layers (H) identified in pit 94-6 are noted.

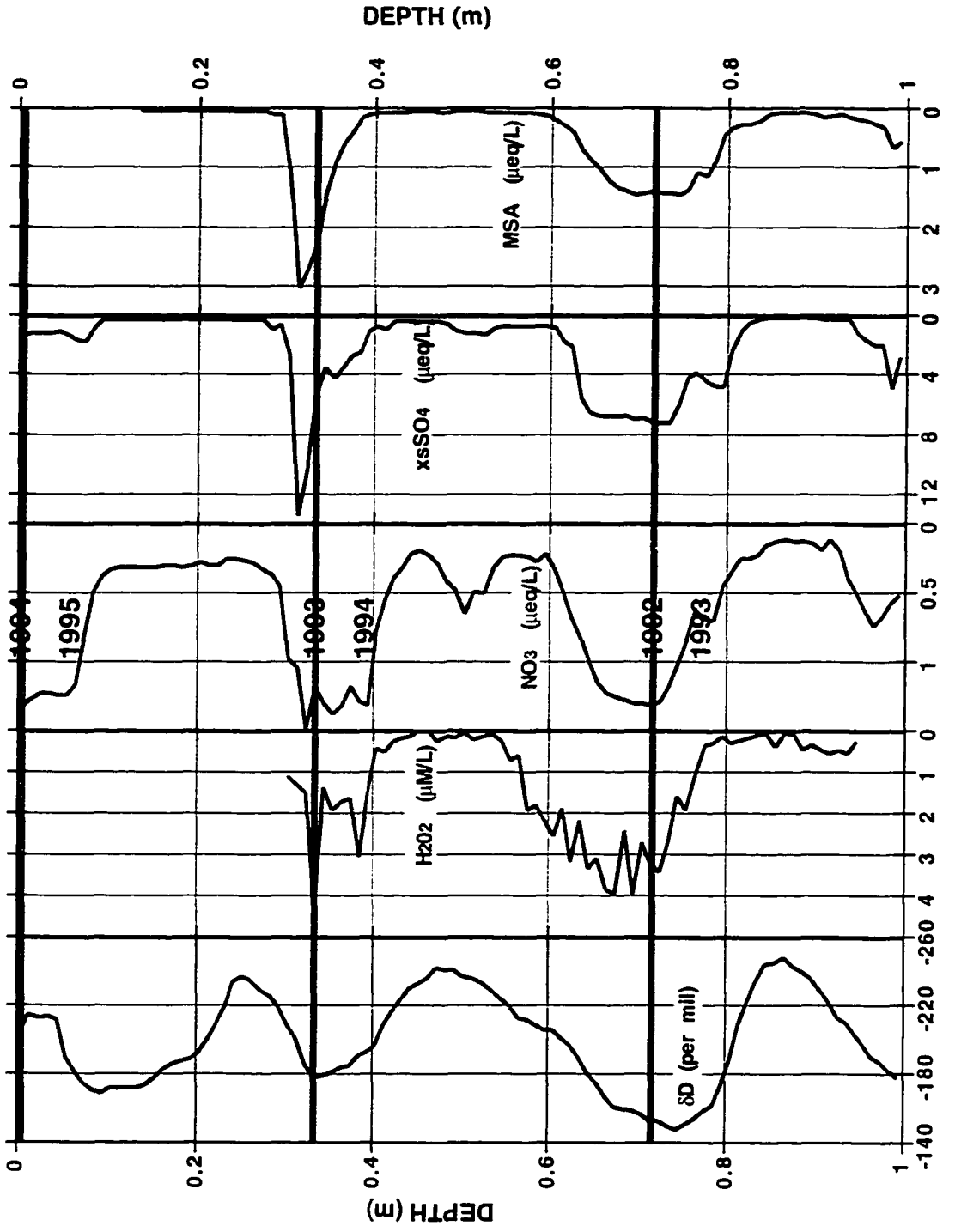

Figure III.4. Comparison of deuterium (δD), H_2O_2, and major ion concentrations (NO_3, $nssSO_4$, and MSA) in pit 94-6.

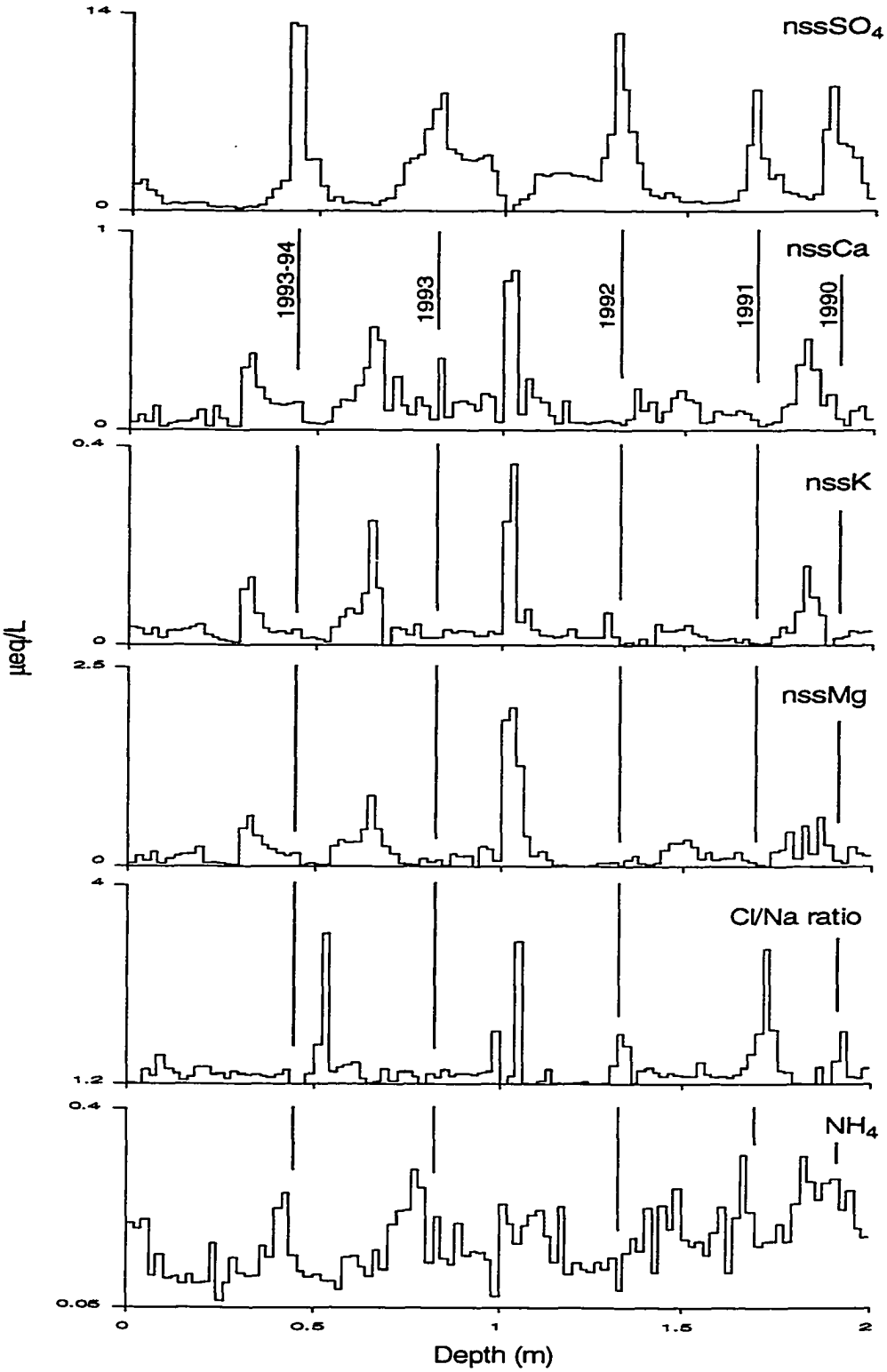

Figure III.5. Comparison of $nssSO_4$, Ca, K, and Mg concentrations, Cl/Na ratios, and NH_4 concentrations in pit 94-1. The temporal pattern of variability demonstrated for these species in pit 94-1 is consistent with other pits.

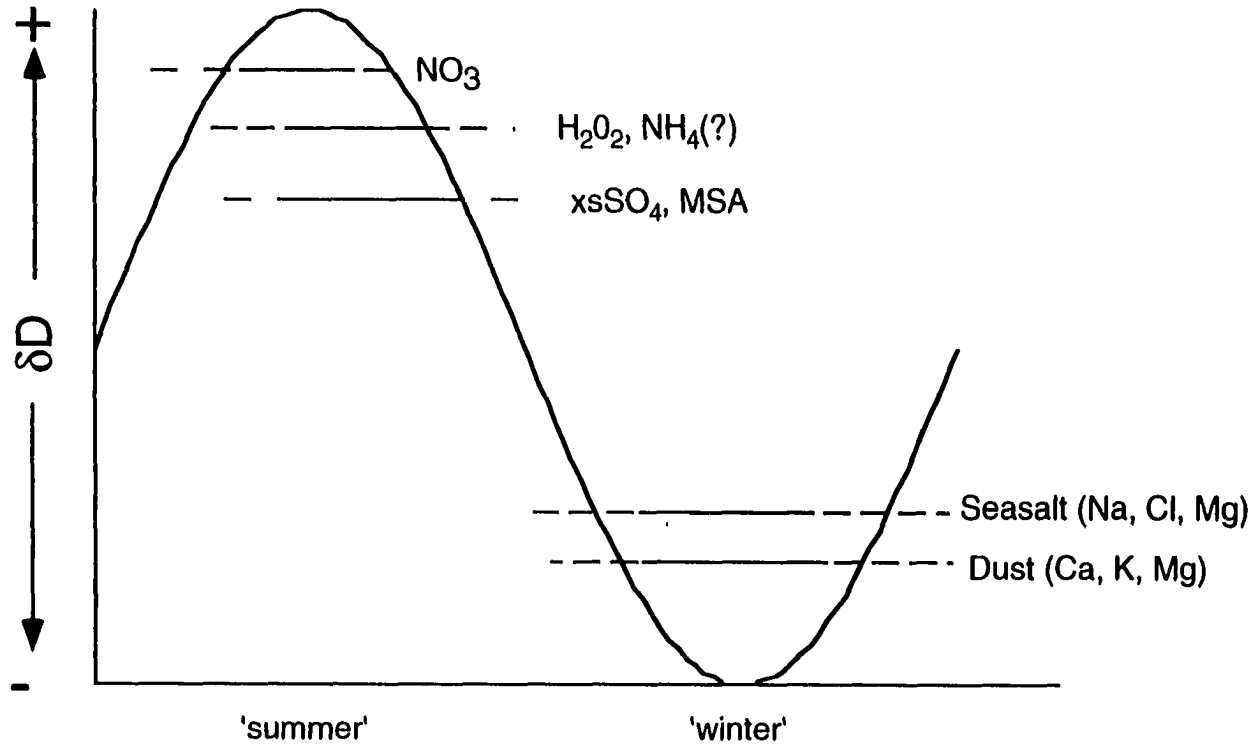

Figure III.6. Summary of seasonal input timing at Siple Dome, relative to an idealized curve (after Whitlow et al., 1992). Soild lines indicate when maximum concentrations frequently occur, and dashed extensions represent the range where peaks are sometimes noted.

Match Point	Date	SSM/I 37 GHz TB(K)	δD (‰)
94/1-17	11/11/94	222.6	-169.4
94/1-16	10/3/94	212	-173.6
94/1-15	7/14/94	213	-189.1
94/1-14	5/14/94	196.1	-237.2
94/1-13	3/6/94	203.3	-226.4
94/1-12	1/1/94	225.7	-177.9
94/1-11	11/25/93	220.8	-185.1
94/1-10	10/18/93	213.2	-196.8
94/1-9	8/9/93	192.2	-241.6
94/1-8	6/17/93	212.1	-237
94/1-7	4/21/93	210.7	-213.2
94/1-6	3/28/93	202.2	-205.9
94/1-5	2/15/93	219.5	-160.6
94/1-4	1/17/93	227.7	-148.1
94/1-3	12/14/92	221.5	-161.9
94/1-2	8/31/92	186.6	-247.8
94/1-1	3/24/92	208.8	-213.1

Table III.1. Summary of information derived from δD/brightness temperature comparison. Matchpoint and date refer to specific tie lines and corresponding brightness temperature dates in Figure III.3.

Pit	*1994*	*1993*	*1992*	*1991*	*1990*	*1989*	*1988*	*Mean*
94-2	14.63	21.94	17.52	19.00				18.27
94-4	13.43	18.92	19.77	8.86	12.69			14.73
94-1	10.97	10.24	14.20	12.68	5.60			10.74
94-6	11.63	12.60	13.25					12.49
94-3	9.15	18.51	21.62	15.25	7.70	9.68		13.65
94-5	5.21	13.03	6.06	12.37	3.78	5.73	7.75	7.70

Table III.2. Estimated annual layer thickness and average accumulation rates ($g/cm^2/yr$) for 1994 Siple Dome snowpits based on chemical, isotopic, and stratigraphic signals.

IV. SPATIAL VARIABILITY AND RELATIONSHIPS BETWEEN GLACIOCHEMISTRY AND ACCUMULATION RATE AT SIPLE DOME AND MARIE BYRD LAND, WEST ANTARCTICA

Section IV will be submitted to Journal of Geophysical Research
(full citation appears in the Complete List of References)

IV. SPATIAL VARIABILITY AND RELATIONSHIPS BETWEEN GLACIOCHEMISTRY AND ACCUMULATION RATE AT SIPLE DOME AND MARIE BYRD LAND, WEST ANTARCTICA

ABSTRACT

Snowpit and shallow core records are used to evaluate the spatial variability of glaciochemistry and accumulation rate at Siple Dome and Inland West Antarctica (IWA). Analysis of full snowpit (4-7 years) records indicates negligible glaciochemical spatial variability at Siple Dome, while in IWA there is significant variability in all species over this period. Examination of annual chemical records from snowpits and shallow cores (30 years) suggests the possible influence of the Siple Dome ice divide and the West Antarctic regional ice divide on glaciochemical spatial variability in the two regions. Glaciochemical concentrations are not related to accumulation rate in either region, suggesting that a simple flux model is insufficient for explaining concentration changes, and that independent climatic information can be derived from concentration and accumulation rate records. Accumulation rate gradients in the two regions are linked to dominant moisture transport pathways and possible orographic effects caused by ice divides. A composite mean annual accumulation rate record from Siple Dome shows an overall similarity to ECMWF-modeled moisture flux, and suggests that the overall control on mass balance in the area is the strength and position of the Amundsen Sea Low pressure system.

INTRODUCTION

Records contained in the snow and ice of polar ice sheets contain highly detailed information about past atmospheric conditions and composition. Such records, developed from snowpit, firn and ice core samples, have been used to document a variety of climatic phenomena, including rapid climate change events, anthropogenic impacts, and volcanic events (e.g., Mayewski et al., 1986; Mayewski et al., 1997; Zielinski et al., 1997). Before long records can be interpreted, however, detailed examination of modern conditions must be made (Mayewski et al., 1990; Mulvaney and Wolff, 1994; Yang et al., 1996; Kreutz and Mayewski, in review). To date, the most detailed ice core records over the past 110,000 years have come from the Northern Hemisphere, specifically the Greenland Ice Sheet (e.g., Mayewski et al., 1997; Johnsen et al., 1997). Following the success of these coring projects, focus has now shifted to the Southern Hemisphere, in an attempt to

determine the global, extent, timing, and phasing of significant climatic events. Because of promising results from glaciochemical (Mayewski et al., 1995) and geophysical (Raymond et al., 1995) reconnaissance at Siple Dome, West Antarctica (Fig. IV.1), a current U.S. project is drilling to bedrock in an attempt to produce a high-resolution, multiparameter, ~100,000 year paleoclimatic record from the area.

To ensure accurate paleoclimatic interpretations based on West Antarctic ice core records, it is crucial to have a knowledge of the spatial representativeness of any given sample site and an understanding of how signals in the ice core reflect environmental change. Specifically, the value of the ice core record depends on an understanding of: 1) the glaciological regime at the core site, 2) spatial variability of chemical and isotopic species (e.g., Mayewski et al., 1987), 3) input timing of these species (Section III), 4) sources of these species (Section II), 5) physical controls on species deposition (e.g., Cunningham and Waddington, 1993), and 6) air/snow fractionation of various species (e.g., Dick and Peel, 1985; Dibb, 1996) . This paper focuses on the spatial variability of major ion concentrations and accumulation rate in two regions of West Antarctica, Siple Dome and Inland West Antarctica (IWA; Fig. IV.1). In particular, the effect of ice divides in both regions on glaciochemical concentrations and moisture flux is addressed, as is the relationship between accumulation rate and chemical concentration. Sampling strategies in the two regions allows these relationships to be investigated in different spatial and temporal detail. At Siple Dome, extensive snowpit sampling provides a detailed description of glaciochemical and accumulation rate variability in the area. The snowpit records, however, are limited in terms of length (5-10 years). In contrast, the distance between sites in IWA (~60-70 km) precludes a spatial investigation as detailed as that at Siple Dome, however the longer IWA records allow investigation of both general spatial and temporal trends in the region.

METHODS

A total of 14 snowpits were sampled at Siple Dome and Inland West Antarctica during the 1994/95 and 1996/97 austral field seasons (Fig. IV.1). Details of pit location, sampling depth, and resolution are given in Table IV.1. Snowpit sampling was performed by workers wearing non-particulating suits, polyethylene gloves, and particle masks. Samples were collected into precleaned polyethylene containers for frozen shipment and stored below -15°C until melting immediately prior to chemical analysis. Analysis of major cations (Na, K, NH_4, Mg, Ca), anions (Cl, NO_3, SO_4), and methanesulfonic acid (MSA) in core and snowpit samples was performed at the University of New Hampshire

using Dionex 4000 series instruments. Cations were analyzed via suppressed chromatography with a Dionex CS12 column, 0.125 ml loop, and 20 m*M* MSA eluent. Anions were analyzed with a Dionex AS11 column, 0.075 ml loop, and 6.0 m*M* NaOH eluent. MSA measurements were made with an AS11 column, 1.5 ml loop, and 0.5 m*M* NaOH eluent. Dating of samples in Siple Dome and IWA snowpits was accomplished via techniques described in Kreutz et al. (in review). Partitioning of marine-influenced species (Na, Cl, Mg, Ca, K, SO_4) into seasalt (ss) and nonseasalt (nss) fractions was done using standard seawater ratios according to O'Brien et al. (1995) and Kreutz et al. (in press).

To further test the dating scheme outlined in Kreutz et al. (in review), we compare $nssSO_4$ and β-activity profiles in firn cores from Siple Dome and IWA. Cores (Table IV.1) were processed at sub-annual resolution (6-12 samples/year) and analyzed for ion content as above. Gross β-activity was measured on 20 and 25 cm samples using a gas-flow proportional counter. Maxima in each β-activity profiles is assumed to represent the global peak reached prior to the 1963 Atmospheric Test Ban Treaty, which reached Antarctica during the austral summer 1964/65 due to atmospheric transport times (Crozaz, 1969). In each core, it is possible to accurately count back to the 1964/65 β chronostratigraphic horizon using summer $nssSO_4$ peaks, lending further evidence that this method is an accurate dating tool.

GLACIOCHEMICAL SPATIAL VARIABILITY

Previous studies in Greenland have investigated glaciochemical spatial variability in detail, and suggested that, particularly for aerosol-associated species, spatial variability is sufficient to impact data interpretation (Dibb, 1996). For example, within a single snow event, traverse sampling indicates substantial variability in the deposition of natural radioactive nuclide tracers of submicron aerosols. Because the atmospheric distribution of these tracers is presumed to be fairly constant over 60 km scales, this example reflects variability imparted by air to snow transfer of submicron aerosol plus spatial variability in the depth of snow that accumulated from this storm at the different spots sampled. This example highlights the extreme spatial variability that can occur during single events. Daily, and more frequent, surface snow sampling at Summit, Greenland, has shown that the concentrations of aerosol-associated ions in adjacent replicates collected in succession from a single stratigraphic layer can vary by as much as a factor of two. Some of the variability can be related to specific events like wind storms or fog deposition (Bergin et al., 1995), but detailed understanding of the causes of this small scale variability is lacking. Similar variability is expected in species deposited on an event-driven basis, such as seasalt

species. Some degree of temporal averaging is likely accomplished during the firnification process, and often by the sampling resolution chosen for a pit or core study. Several studies have investigated the spatial variability of annual glaciochemical signals, and found that, in general, spatial changes at this level of averaging are often low enough that one snowpit or core record can be assumed to be representative of a larger region (Mayewski et al., 1987, 1990; Yang et al., 1996; Zielinski et al., 1997). Likewise, because one goal of glaciochemical research in West Antarctica is to correlate time-series mean annual records of aerosol-associated species with meteorological records, it is important to understand how representative a single core record from a particular area of West Antarctica is of a larger region.

Siple Dome

Mean ion concentrations for the 1996 Siple Dome snowpits are given in Table IV.2 (mean values for 1994 pits in Kreutz and Mayewski [in review]). Temporal variance in concentration for each species and each pit is large. A two-sided t-distribution test with unequal variances was applied to mean pit concentrations, and indicates no significant difference between pits for all species. Therefore, the t-test results suggest that on timescales represented by mean pit values (5-7 years), glaciochemical spatial variability across Siple Dome is negligible. This result is shown in Fig. IV.4. To further investigate the issue of spatial variability at Siple Dome, chemical records from the 11 snowpits and 3 firn cores were examined via the analysis of variance (ANOVA) technique. The ANOVA method was chosen to compare sample means as it is able to separate random and controlled-factor error, and is less sensitive to sample populations with large variance (Miller and Miller, 1993).

Siple Dome snowpits were separated into two groups (north and south) according to their location relative to the Siple Dome ice divide (Fig. IV.2), in order to test whether possible micrometeorological processes associated with the ice divide (N. Nereson, pers. commun., 1997) have a discernible influence on chemical variability. ANOVA results are presented in Table IV.3. Concentrations tested over the total pit range (5-7 years integrated) indicates there is no significant difference in any species (95% confidence level) between pits grouped on either side of the divide or over the entire area, consistent with t-test results. Significance is higher for those species deposited mainly in late spring/summer (NO_3, SO_4, MSA), as opposed to species derived from marine and continental sources (Na, Cl, Mg, K, and Ca). The same statistical (ANOVA) method was applied to samples from within 3 annual layers common to all Siple Dome snowpits: 1992, 1993, and 1994 (Table IV.3). For sulfur (SO_4 and MSA) and NO_3 species, there is no

significant difference across the entire area in any of the three annual layers. However, in the 1994 layer, pits on the South side of the divide are not correlated with respect to SO_4 and MSA. Ca and K demonstrate high variability within annual layers, both across the entire area and on each side of the divide. Seasalt species (Na, Cl, and Mg) display no significant difference in the 1993 and 1994 layers. In the 1992 layer, however, there is a significant difference across the entire area. This is due to extremely high seasalt concentrations in pits on the north side of the divide in the 1992 layer. While there is no significant difference in pits grouped on either side of the divide, the influence of the single storm event on correlations across the entire region can be seen by the low P value in the all pit case (Table IV.3).

Glaciochemical spatial variability on an annual basis can be further tested by using shallow firn core records on either side of the ice divide (Table IV.1). Correlation coefficients for the two cores on the north side of the divide (N50E50 and the 1994 core) indicate significant correlations between 32-year records (common period of overlap in each core) of every species except NH_4. In contrast, correlations across the divide (between N50E50 and S50E50 and between the 1994 core and S50E50) indicate significant correlations only for NO_3 and SO_4. While this analysis does not provide information on each individual annual layer (as above in ANOVA analysis), and is also susceptible to possible dating errors, it does suggest that a single core record on the north side of the divide is representative of the northern region on an annual basis.

Inland West Antarctica

Mean ion concentrations for the three IWA snowpits (Table IV.1) are presented in Kreutz and Mayewski (in press). The contribution of each species to the total ion burden in the three snowpits is shown in Fig. IV.4. Using ANOVA analysis on the full pit records indicates significant differences for all species except Ca, NO_3, and MSA. Because ANOVA tests on entire pit records reveal significant differences on an interannual basis, individual annual layers were not tested from the IWA pits.

Correlation analyses were performed on mean annual chemical records from the three IWA cores (Table IV.1) for the period 1963-1994. Although longer annual records from these three cores are available, this period was chosen because it likely represents the best-dated portion of the record (based on β profiles). Unlike the three shallow cores used at Siple Dome, which have a total separation of 10 km, the IWA cores are spaced over 160 km. Not surprisingly, correlation of RIDSA versus RIDSB and RIDSA versus RIDSC annual records reveals no significant correlations for any species (except SO_4 in cores RIDSA and RIDSC). However, mean annual records of several species (Na, Cl, Mg,

NH_4, Ca, and NO_3) are correlated between RIDSB and RIDSC cores. These results suggest that there may be a different atmospheric circulation regime responsible for transporting several species to the RIDSA site, while the RIDSB and RIDSC sites are influenced by a separate atmospheric regime.

ION CONCENTRATION VS. FLUX

Glaciochemical spatial variability discussed above could be related to two overall causes: 1) Changes in atmospheric circulation and source regions, if chemical concentration is independent of snow accumulation rate; 2) changes in snow accumulation rate, if chemical concentration depends on snow accumulation rate. To investigate the spatial relationship between accumulation rate and chemical concentration at Siple Dome, annual chemical concentrations were correlated with annual accumulation rates. As above, the accumulation rate/concentration relationship was tested for pits on either side of the Siple Dome ice divide, as well as across the entire region. Results of the analysis are given in Figure IV.5 and Table IV.5. The only significant correlation found is between NO_3 and accumulation rate in pits on the South (lower accumulation) side of the ice divide.

Empirical orthogonal function (EOF) analysis may be used to further test the relationship between concentrations and accumulation rate (Meeker et al., 1997). If accumulation rate and concentration are related, an EOF mode which explains a high percentage of variance in both should be identified. EOF results for the period 1963-1994 in the 1994 Siple Dome core and the three IWA cores is presented in Table IV.6. In the Siple Dome, RIDSA, and RIDSB cores, the majority of accumulation rate variance is partitioned on the third EOF (EOF3). In these records, EOF3 does not explain a large portion of variance of any chemical species, suggesting that there is no relationship between chemical concentration and accumulation rate over this time period. In the RIDSC core, a majority of the accumulation rate variance is split between EOF2 and EOF3. EOF2 and EOF3 also explain ~20-50% of the variance of NH_4, NO_3, and SO_4, which may indicate that there is some relationship between summer precipitation and deposition of these species at this site.

SPATIAL VARIABILITY IN ACCUMULATION RATE

Previous studies of Antarctic precipitation indicate that disproportionately large moisture fluxes occur in West Antarctica, where cyclonic systems are able to penetrate inland (Lettau, 1969). The passage of cyclonic storms over West Antarctica is frequent, although

the location of the major tropospheric troughs and ridges, and hence the advection of moisture, varies from month to month and from year to year (Rubin and Giovinetto, 1962). The relative frequency of one type of cyclone trajectory or one type of circulation pattern is not necessarily the deciding factor in the precipitation regime (Rubin and Giovinetto, 1962). In view of the low absolute amount of precipitation in the region, it is possible that only a few storms during a particular season can deposit much of the total accumulation. Several lines of evidence (Bromwich, 1988), however, demonstrate that the majority of Antarctic precipitation falls during the winter, when the average atmospheric moisture content is low. This, in conjunction with the zonally averaged dominance of the transient eddy moisture fluxes, suggests that the intensity of cyclonic activity is the key aspect of precipitation generation (Bromwich, 1988). Topographically forced moisture transport convergence is responsible for the meridional precipitation distribution in the Antarctic, with large amounts over the marginal ice slopes and small values in the continental interior. Variations in amounts of zonal precipitation are linked with the quasi-stationary cyclones in the circumpolar low-pressure trough and ultimately to the positions of the long waves in the hemispheric circulation (Bromwich, 1988). Penetrations far into the continent of warm, moist air masses with their abundant precipitation are associated with marked southerly wind through a deep tropospheric layer. The topography of coastal and central West Antarctica appears to play a major role in channeling incoming moisture into fairly well-defined pathways. In particular, a trough bewteen the Executive Committee Range (~3000 m elevation) and Pine Island Bay (Fig. IV.1) provides a pathway for frontal systems to migrate onto the polar plateau. Potential temperature isotherms (Hogan, 1997) support this view, showing maximum values in a narrow band well inland from the coast. In addition, previous compilations of accumulation rate estimates in West Antarctica suggest that the dominant storm track follows the regional ice divide (Fig. IV.1), with higher accumulation rates being located on the windward and within ~20 km of the leeward side of the divide.

Inland West Antarctica

Results from the three IWA cores suggest a steep accumulation rate gradient in Marie Byrd Land, decreasing by a factor of ~2.5 along the 160 km traverse (Fig. IV.2 and Table IV.7). In addition, the relative change between sites A and B (60% increase) is much larger than that between sites C and B (33% increase). Our estimate (11.1 g/cm^2/yr) from Site C, ~3 km from Byrd Station, is consistent with previous estimates (Rubin and Giovinetto, 1962; Vickers, 1966; Gow et al., 1972; Whillans, 1978). The large mass balance estimate for Site A may be related to orographic effects on air masses advecting from the Amundsen Sea (Fig. IV.1). In a similar study traversing up-glacier from Byrd,

Whillans (1978) previously noted a steep accumulation gradient in the same vicinity as Site A. In addition, Whillans (1978) reported that this gradient is consistent over different time periods studied (1964-67 and 1968-1973). Several factors contribute to mean accumulation rate, especially for sites in close spatial proximity (e.g., surface microrelief due to snow drifts and sastrugi), but in this case the gradient is likely due to changes in atmospheric moisture transport. Therefore, it appears that accumulation rate conditions in this region are quite sensitive to the site position relative to the major moisture flux, probably driven parallel to the regional ice divide by topographic effects. As suggested by Whillans (1978), two regimes may exist in this region of West Antarctica: one near the regional ice divide, where the accumulation rate is related to orographic effects on air masses coming from the Amundsen Sea, and a second on the lee side of the ice divide where snow accumulation is more related to uniform radiational cooling.

Siple Dome

Spatial gradients in accumulation rate can also be studied at Siple Dome based on snowpit and shallow core results. The transect of snowpits at Siple Dome (Fig. IV.2), demonstrates a distinct decrease in the number of annual chemical signals present in pits on the south side of the divide (Fig. IV.6). Snowpit estimates indicate a two-fold decrease in accumulation rate along the 60 km transect (Table IV.7). Accumulation rate estimates from shallow cores suggest that this gradient (within ±5 km of the ice divide) has persisted for at least the last 30 years (Table IV.6). The north-south accumulation gradient noted at Siple Dome is consistent with accumulation estimates from the Ross Ice Shelf (Herron and Langway, 1978; Warburton and Young, 1981), which suggest the main moisture source for the region is the Ross and Amundsen Seas.

Moisture flux into a selected region of West Antarctica, which includes Siple Dome, was modeled by Cullather et al. (1996) using ECMWF numerical analyses. The computed interannual trend in moisture convergence for the region (Fig. IV.8) was compared to the Southern Oscillation index, and found to have a similar trend over the period 1980-1995 (Cullather et al., 1996). To compare the model results to observational data at Siple Dome, a composite accumulation rate record was derived from the N50E50, S50E50, and 1994 core records. This approach was taken to minimize potential dating errors, and topographic effects on accumulation rate related to the Siple Dome ice divide. The composite mass balance record displays an overall similarity to the modeled moisture flux for the region (Fig. IV.7). Because the modeled moisture flux is primarily driven by changes in the strength and position of the Amundsen Sea Low pressure system, the similarity of the two

records lends further support to the hypothesis that the main moisture source region for Siple Dome is the Ross and Amundsen Seas.

CONCLUSIONS

In this paper, spatial variability in glaciochemistry and accumulation rate, as well as the relationship between the two parameters, was investigated in two regions of West Antarctica. Glaciochemical spatial variability at Siple Dome is negligible on 5-7 year timescales, however variability within annual layers can be significant. Some of the noted variability may be related to the Siple Dome ice divide, particularly in the case of seasalt species. Glaciochemical spatial variability in IWA is significant between sites for the most recent 3-5 years. Correlation of longer (30 year) annual records suggests that the sites farthest removed from the regional ice divide are more closely related than the site nearest the ice divide, possibly related to orographic effects. Glaciochemical concentrations are not directly related to accumulation rate at any of the sites, suggesting that a simple flux model is not sufficient to explain changes in chemical concentration. Rather, independent climatic information can be derived from concentration and accumulation rate records. The sharp gradient in accumulation rate noted in IWA is likely related to dominant storm tracks and topographic effects in the region. Therefore, two separate atmospheric regimes appear to exist in the region based on glaciochemical and accumulation rate results. The accumulation rate gradient at Siple Dome is consistent with modeling and other observational results, suggesting that Amundsen Sea Low pressure system has a large role in moisture transport into the region.

ACKNOWLEDGMENTS

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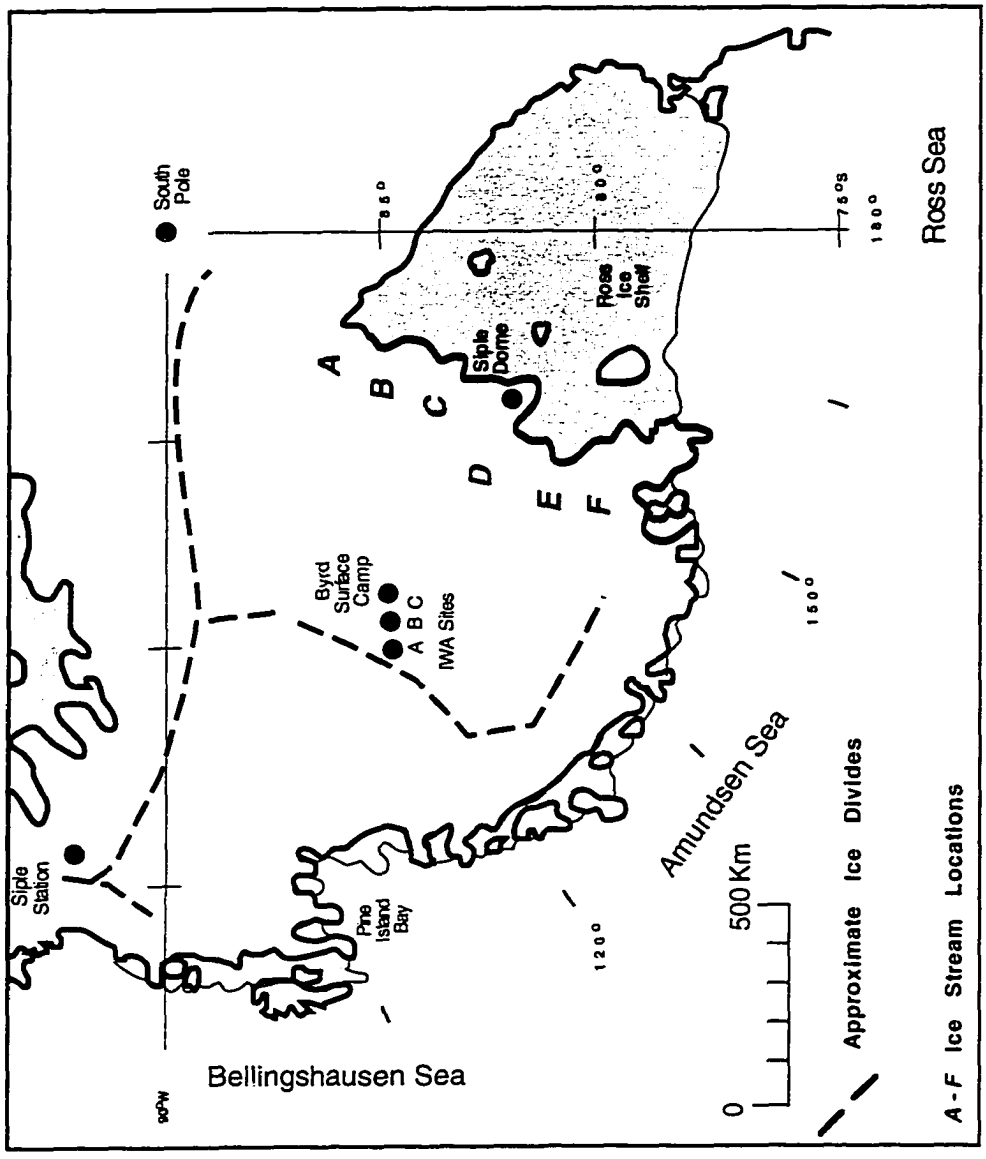

Figure IV.1. Location map for West Antarctic sites.

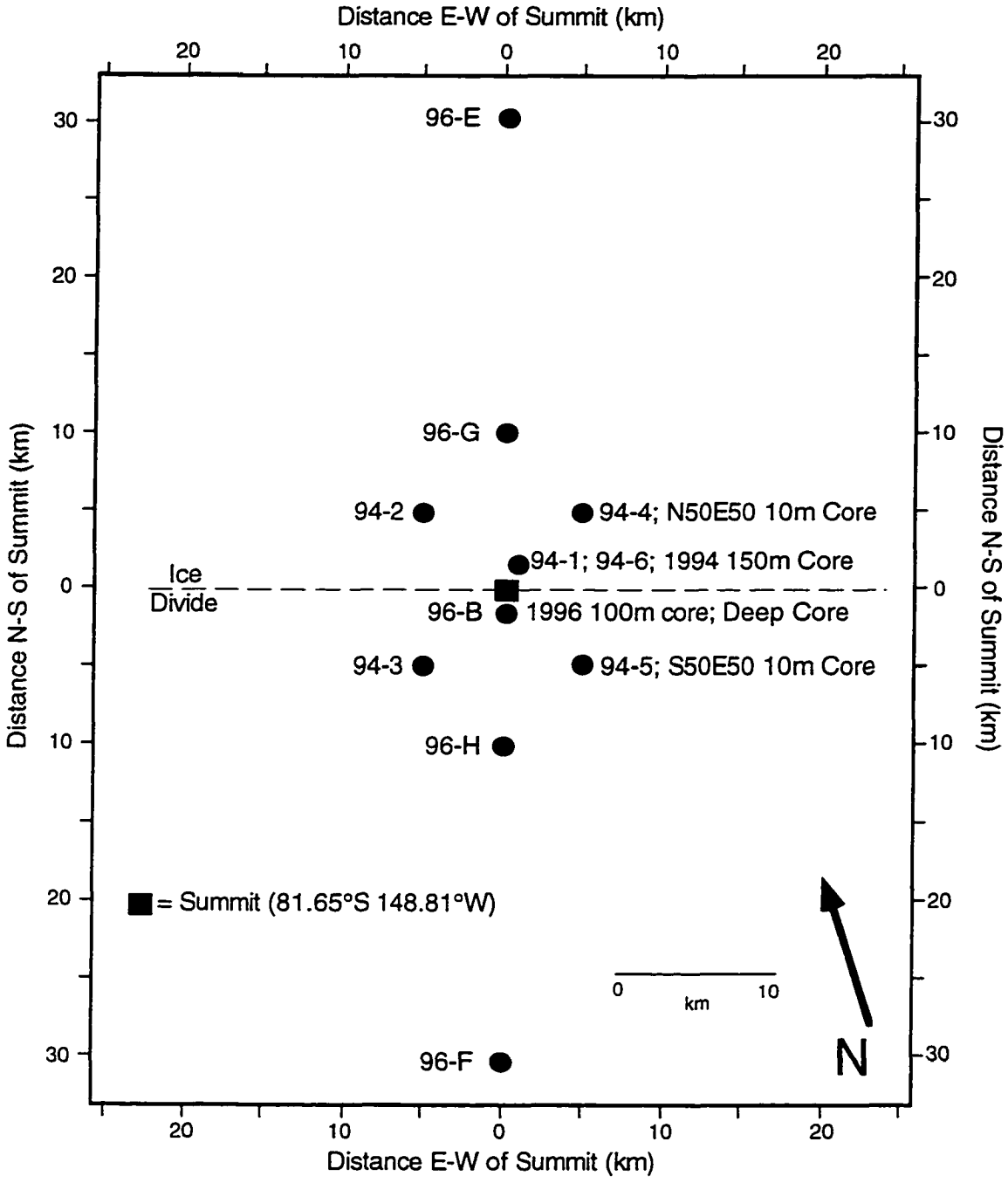

Figure IV.2. Location map for Siple Dome snowpits and cores.

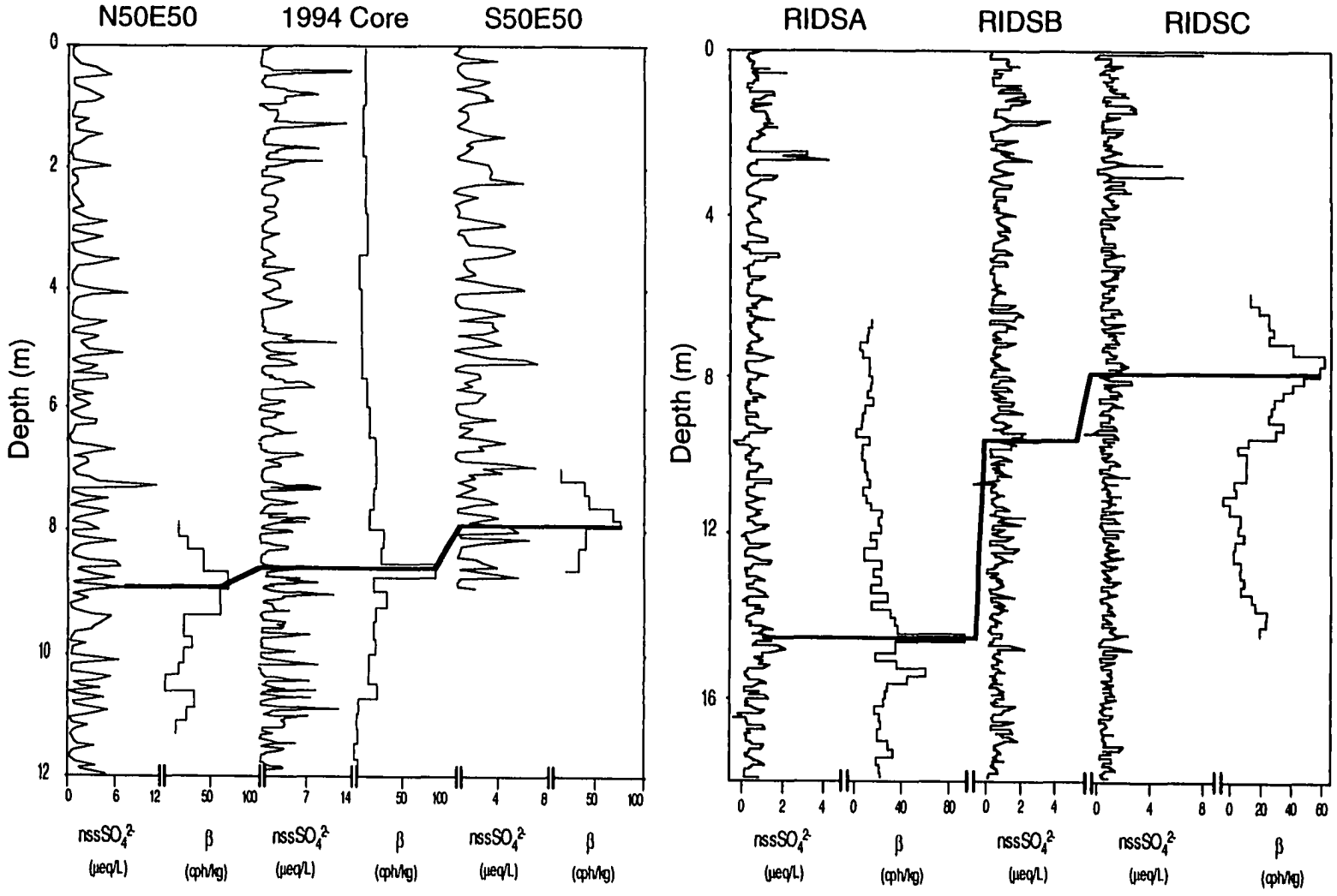

Figure IV.3. Beta activity and $nssSO_4^{2-}$ profiles from Siple Dome and Inland West Antarctic cores. The thick black lines correspond to the 1964/65 time horizon.

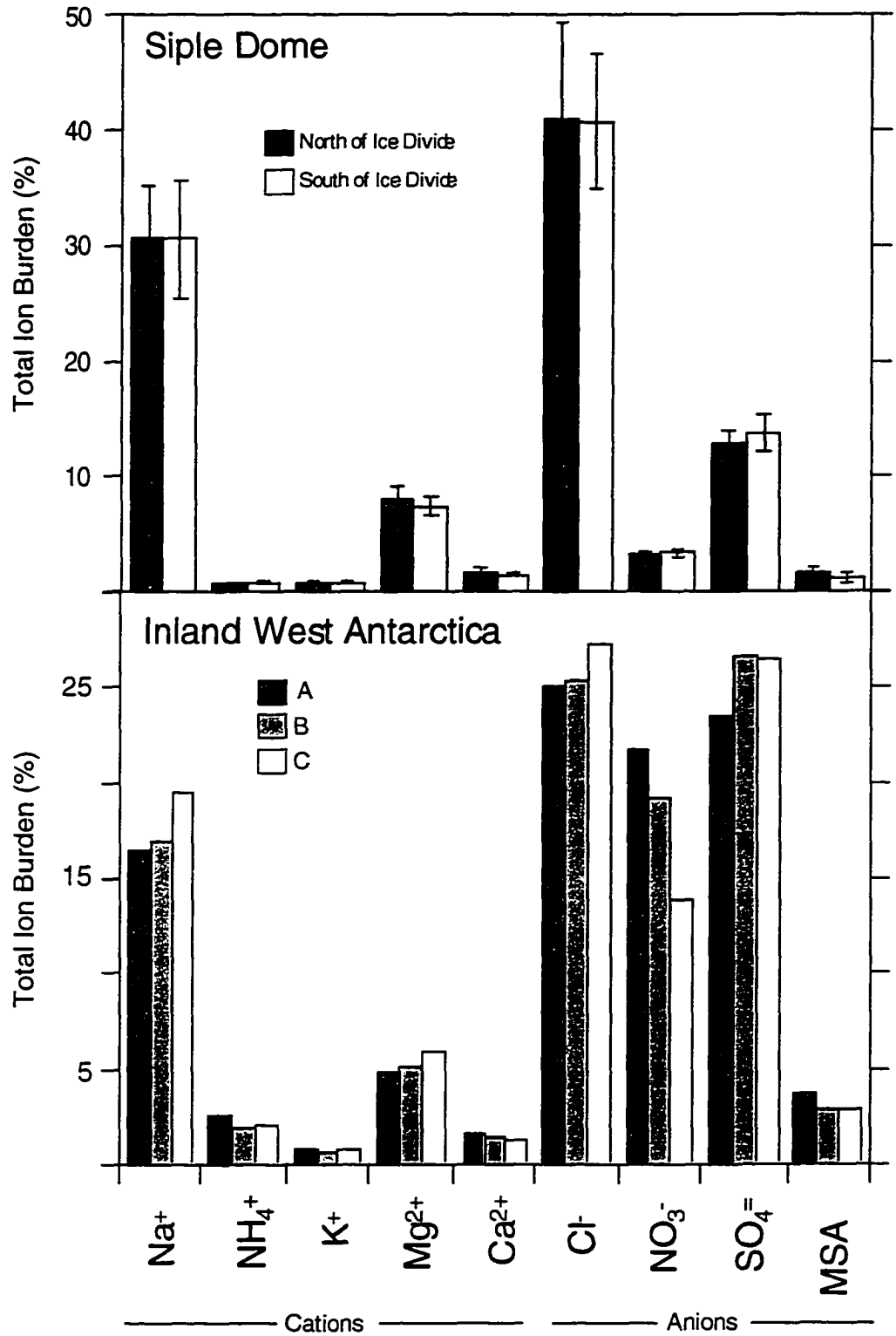

Figure IV.4. Relative contribution of chemical species to the total ion burden at Siple Dome and IWA sites. Error bars represent standard error of mean pit values on the North and South side of the Siple Dome ice divide.

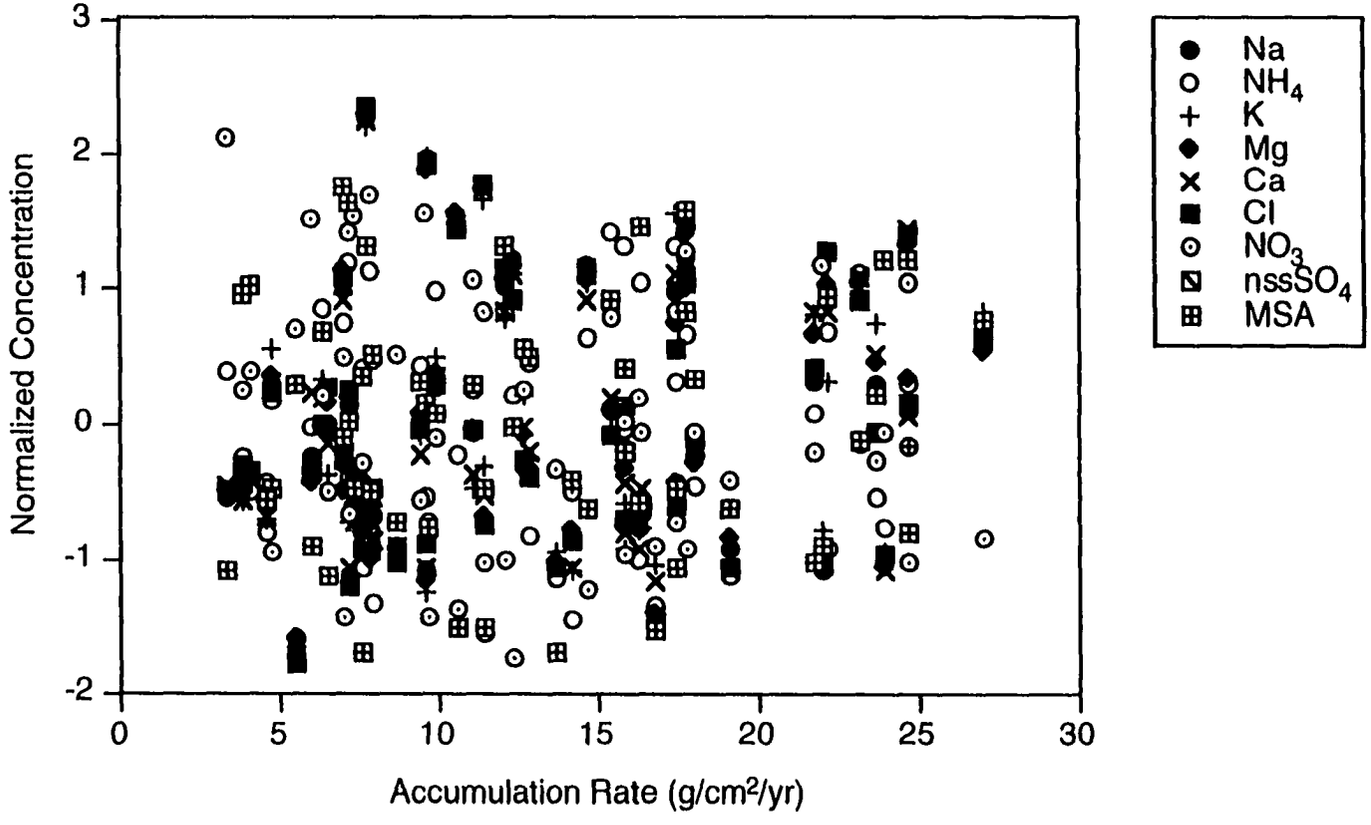

Figure IV.5. Normalized mean annual species concentrations vs. mean annual accumulation rate in Siple Dome snowpits.

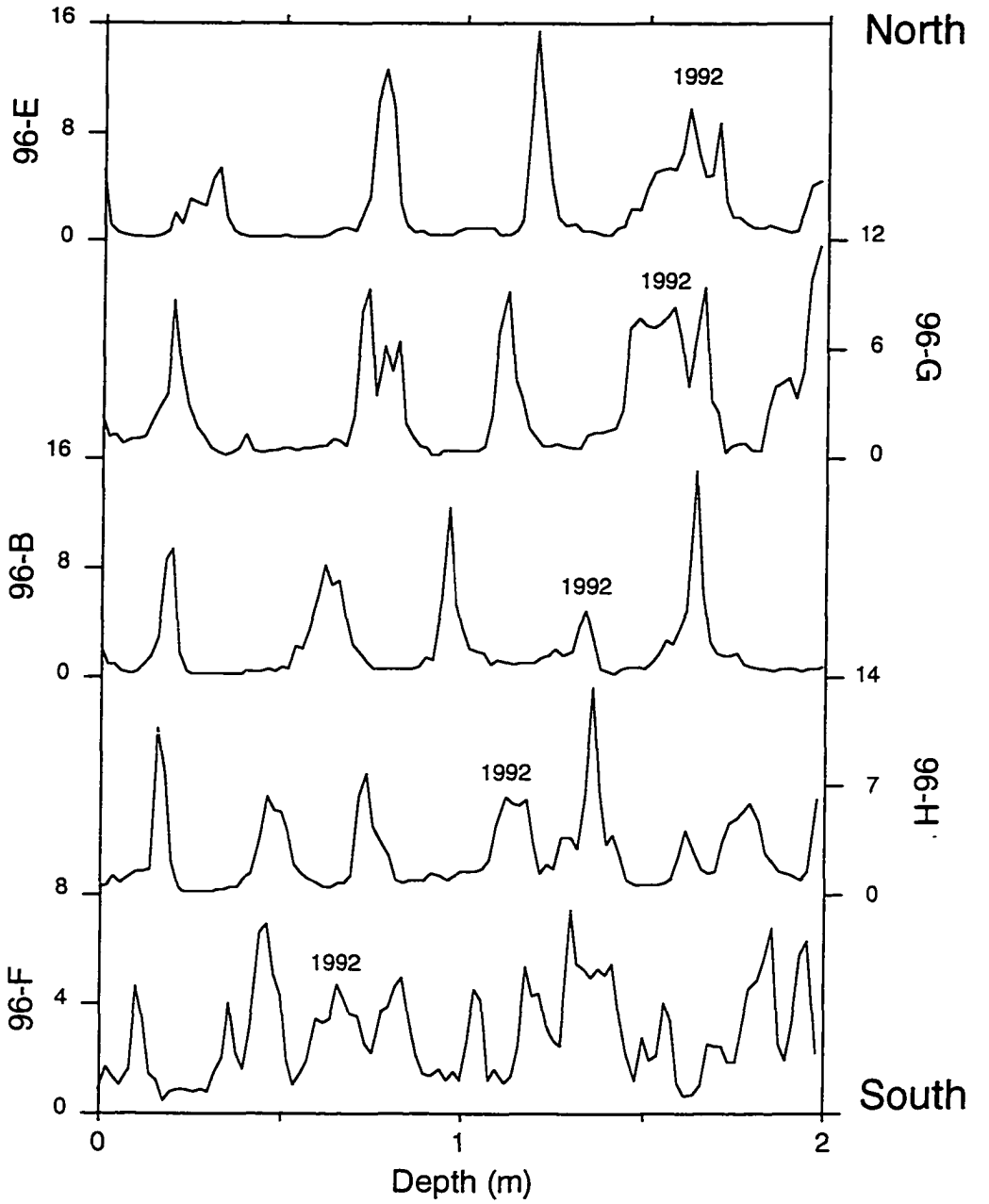

Figure IV.6. Nonseasalt (nss) SO_4 concentrations for 1996 Siple Dome snowpits, arranged from 30 km north of the ice divide (96-E) to 30 km South of the ice divide (96-F).

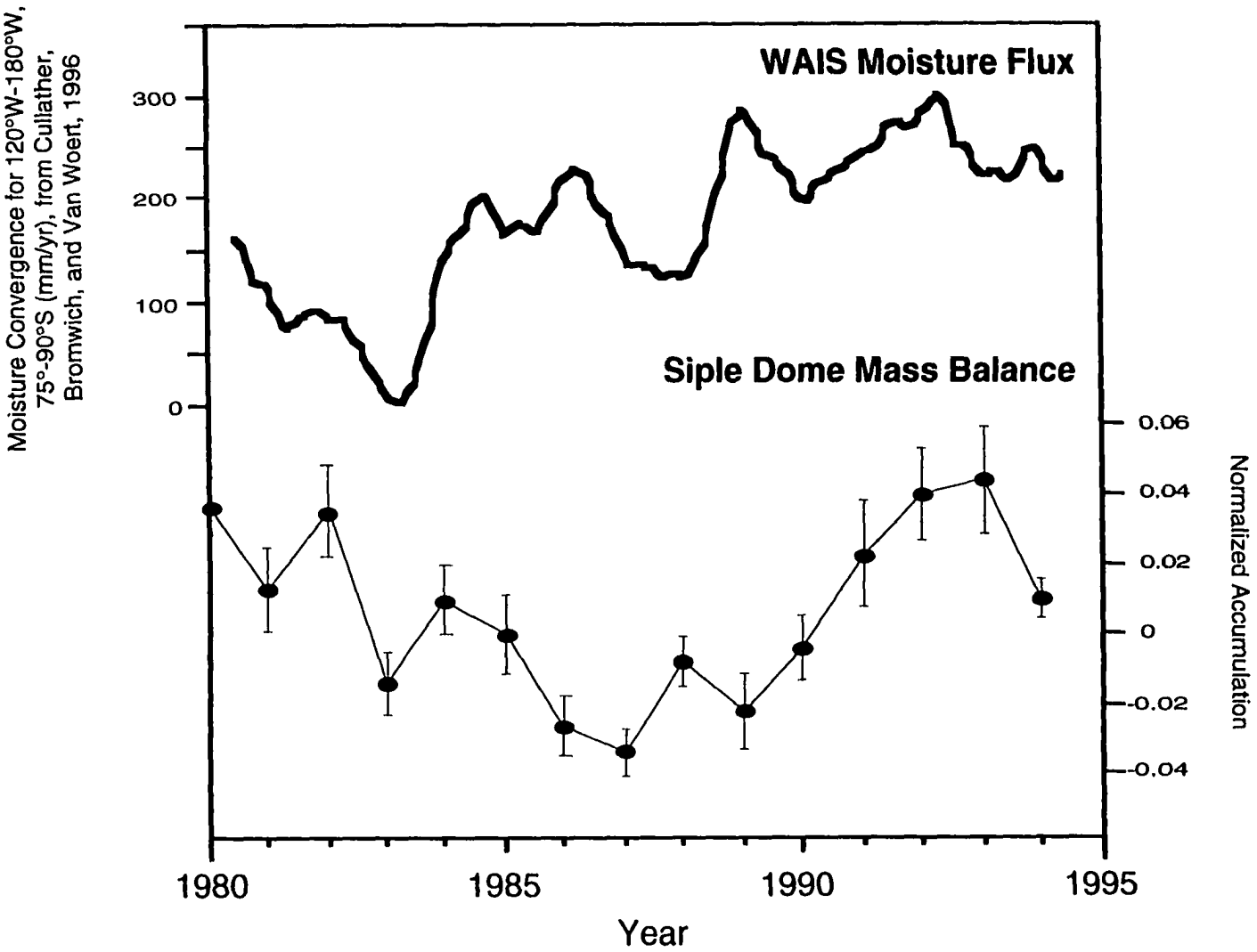

Figure IV.7. Comparison of modeled moisture flux into the South Pacific moisture convergence sector (includes Siple Dome; from Cullather et al., 1996) and composite Siple Dome accumulation rate record for the period 1980-1994.

	Location	Depth (m)	Sample Interval (cm)	Time Period Covered (year AD)
Snowpits				
Siple Dome				
1996-E	81°18.14'S, 148°18.14'W	2	2	1992-1996
1996-G	81°34.25'S, 148°35.85'W	2	2	1992-1996
1996-B	81°39.53'S, 148°48.72'W	4	2	1984-1996
1996-H	81°44.37'S, 148°58.61'W	2	2	1989-1996
1996-F	81°54.51'S, 149°20.22'W	2	2	1987-1996
1994-1	81°38.55'S, 148°46.36°W	4	2	1983-1994
1994-2	81°40.17'S, 149°00.42'W	2	2	1990-1994
1994-3	81°41.02'S, 149°11.15'W	2	2	1989-1994
1994-4	81°37.28'S, 148°26.02'W	2	2	1990-1994
1994-5	81°42.33'S, 148°36.17'W	2	2	1988-1994
1994-6	81°38.40'S, 148°46.46°W	1	1	1992-1994
IWA				
1995-A	78°44.00'S, 116°20.00'W	2	2	1992-1995
1995-B	79°27.66S 118°02.68'W	2	2	1991-1995
1995-C	80°00.85'S 119°33.73'W	2	2	1990-1995
Cores				
Siple Dome				
N50E50	81°41.02'S, 149°11.15'W	12	5	1952-1994
SDM 1994	81°38.55'S, 148°46.36°W	150	2	842-1994
S50E50	81°42.33'S, 148°36.17'W	9	5	1962-1994
IWA				
RIDSA	78.73°S 116.33°W	150	3	1506-1995
RIDSB	79.46°S 118.05°W	60	3	1690-1995
RIDSC	80.01°S 119.56°W	60	3	1594-1995

Table IV.1. Siple Dome and Inland West Antarctica (IWA) snowpit, firn and ice core location and sampling information.

	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	$SO_4^=$	MSA	Ion Balance
					96-B					
mean	7.15	0.15	0.19	1.69	0.32	9.04	0.58	2.21	0.22	-2.91
std. dev.	6.05	0.05	0.15	1.27	0.26	6.80	0.42	2.56	0.24	
median	5.57	0.14	0.14	1.33	0.25	7.33	0.47	1.21	0.13	
					96-E					
mean	6.32	0.12	0.16	1.44	0.24	7.73	0.70	2.28	0.34	-3.06
std. dev.	6.36	0.07	0.17	1.32	0.24	6.71	0.70	2.97	0.44	
median	4.13	0.10	0.10	1.04	0.17	5.34	0.53	0.88	0.13	
					96-F					
mean	7.52	0.17	0.19	1.66	0.31	9.54	0.77	2.88	0.10	-3.81
std. dev.	8.86	0.07	0.18	1.65	0.35	9.55	0.48	1.71	0.11	
median	5.11	0.16	0.14	1.13	0.21	7.28	0.76	2.47	0.07	
					96-G					
mean	7.58	0.12	0.18	1.77	0.33	9.73	0.69	2.67	0.37	-3.76
std. dev.	8.30	0.07	0.17	1.63	0.32	9.43	0.46	2.88	0.45	
median	5.42	0.10	0.14	1.29	0.24	7.77	0.60	1.22	0.13	
					96-H					
mean	5.88	0.13	0.15	1.36	0.25	7.46	0.72	2.54	0.25	-3.49
std. dev.	4.68	0.05	0.10	1.04	0.19	5.06	0.43	2.41	0.23	
median	4.49	0.13	0.12	1.06	0.17	6.11	0.72	1.46	0.17	

Table IV.2. Summary of the soluble ionic composition of snow from 1996 Siple Dome snowpits. All concentrations are in μeq/L.

	Na^+			NH_4^+			Ca^{2+}			K^+			NO_3^-			$SO_4^{=}$			MSA		
Siple Dome	N	S	A	N	S	A	N	S	A	N	S	A	N	S	A	N	S	A	N	S	A
Total Pit																					
F	2.23	1.37	1.83	2.24	2.01	2.12	2.15	1.83	2.05	2.29	2.81	1.95	1.11	1.17	1.69	0.42	2.28	0.93	1.04	0.69	1.36
P-value	0.06	0.26	0.09	0.08	0.10	0.09	0.07	0.12	0.05	0.06	0.04	0.06	0.35	0.32	0.10	0.80	0.06	0.50	0.38	0.50	0.24
1994																					
F	0.86	1.10	1.22	4.28	1.61	4.73	3.32	0.39	2.87	0.82	0.06	0.61	0.57	1.56	2.01	0.78	2.54	2.10	0.63	5.07	1.02
P-value	0.49	0.36	0.29	0.00	0.21	0.00	0.02	0.76	0.01	0.52	0.98	0.77	0.64	0.35	0.06	0.54	0.01	0.06	0.64	0.02	0.42
1993																					
F	1.90	0.07	1.57	2.07	4.51	4.91	2.30	5.63	3.04	1.59	4.32	3.23	0.15	0.30	0.20	0.50	1.09	0.66	0.59	1.36	0.89
P-value	0.12	0.93	0.15	0.09	0.02	0.00	0.08	0.00	0.01	0.20	0.02	0.03	0.96	0.82	0.99	0.73	0.36	0.73	0.67	0.27	0.52
1992																					
F	1.82	0.44	3.12	0.91	1.88	0.79	2.94	1.10	1.83	2.50	1.46	2.71	1.26	1.05	1.18	1.02	0.25	0.61	1.74	1.52	1.81
P-value	0.13	0.64	0.02	0.46	0.17	0.60	0.04	0.36	0.09	0.07	0.24	0.01	0.40	0.52	0.45	0.40	0.86	0.77	0.16	0.25	0.09
IWA																					
F		5.26			6.56			2.37			6.92			1.80			7.31			1.04	
P-value		0.00			0.00			0.09			0.00			0.17			0.00			0.35	

Table IV.3. Analysis of variance (ANOVA) results from Siple Dome and IWA snowpit data. Results from analysis of Cl and Mg are similar to Na, and are therefore not given. F values indicate the between group/within group variance ratio, and P values are probability estimates based on a one-sided t-test ($P>0.05$ is significant at 95% c.l.). For Siple Dome, data were grouped and analyzed for pits only on the North (N) and South (S) sides of the Siple Dome ice divide, and for all pits together (A).

	Na^+	NH_4^+	Ca^{2+}	K^+	NO_3^-	SO_4^{2-}
Siple Dome						
1994 Core vs. N50E50	**0.46**	0.03	**0.30**	**0.40**	**0.31**	**0.28**
1994 Core vs. S50E50	0.20	0.15	-0.01	0.17	**0.26**	**0.33**
N50E50 vs. S50E50	0.12	-0.10	-0.14	-0.15	**0.31**	**0.28**
IWA						
RIDSA vs. RIDSB	-0.10	-0.20	0.01	0.18	-0.27	**-0.33**
RIDSA vs. RIDSC	-0.08	0.02	-0.18	-0.11	-0.06	**0.34**
RIDSB vs. RIDSC	**0.26**	**0.37**	**0.29**	0.16	**0.26**	**-0.26**

Table IV.4. Correlation coefficients for core chemistry records (1963-1994). Significant values (95% c.l.) are in bold.

Species	*r value North (n=25)*	*r value South (n=36)*	*r value Total (n=61)*
Na^+	0.10	0.23	0.15
NH_4^+	-0.14	0.22	0.06
K^+	0.15	0.22	0.16
Mg^{2+}	0.13	0.23	0.16
Ca^{2+}	0.17	0.22	0.17
Cl^-	0.11	0.19	0.13
NO_3^-	0.06	**-0.33**	-0.15
$SO^{4=}$	0.20	0.01	0.07
MSA	0.20	0.01	0.07

Table IV.5. Regression statistics for mean annual species concentration and mean annual accumulation rate in Siple Dome snowpits. Significant values (95% c.l.) are in bold.

Siple Dome

	Eigenvector Components			% Variance Explained		
Species	EOF1	EOF2	EOF3	EOF1	EOF2	EOF3
Na^+	0.98	-0.63	0.08	95.6	0.4	0.7
Cl^-	0.91	-0.30	-0.05	83.5	8.9	0.3
Mg^{2+}	0.97	-0.15	-0.01	94.4	2.2	0.2
Ca^{2+}	0.94	-0.06	0.19	89.1	0.4	3.4
K^+	0.96	-0.01	0.18	92.5	0.0	3.1
NH_4^+	0.44	0.66	-0.01	19.1	43.6	0.1
NO_3^-	-0.16	0.88	-0.09	2.6	77.7	0.9
SO_4^{2-}	0.29	0.89	-0.01	8.9	78.3	0.0
MSA	0.22	0.79	0.03	5.0	62.8	0.1
H_2O	-0.42	0.08	0.90	17.7	0.6	80.9
			Total	41.2	13.4	11.1

RIDS95A

	Eigenvector Components			% Variance Explained		
Species	EOF1	EOF2	EOF3	EOF1	EOF2	EOF3
Na^+	0.97	-0.02	-0.03	94.3	0.1	0.1
Cl^-	0.97	-0.01	-0.01	94.5	0.0	0.0
Mg^{2+}	0.97	-0.03	-0.01	93.7	0.1	0.0
Ca^{2+}	0.61	0.05	-0.19	36.6	0.3	3.7
K^+	0.82	-0.08	0.19	66.7	0.6	3.6
NH_4^+	0.45	0.24	0.41	20.6	5.9	16.5
NO_3^-	-0.23	0.79	-0.01	5.1	63.9	0.0
SO_4^{2-}	0.13	0.80	0.05	1.6	63.1	0.3
MSA	-0.02	0.79	0.28	0.1	61.8	7.7
H_2O	-0.20	-0.39	0.84	3.9	15.1	70.9
			Total	41.7	21.1	10.3

RIDS95B

	Eigenvector Components			% Variance Explained		
Species	EOF1	EOF2	EOF3	EOF1	EOF2	EOF3
Na^+	0.97	0.06	-0.02	95.2	0.4	0.1
Cl^-	0.97	0.09	-0.01	93.7	0.8	0.0
Mg^{2+}	0.98	0.00	-0.01	95.7	0.0	0.0
Ca^{2+}	0.96	0.13	0.00	92.9	1.6	0.0
K^+	0.67	0.30	0.00	45.2	9.2	0.0
NH_4^+	0.58	0.06	0.10	33.6	0.4	1.1
NO_3^-	-0.38	0.84	0.18	14.5	71.1	3.4
SO_4^{2-}	-0.16	0.92	0.20	2.7	85.2	4.1
H_2O	0.09	-0.38	0.92	1.0	14.3	83.8
			Total	52.7	20.3	10.3

RIDS95C

	Eigenvector Components			% Variance Explained		
Species	EOF1	EOF2	EOF3	EOF1	EOF2	EOF3
Na^+	0.98	0.13	-0.06	96.7	1.7	0.4
Cl^-	0.97	0.14	-0.12	94.6	2.1	1.3
Mg^{2+}	0.98	0.10	-0.08	97.2	1.0	0.6
Ca^{2+}	0.95	0.00	-0.04	86.3	0.0	0.2
K^+	0.93	0.20	-0.20	86.3	4.1	4.1
NH_4^+	0.52	-0.54	-0.15	27.2	29.6	2.2
NO_3^-	0.44	-0.51	0.57	20.0	25.6	32.9
SO_4^{2-}	0.51	-0.46	0.25	25.9	21.3	6.5
H_2O	0.28	0.64	0.62	8.1	41.9	38.5
			Total	60.6	14.2	9.7

Table IV.6. Joint empirical orthogonal function analysis of annual chemical and accumulation rate time-series for the period 1962-1994 in Siple Dome and Inland West Antarctica cores.

Location	Position Relative to Local Ice Divide (km)	Dating Method	Mean Accumulation Rate ($g/m^2/yr$)
Siple Dome			
N50E50 Core	5	β, chemistry	14.5
1994 Core	0.7	β, chemistry	12.5
S50E50 Core	-5	β, chemistry	11.6
Pit 96-E	30	chemistry	18.2
Pit 96-G	10	chemistry	17.3
Pit 94-2	5	chemistry	18.3
Pit 96-B	-0.5	chemistry	12.2
Pit 94-3	-5	chemistry	13.7
Pit 96-H	-10	chemistry	11.4
Pit 96-F	-30	chemistry	9.5
IWA			
RIDSA	-20	β, chemistry	23.7
RIDSB	-110	chemsitry	14.8
RIDSC	-180	β, chemistry	11.1

Table IV.7. Mean accumulation rate estimates for Siple Dome and Inland West Antarctic sites. Note that estimates from Siple Dome snowpits represent 4-10 years of deposition (1984-1994), whereas core estimates are for the period 1964-1994.

V. POST-DEPOSITIONAL PROCESSES IN WEST ANTARCTIC GLACIOCHEMICAL RECORDS

Section V has been accepted for publication in Annals of Glaciology (full citation appears in the Complete List of References)

V. POST-DEPOSITIONAL PROCESSES IN WEST ANTARCTIC GLACIOCHEMICAL RECORDS

ABSTRACT

High-resolution (>10 samples/year) glaciochemical analyses covering the last 110 years from a Siple Dome, Antarctica, ice core reveal limited migration of certain soluble ionic species (methanesulfonate [MSA], NO_3^-, and Mg^{2+}). The observed chemical migration may be due in part to seasonal alternation between less acidic winter (from high seasalt concentrations) and more acidic summer (from high marine biogenic acid concentrations) layers, common at coastal sites such as Siple Dome. Exact mechanisms to explain the migration are unclear, although simple diffusion and gravitational movement are unlikely as new peaks are formed where none previously existed in each case. Initial migration of each species is both shallower and earlier at Siple Dome than at other sites in Antarctica where similar phenomena have been observed, which may be related to the relatively low accumulation rate at Siple Dome (~11 $g/cm^2/yr$). Migration appears to be limited to either the preceding or following seasonal layer for each species, suggesting that paleoclimatic interpretations based on data with lower than annual resolution are not likely to be affected.

INTRODUCTION

Obtaining paleoatmospheric information on both regional and global scales is a key objective in ice-core research. The basis for such reconstructions is the fact that concentrations of chemical species found in snow and ice are determined in part by the atmospheric concentrations of those species, and additionally by depositional and post-depositional processes. For certain soluble species (i.e., non-volatile seasalt and crustally-derived ions), reconstruction of relative changes in paleoatmospheric concentrations is possible because post-depositional changes are negligible. For other species, such as NO_3^- and H_2O_2, both depositional and post-depositional processes in snow and ice can alter preserved concentrations of certain species, making interpretation of past atmospheric concentrations more difficult (Dibb, 1996). Post-depositional processes in most cases do not significantly alter long-term average concentrations, but can affect short-term (i.e., sub-annual scale) fluctuations as well as the amplitude and timing of chemical signal seasonality (Wolff, 1996).

An example of such a process is the recently observed post-depositional migration of methanesulfonate (MSA), an oxidation product of marine biogenically-produced dimethylsulfide (Wolff, 1996). A shift from summer (near the surface) to apparent winter (below ~5-10 m depth) MSA deposition has been observed in Antarctic ice cores from Dolleman Island (Mulvaney et al., 1992), Byrd Station (Langway et al., 1994), the Filchner-Ronne Ice Shelf (Minikin et al., 1994), and Berkner Island (Wagenbach et al., 1994). Because a change in the seasonal production and deposition of MSA is not likely (Mulvaney et al., 1992), migration of MSA relative to excess (xs) SO_4^{2-} (which continues to peak during $\delta^{18}O$ maxima in the Dolleman Island core, and is therefore assumed to remain in place after summer deposition) is thought to have occurred. Interpretation of MSA/xsSO_4^{2-} molar ratios (R) at these sites, especially where high resolution sampling is performed (>5 samples/year), can be seriously complicated by post-depositional migration of MSA (Mulvaney et al., 1992). This phenomenon, however, has not yet been documented at enough sites to provide a clear spatial understanding of where and under what conditions it occurs.

Like MSA, post-depositional processes are known to affect NO_3^- concentrations in snow and ice. There is compelling evidence for HNO_3 loss in surface snow at low-accumulation rate sites (Mayewski and Legrand, 1990; Dibb and Whitlow, 1996), possibly through photochemical degradation or degassing (Neubauer and Heumann, 1988). Diffusive smoothing of seasonal NO_3^- patterns in firn has also been noted (Wolff, 1996). Further, NO_3^- depletion has been observed in ice layers impacted by deposition of volcanically-derived acids (mainly H_2SO_4) (Laj et al., 1993; Yang et al., 1996). While it is possible that changes in the atmospheric nitrogen cycle are responsible for decreased NO_3^- deposition during volcanic eruptions, an alternate explanation involves post-depositional migration of NO_3^- from the highly acidic volcanic ice layers (Wolff, 1996). Clearly, the behavior of NO_3^- in acidic firn and ice layers needs to be understood so that proper interpretations of glaciochemical data can be made.

Chemical species derived from seasalt aerosols (viz., Na^+, Cl^-, Mg^{2+}, K^+, Ca^{2+}), which can be used as proxy indicators of past atmospheric circulation strength (e.g., Mayewski et al., 1994), are considered to be conservative, non-reactive, and therefore fixed in place after deposition in most locations. Wolff (1996), however, demonstrated that Mg^{2+} concentrations peak on either side of Na^+ winter maxima in the Dolleman Island ice core, causing disruption in standard Mg^{2+}/Na^+ marine ratios. Although the migration of Mg^{2+} in the Dolleman Island core was confined within the same annual layer, paleo-atmospheric circulation reconstructions based on multivariate statistical techniques (e.g., Mayewski et al., 1994) could potentially be affected by such migration. The problem may be enhanced

in ice age ice (in both Antarctica and Greenland), where seasalt concentrations can be ~30-40 times higher than modern values (Palais and Legrand, 1985). Dolleman Island is the only location so far where this phenomenon has been observed, therefore a more thorough investigation of the problem is needed to determine under what conditions it occurs.

In this paper, we present results from a Siple Dome, Antarctica (81.65°S 148.81°W; Fig. V.1) ice core glaciochemical record and investigate migration of the soluble chemical species described above. Compared to other sites where similar ion migration phenomena have been observed, Siple Dome is unique due to its high seasalt and marine biogenic acid concentrations and relatively low accumulation rate (~11 cm ice/yr; Kreutz et al., 1997). One result of these physical characteristics is a seasonal alternation between deposition of more acidic summer layers (H_2SO_4, HNO_3, MSA) and less acidic winter layers (seasalt). Because both seasalt concentrations and accumulation rate have been suggested as possible controls on species migration (Wolff, 1996), Siple Dome provides an ideal location to investigate these processes.

METHODS

During the 1994/95 field season, a 150 m core was drilled ~3 km NNE of the summit of Siple Dome (10 m temperature= -25°C; Mayewski et al., 1995; Fig. V.1). In addition, 5 snowpits were sampled in November 1994; a 4 m pit at the drillsite, and 2 m pits at each corner of a 10 km x 10 km surveyed grid centered at the drillsite (Fig. V.1). Snowpit sampling and ice core collection was performed by workers wearing non-particulating suits, polyethylene gloves, and particle masks. A 2 cm interval was used in snowpit sampling.

Core samples were processed in a cold room at temperatures not exceeding -12°C, by individuals wearing precleaned polyethylene gloves and particle masks. All tools and containers used were thoroughly precleaned using ultrapure water. The upper 2 m of core were not processed due to poor core quality. As there is reasonable agreement between chemistry data from 2-4 m depth in the core and the 4 m coresite snowpit, the upper 2 m of Pit 1 are used to create a continuous 24 m core record. Blanks of frozen ultrapure water prepared at frequent intervals indicate that sample containers and techniques were free of contamination. Analysis of major cations (Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}), anions (Cl^-, NO_3^-, SO_4^{2-}), and MSA in core and snowpit samples was performed at the University of New Hampshire using Dionex 4000 series instruments. Cations were analyzed via suppressed chromatography with a Dionex CS12 column, 125 µl loop, and 20 m*M* MSA eluent. Anions were analyzed with a Dionex AS11 column, 75 µl loop, and 6m*M* NaOH

eluent. MSA measurements were made with an AS11 column, 1.5 ml loop, and 0.5m*M* NaOH eluent.

Core and snowpit records were dated using well-preserved annual chemical signals in both discrete and continuous melter sampling (notably $xsSO_4^{2-}$ [see below] and Cl^-), beta radioactivity profiles, snowpit and core stratigraphy, and volcanic marker horizons (Mayewski et al., 1995; Kreutz et al., 1997). Based on the depth/age scale developed for the core, the 1150-year average accumulation rate is ~11.5 cm ice/yr. The upper 24 m of the core was sampled at 2 cm intervals to provide a high resolution (at least 8 samples/year) glaciochemical record of the past 110 years.

Calculation of seasalt (ss) and nonseasalt (or excess[xs]) portions of chemical species in Siple Dome snowpit and core samples is based on bulk seawater ratios according to the formula (Delmas, 1992):

$$\text{excess} = \text{total} - (Na^+ * k)$$

Na^+ is used as the reference species as it was found to be the most conservative seasalt element at Siple Dome (Kreutz et al., 1997). Using a k value which reflects bulk seawater $[SO_4^{2-}]/[Na^+]$ mass ratio (0.252), calculations for winter snow and firn samples often lead to negative $xsSO_4^{2-}$ estimates at Siple Dome and other Antarctic coastal sites (Wagenbach et al., 1988; Gjessing, 1989; Mulvaney et al., 1992; Minikin et al., 1994). The deficit suggests that fractionation must be occurring between bulk seawater and seasalt aerosol during parts of the year, but how such fractionation occurs is unclear. One possibility (Ducroz, 1996) is precipitation of Na_2SO_4 in seawater below 8°C, resulting in a brine solution that is depleted in SO_4^{2-} (the relative depletion of Na^+ would be negligible since it is present in much higher concentrations). To correct for this problem, winter layers were separated for each snowpit and the upper 6 m of core. SO_4^{2-} and Na^+ were plotted to calculate the slope (k). Our results (Table V.1) are similar to those obtained at other Antarctic sites. Therefore, we have used a k value of 0.1 to calculate Siple Dome snowpit and ice core $xsSO_4^{2-}$ values. Because there is no evidence for SO_4^{2-} fractionation during summer months, and our calculation is not seasonally dependent, summer $xsSO_4^{2-}$ values may be overestimated in some cases.

RESULTS AND DISCUSSION

MSA

MSA and $xsSO_4^{2-}$ concentrations from the upper 2 m of the Siple Dome core are presented in Figure V.2. The two species are in phase through the upper 1.5 m (approximately 3.5 years). In addition, the last 3 years of MSA and $xsSO_4^{2-}$ maxima

correspond with summer δD peaks. These findings are consistent with aerosol measurements at Neumayer Station, which are well correlated with the annual DMS cycle measured at the sub-Antarctic Macquairie Island (Gillet et al., 1993), suggesting that the three are directly related (Wagenbach, 1996). Likewise, $xsSO_4^{2-}$ and MSA concentrations in surface snow from coastal locations (Filchner-Ronne Ice Shelf [Minikin et al., 1994]) and inland (South Pole [Whitlow et al., 1992]; Dronning Maud Land [Osada, 1994]) locations demonstrate strong seasonal signals that both peak in the summer. The $xsSO_4^{2-}$/MSA relationship observed in the upper 1.5 m of the core (coeval existence in the first 3.5 years; not in depth due to small differences in accumulation rate between the north and south sides of the Siple Dome ice divide) is consistent in all Siple Dome snowpits collected in 1994 (Fig. V.1).

Below 1.5 m in the core, MSA peaks occur slightly before (deeper) than $xsSO_4^{2-}$ peaks (Fig. V.3). As previously discussed, we assume that this represents post-depositional migration of MSA and not a significant shift in deposition timing. This pattern (the first sign of MSA migration after the first 3 years) is spatially consistent over the 10 km x 10 km grid on which 6 snowpits were collected (Fig. V.1). Apparent initial migration of MSA at Siple Dome after 3 years is earlier than at Dolleman Island (4.4 m, or ~5 years; Mulvaney et al., 1992), Byrd Station (4.6 m, or ~13 years; Langway et al., 1994), Berkner Island (3.5 m, or ~12 years; Wagenbach et al., 1994), and the Filchner-Ronne Ice Shelf (1.8 m, or ~8 years; Minikin et al., 1994).

Deeper in the core, MSA and $xsSO_4^{2-}$ peaks are clearly out of phase (Fig. V.3). Specifically, below 2 m depth (selected 2m sections of the core are presented in Fig. V.3), there is no place where MSA and $xsSO_4^{2-}$ are in phase. This situation is unlike Dolleman Island and Byrd Station cores, which contain a transition zone where the MSA/$xsSO_4^{2-}$ relationship is both in and out of phase. At Siple Dome, MSA migration appears to occur early and without a transition zone. At least one MSA peak exists between each $xsSO_4^{2-}$ peak, suggesting that the distance of MSA migration must be limited to one season.

Composite mean annual chemical cycles from different depths in the core (Fig. V.4) also indicate MSA migration. Values of $xsSO_4^{2-}$ consistently peak during the austral summer in three different core sections. MSA values also indicate peak values during summer months in upper core samples. In the two lower sections, however, MSA values clearly have shifted to winter peaks. The apparent decrease in amplitude may be a function of fewer samples per year deeper in the core, and also the possible role of the prolonged early 1990's El-Ninó-Southern Oscillation (ENSO) event (Trenberth and Hoar, 1996) in producing very high MSA values in surface snow (~1991-1994). Although the reduction in amplitude would suggest diffusive smoothing of MSA, peak shapes appear to remain

sharp and well-defined throughout the upper 24 m (Fig. V.3) and therefore the amount of diffusive smoothing must be limited.

NO_3^-

NO_3^- concentrations from the upper 2 m of the Siple Dome core are presented in Figure V.2. Peak values of NO_3^- occur on the rising limb of δD cycles and slightly earlier than $xsSO_4^{2-}$ peaks (Fig. V.2), suggesting that NO_3^- deposition occurs during late spring when the polar vortex initially breaks down. This is consistent with other observations of the annual NO_3^-cycle in Antarctic surface snow and air (Mayewski and Legrand, 1990; Savoie et al., 1992; Whitlow et al., 1992; Mulvaney and Wolff, 1993; Minikin et al., 1994; Osada, 1994; Wagenbach, 1996). This pattern (no apparent movement of NO_3^- relative to $xsSO_4^{2-}$ in the upper 2m) is spatially consistent over the 10 km x 10 km grid on which 5 snowpits were collected. Unlike very low accumulation rate sites (i.e., South Pole, Vostok), there is no indication of significant NO_3^- depletion in buried snow layers due to post-depositional degassing of NO_3^- at Siple Dome (Fig. V.2).

NO_3^- concentrations are plotted vs. $xsSO_4^{2-}$ (summer indicator) for selected core sections in Fig. V.5. NO_3^- concentrations consistently peak slightly earlier than $xsSO_4^{2-}$ to a depth of 8.5 m. In the 8.5-10 m section, the phase $NO_3^-/xsSO_4^{2-}$ relationship becomes confused. Below 10 m (10-12 m), it appears that NO_3^- has migrated into the winter layer in some places, but is still in phase with $xsSO_4^{2-}$ in other places. By 14-16 m, NO_3^- has clearly moved into winter layers during every annual cycle. Likewise, in the 18-20 m section, NO_3^- and $xsSO_4^{2-}$ are anticorrelated. In each core section, there is at least one NO_3^- peak for every $xsSO_4^{2-}$ peak, suggesting that the distance of NO_3^- migration must be limited to one season.

Composite mean annual NO_3^- values (Fig. V.4) indicate summer peaks in upper core samples. In 1960-68 samples, there is still indication of summer NO_3^- peaks, although the signal is much less pronounced than during 1988-1994. In 1910-1922 samples, NO_3^- values have shifted to winter peaks. There appears to be some loss of signal amplitude with increasing depth, which may be related to sampling resolution and/or diffusive smoothing. The amount of diffusive smoothing occurring must be limited, as NO_3^- peaks retain a sharp character throughout the entire 24 m of detailed core data (Fig. V.5).

Mg^{2+}

Mg^{2+} concentrations in the upper 2 m of the Siple Dome ice core are presented in Fig. V.2. Mg^{2+} and Na^+ are well correlated (and in the ss ratio), suggesting that the majority of Mg^{2+} at Siple Dome is derived from seasalt aerosol (Fig. V.3). Peaks in Mg^{2+} and Na^+

generally occur during δD minima, indicating the majority of seasalt is deposited during the winter. Aerosol measurements at Antarctic coastal (Neumayer [Wagenbach, 1996] and Mawson [Savoie et al., 1992]) and inland (South Pole [Tuncel et al., 1989]) stations, as well as surface snow measurements (Whitlow et al., 1992; Osada, 1994) also reveal a seasonal cycle in seasalt which peaks in the winter season. However, short-term seasalt increases have also been observed throughout the year at Mawson and Neumayer Stations, and are linked to local storm activity (Wagenbach, 1996). A similar situation is observed at Siple Dome, where input of seasalt occasionally occurs during summer (i.e., 1992, 1993). Because the seasalt cycle is out of phase with seasonal sea ice fluctuations, transport of seasalt aerosols during the winter season is most likely by rapid long-range advection from large open water areas as well as from local polynias opened by heavy storm winds (Wagenbach, 1996). The correlation between Na^+ and Mg^{2+} is consistent in the top 2 m of other Siple Dome snowpits (Fig. V.1).

The first indication of Mg^{2+} migration (relative to Na^+) occurs at 9.65 m depth in the core, and continues to occur throughout the remaining 14 m of detailed data (Fig. V.6). As in the Dolleman Island core (Wolff, 1996), migration of Mg^{2+} is characterized by Mg^{2+} peaks forming on either side of a Na^+ peak. The first indication of Mg^{2+} migration at Dolleman Island occurs below about 10 m (Wolff, 1996). Therefore, comparison of the problem in the two cores suggests that Mg^{2+} migration begins at a similar depth, but at different times (~33 years at Siple Dome; ~13 years at Dolleman Island). The lowest Na^+ concentration where Mg^{2+} migration occurs at Siple Dome appears to be ~15 μeq/l. Nearly every (but not all) Na^+ peak above 15 μeq/l has Mg^{2+} peaks formed on either side. Based on limited data (39.6-42.5 m), a similar Na^+ threshold exists at Dolleman Island (Wolff, 1996).

Comparison of mean annual Mg^{2+} and Na^+ cycles (Fig. V.4) indicates coeval winter peaks in upper core samples. In 1960-68 samples, there is still an identifiable winter Mg^{2+} peak, however it is weaker than the upper core portion. In 1910-1922 samples, Mg^{2+} is clearly peaking in the summer. This 2 m section of core (18-20 m; Fig. V.6) contains a number of Mg^{2+} peaks that are directly out of phase with Na^+. There is no apparent reduction in Mg^{2+} peak amplitude, and Mg^{2+} peaks retain a sharp character throughout all 24 m of high-resolution samples.

Possible Mechanisms for Species Migration

Because summer ($xsSO_4^{2-}$, NO_3^- and MSA) and seasalt (Na^+ and Mg^{2+}) species are deposited in phase in the upper portion of the core, we assume that the change in species relationship noted deeper in the core results from post-depositional migration and not a

change in deposition timing. Several different mechanisms could be responsible for the observed migration: 1) diffusion (both vapor phase and within solid ice), 2) gravitational movement, 3) interactions within and outside the ice lattice, 4) migration associated with strongly acidic layers (i.e. volcanic), and 5) formation of insoluble salts (Wolff, 1996).

For MSA, migration may be in the up-core direction where it is first noted (1.5-2 m depth). This would rule out gravitational movement. Likewise, simple diffusion is not likely, as peak shapes near the bottom of the detailed 24 m core section are still sharply defined, and new peaks have been formed where none previously existed. Wolff (1996) has speculated that MSA may form an insoluble salt with one of the seasalt cations, which would then allow continued diffusion as the insoluble salt is a different species and would maintain the gradient. This process would effectively deplete the original peak, and form a new one in the seasalt peak area, similar to what is observed at Siple Dome. Assessing the feasibility of this process is limited by little information on the low-temperature solubility of MSA salts (Wolff, 1996). In addition, the freezing point of Na^+ or Mg^{2+} salts of MSA may be above the temperature of the ice, effectively removing MSA from the liquid phase. Again, there is little information on freezing point curves for Na^+ or Mg^{2+} salts of MSA (Mulvaney et al., 1992). As the most pronounced MSA migration has been noted at sites with high seasalt concentrations (Dolleman Island, Filchner-Ronne Ice Shelf, Siple Dome), it is imperative to understand the reactions between MSA and seasalts to determine if this is the main cause of migration. Another possibility is that MSA is located within veins at a eutectic composition, and therefore could move across an apparent gradient in bulk composition (Mulvaney et al., 1992). Eutectic compositions of strong acids commonly freeze below 0°C, with many remaining liquid at well below the temperature of Antarctic ice. This explanation, however, may not be effective in firn where ice grains have not compacted to form a completely interlinked network of veins, as may be the case in the upper 24 m of the Siple Dome core.

High summer biogenic SO_4^{2-} concentrations in Siple Dome summer layers appear to have a significant effect on NO_3^- concentrations. The average summer SO_4^{2-} maxima in the upper 24 m (6.10 μeq/l) of the Siple Dome core is greater than all but the largest volcanic SO_4^{2-} spikes (e.g., Tambora and 1259 AD events) recorded in Antarctic (Dai et al., 1991; Delmas et al., 1992; Langway et al., 1995) and Greenland ice cores (Laj et al., 1993) over the last 1000 years. NO_3^- migration from summer to winter layers is also seen (but not commented on) in Berkner Island (Wagenbach et al., 1994) and Filchner-Ronne Ice Shelf ice cores (Minikin et al., 1994), coastal sites with comparable seasonal SO_4^{2-} amplitudes as Siple Dome. At all three locations, NO_3^- migration appears to be limited to either the preceding or following winter layer, with peaks forming where none previously

existed. Therefore, like MSA, migration of NO_3^- appears to be limited by winter layers with high seasalt concentrations. Mechanisms to explain this phenomenon have not been studied in detail, but may include decreased sticking probability of the HNO_3 molecule due to increased acidity (Laj et al., 1993). Constant NO_3^- migration (e.g., occurring every year below a certain depth) may be limited to coastal sites where there is an alternation between more acidic summer and less acidic winter layers. Although we can provide no definite cause for NO_3^- migration, it is clear that NO_3^- migration from volcanic layers cannot be ignored when making interpretation of changes in nitrogen atmospheric chemistry during volcanic periods.

The only other ice core location where Mg^{2+} movement has been observed is Dolleman Island, where, like Siple Dome, seasalt concentrations are high (Dolleman Island: ~12.6 μeq/l Na^+, ~3.0 μeq/l Mg^{2+} [Mulvaney et al., 1992]; Siple Dome: ~7.1 μeq/l Na^+, ~2.1 μeq/l Mg^{2+}). Formation of two distinct peaks on either side of a Na^+ peak rules out simple diffusion, which would tend to smooth the record, and gravitational movement of a grain-boundary liquid. Wolff (1996) has suggested that there may be a limited number of cation sites on grain boundaries, and that as the grain grows and surface area decreases, the number of sites may decrease. As seasalt particles (initially present as discrete particles) slowly dissolve, Na^+ may preferentially occupy external sites, while Mg^{2+} is driven away from the high Na^+ and Cl^- region (Wolff, 1996). This mechanism is speculative, and more work on this problem is clearly needed.

Implications for Core Interpretation

Migration of all three species discussed here appears to be limited to either the preceding or following seasonal layer. In the case of MSA and NO_3^-, migration is essentially stopped by the high concentration of seasalt in the winter layer. A similar pattern is observed for MSA at Dolleman Island, where migration continued at least until pore close-off, but never went farther than one year (i.e. into the trough of the previous or following summer). In fact, deeper in the Dolleman Island core, MSA peaks became sharper, and summers became more and more depleted (Wolff, 1996). The maximum extent of Mg^{2+} migration appears to be one season, as with MSA and NO_3^-. In most cases, Mg^{2+} appears to migrate only to the shoulders of Na^+ peaks. Therefore, we would expect that interpretations based on data of greater than annual resolution will not be affected by Mg^{2+} migration.

To fully understand the observed chemical migration phenomena, two approaches are likely needed. First, continued collection of samples from a wide variety of locations in Antarctica (such as those planned as part of the International Trans-Antarctic Scientific Expedition [ITASE, 1996]) will provide a more detailed spatial picture of conditions under

which these phenomena occur. Second, laboratory experiments are needed to investigate the small-scale interactions of chemical species and ice. For example, information on the exact location of impurities within the ice lattice and vapor pressure effects would be useful in investigating species migration. While our results suggest that species migration is limited to less than one annual layer, an ultimate goal of ice-core paleoclimatic reconstructions is to make interpretations on sub-annual scales. To do so with long time-series ice core glaciochemical records in areas where species migration occurs, our understanding of these problems must improve.

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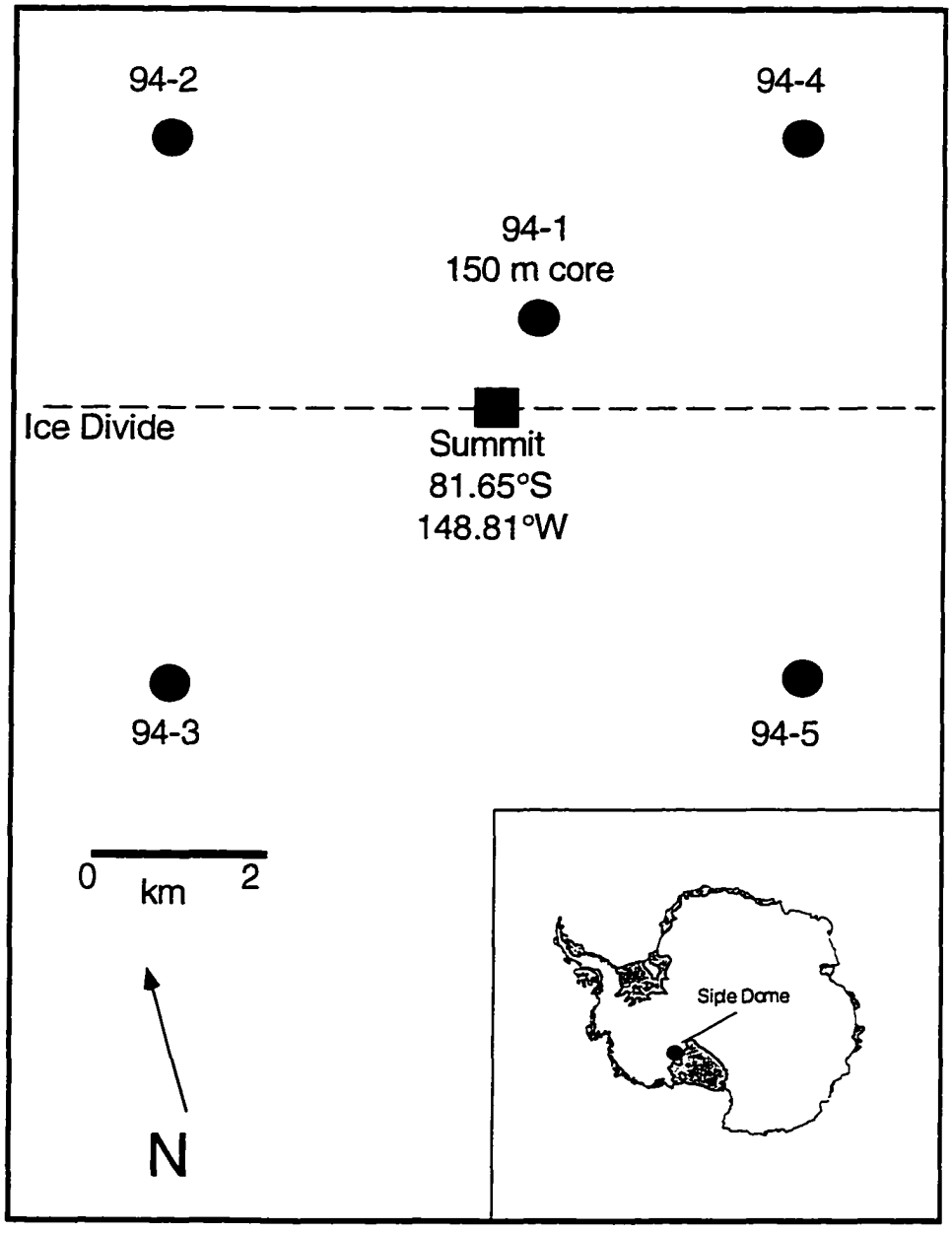

Figure V.1. Location map of 1994 sampling sites on Siple Dome, Antarctica. Pit 94-1 was sampled to 4 m depth, while pits 94-2, 94-3, 94-4, and 94-5 were sampled to 2 m depth. Elevation of the Siple Dome summit is 621 m.

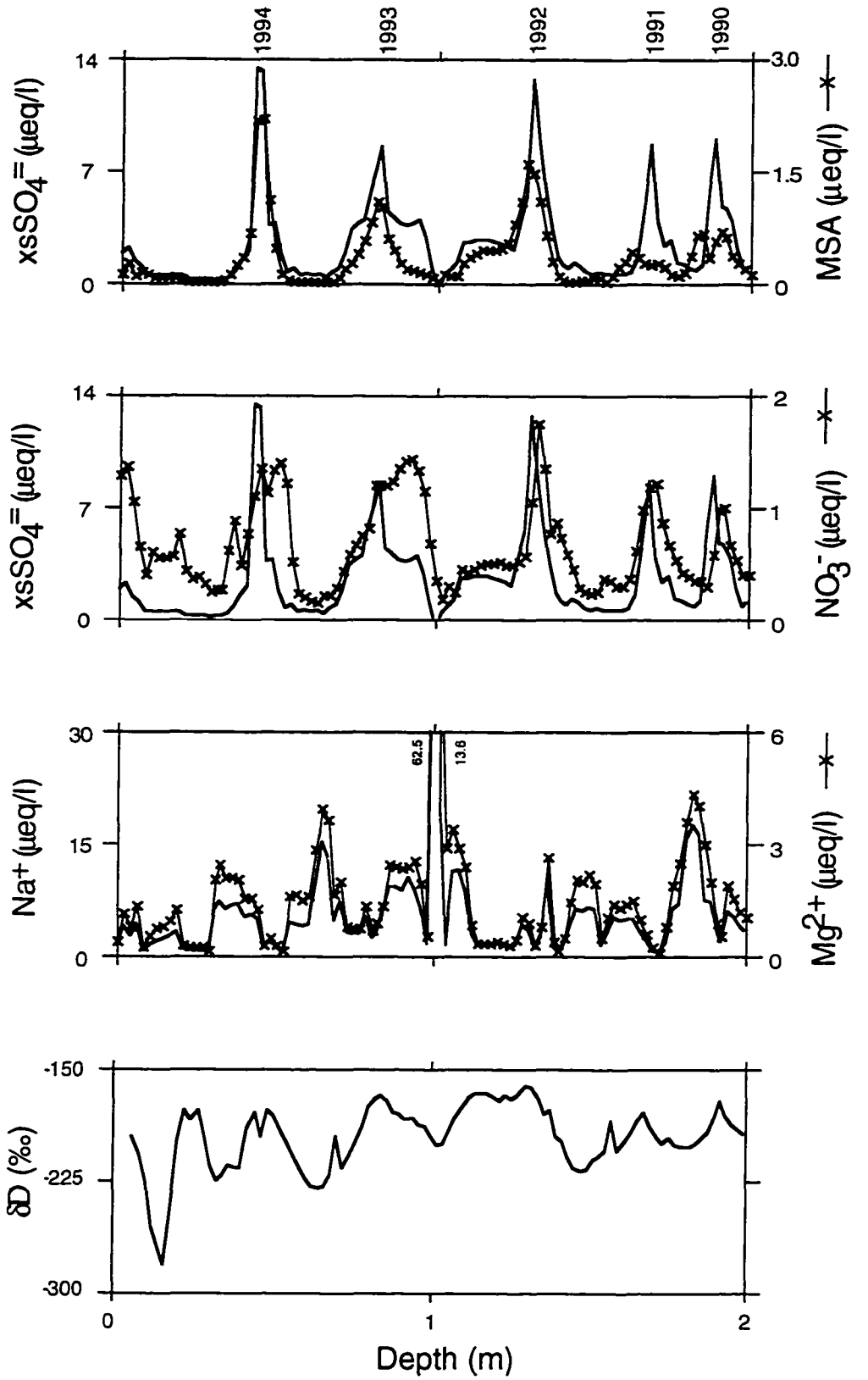

Figure V.2. Glaciochemical and isotopic concentrations in samples (2 cm sample interval) from the upper 2 m of Siple Dome surface snow. Approximately 5.5 years of snow deposition are contained in the 2 m section. Dates above each plot represent January 1 of that year.

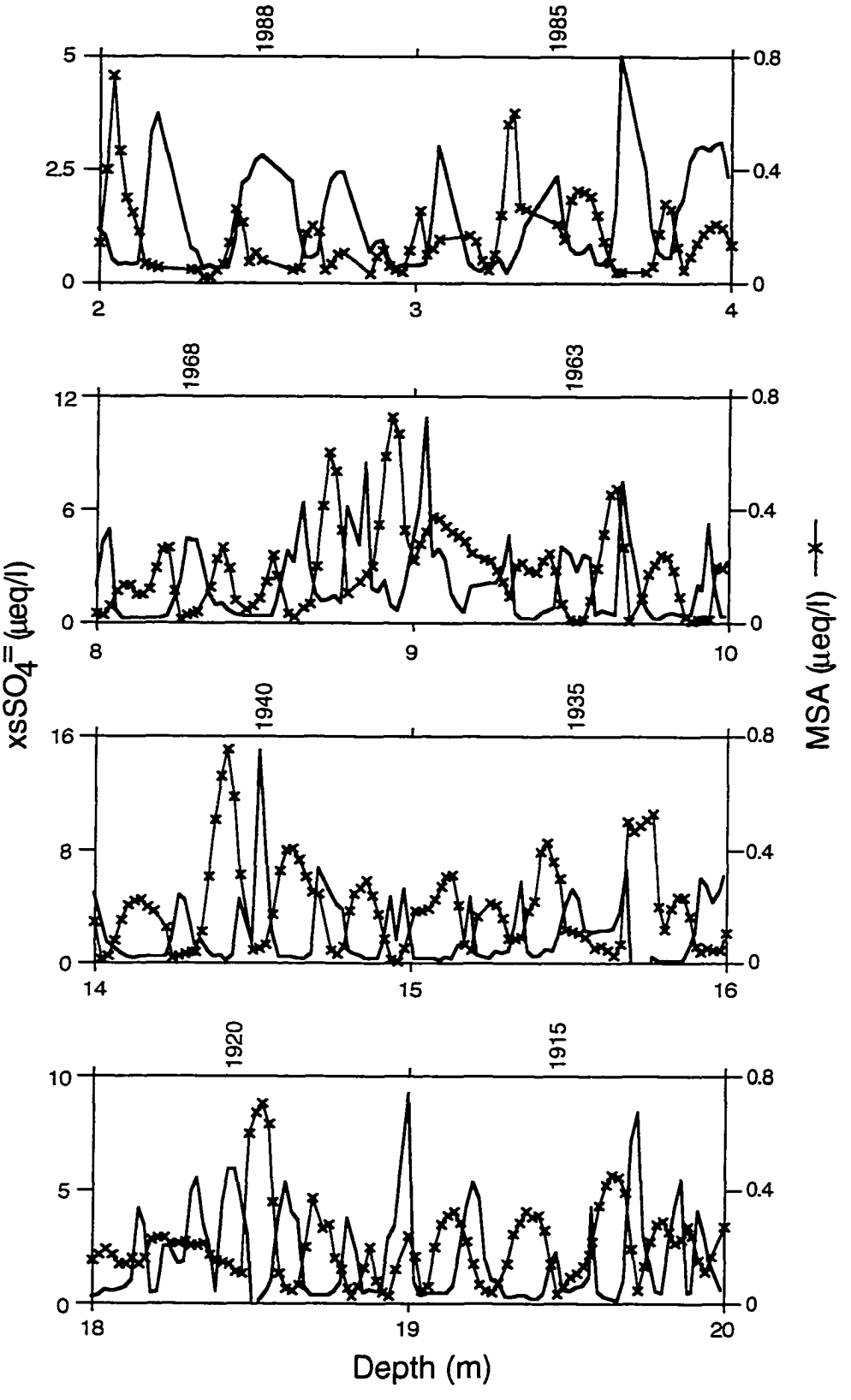

Figure V.3. $xsSO_4^{2-}$ and MSA concentations in samples (2 cm sample interval) from four sections of the Siple Dome ice core. Corresponding dates are given above each plot.

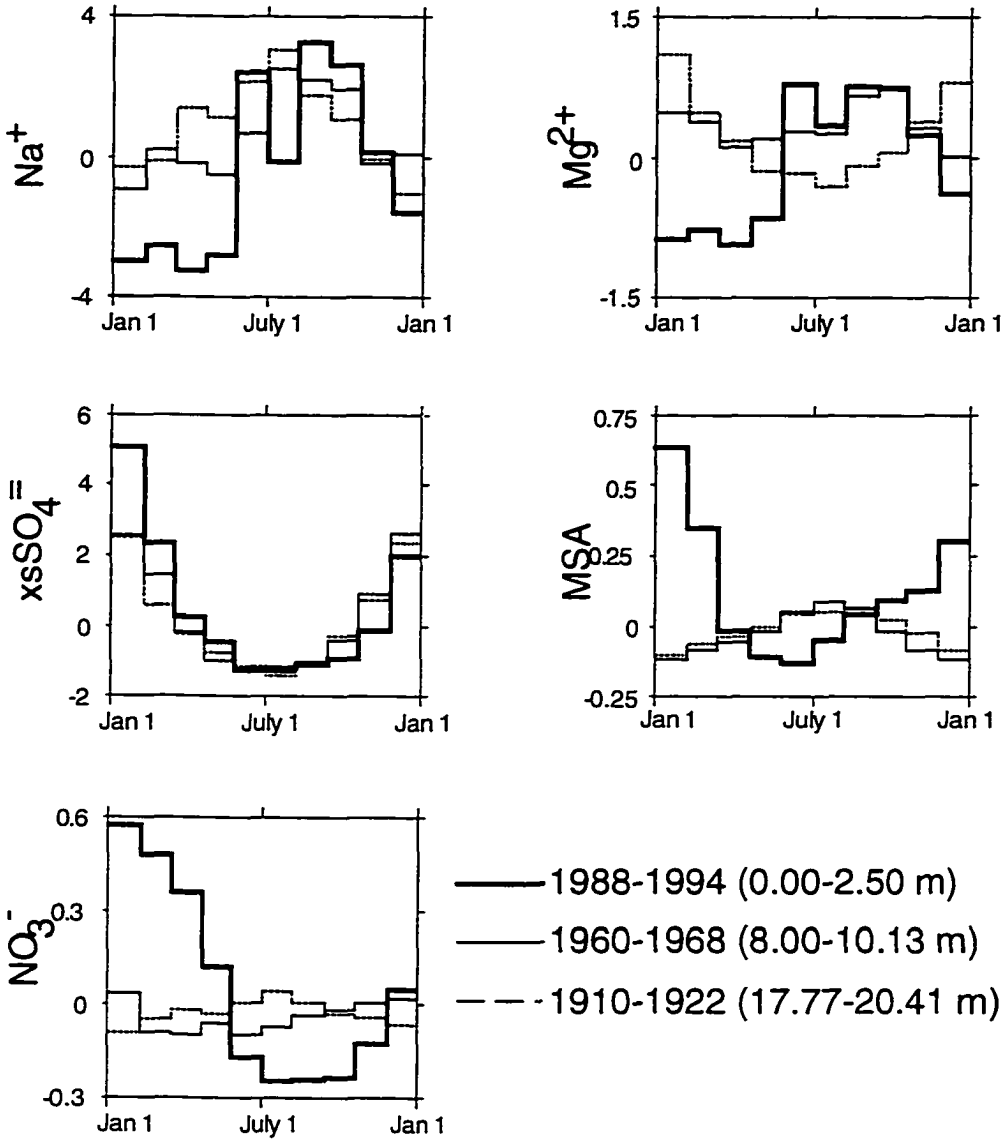

Figure V.4. Mean annual cycles of Na^+, Mg^{2+}, $xsSO_4^{2-}$, MSA, NO_3^- in the upper 24m of the Siple Dome core. Concentration values are given as deviations from the 110-year mean of each species. The thick line corresponds to the near-surface depth interval, which overlaps snowpit samples and the time interval (1988-1994) of the prolonged early 1990's ENSO event, and contains the interval where MSA migration is first noted. The thin line represents the interval where NO_3^- migration is first noted, and the thin dashed line is the interval where pronounced Mg^{2+} migration is observed.

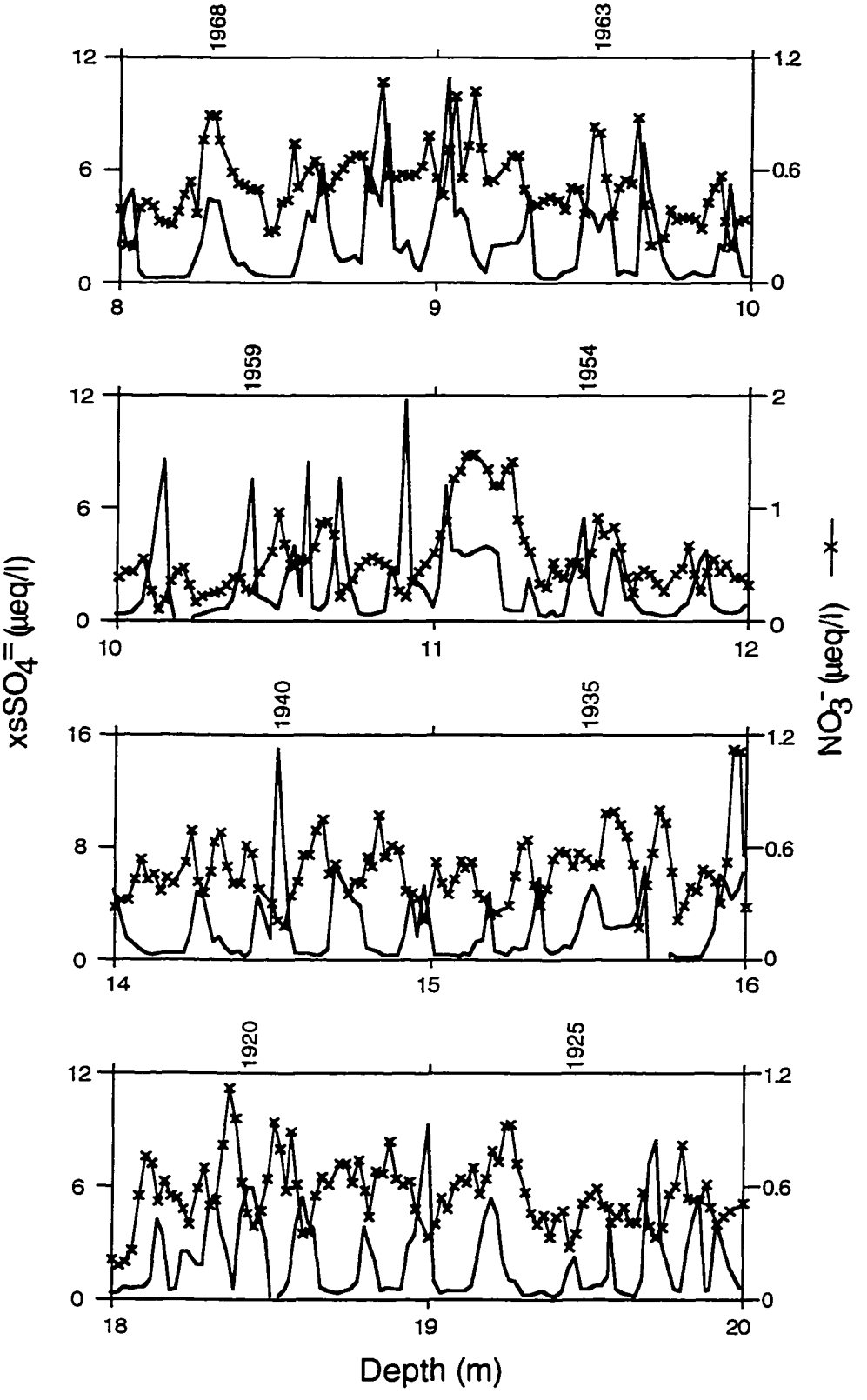

Figure V.5. $xsSO_4^{2-}$ and NO_3^- concentrations in samples (2 cm sample interval) from four sections of the Siple Dome core. Corresponding dates are given above each plot.

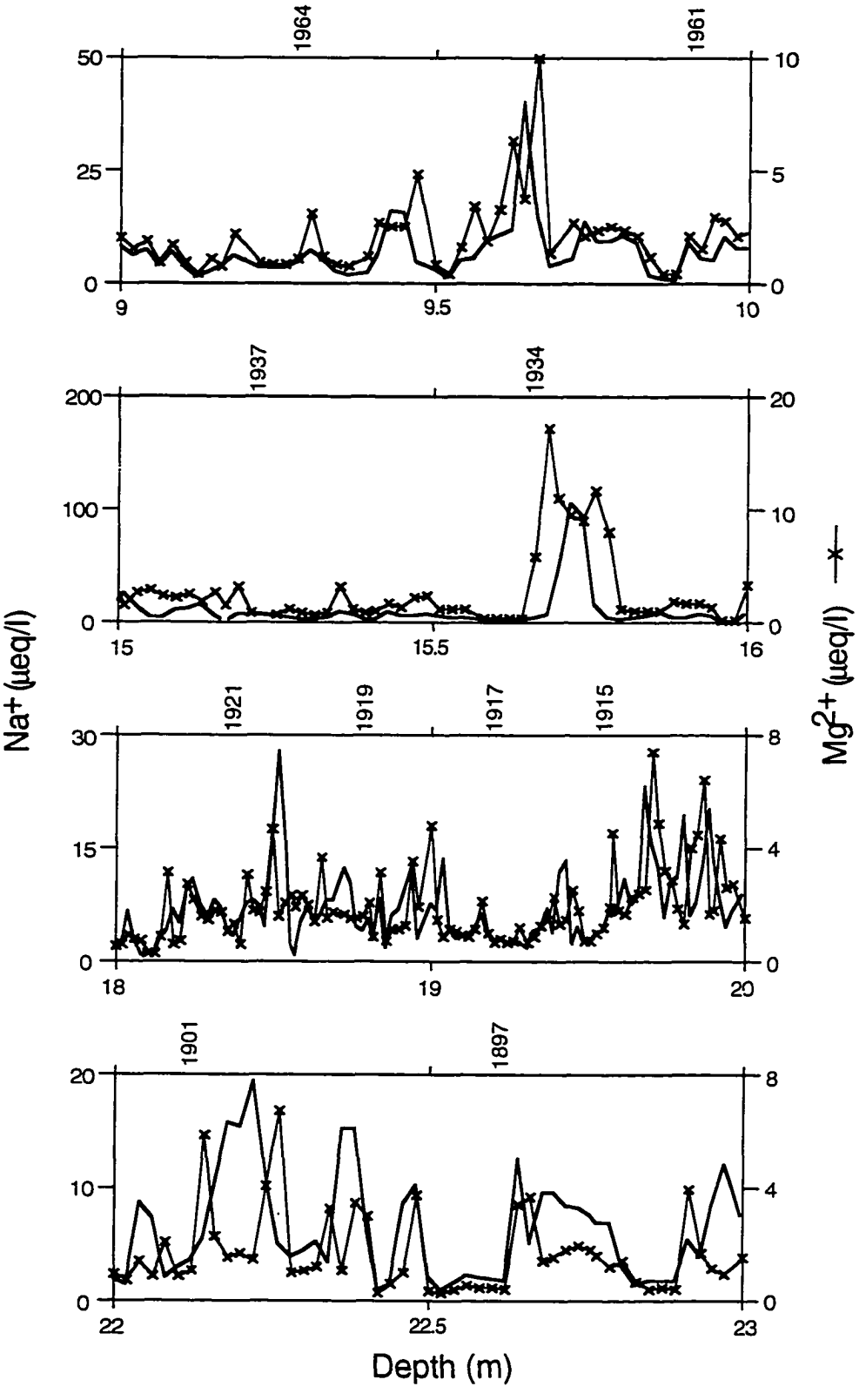

Figure V.6. Na^+ and Mg^{2+} concentrations in samples (2 cm sample interval) from four sections of the Siple Dome core. Corresponding dates are given above each plot.

Location	*Sample Type*	*k*
Coresite	Snow and Firn	0.088
Pit 2	Snow	0.102
Pit 3	Snow	0.139
Pit 4	Snow	0.103
Pit 5	Snow	0.051
Mean		0.096
Bulk seawater		0.252

Table V.1. Estimated SO4 to Na mass ratios (k) in seasalt aerosol at Siple Dome

VI. SEA-LEVEL PRESSURE VARIABILITY IN THE AMUNDSEN SEA OVER THE PAST CENTURY INFERRED FROM A WEST ANTARCTIC GLACIOCHEMICAL RECORD

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VI. SEA LEVEL PRESSURE VARIABILITY IN THE AMUNDSEN SEA OVER THE PAST CENTURY INFERRED FROM A WEST ANTARCTIC GLACIOCHEMICAL RECORD

ABSTRACT

Using numerical operational analyses, sea-ice extent records and station pressure data, we develop an ice core glaciochemical proxy record of interannual climatic variability in the Amundsen Sea region over the past century. More specifically, this record documents lower tropospheric transport of seasalt aerosols based on empirical orthogonal function (EOF) analysis of the high-resolution Siple Dome multivariate ice core chemical time-series record. Using European Center for Medium-Range Weather Forecast (ECMWF) analyses, the relationship between EOF1 and the quasi-stationary Amundsen Sea Low (ASL) pressure system is demonstrated for the period 1985-1994. To calibrate the EOF1 record prior to ECMWF coverage, an index is created using station pressure data from Chatham Island (45°58'S, 189°29'E) and Isle de Pascua (67°10'S, 250°34'E) stations. The EOF1 record is significantly correlated with the index on an annual ($r=0.4$, $p<0.02$) and interannual ($r=0.7$, $p<0.001$) basis, suggesting that the Siple Dome EOF1 record is sensitive to changes in regional meridional circulation strength. Correlation of monthly ECMWF sea-level pressure (SLP) fields and EOF1 annual time series suggests that September-November (austral spring) is the season of maximum seasalt transport to Siple Dome, consistent with previous interpretations and Antarctic station aerosol measurements. No relationship is found between sea-ice extent in the Amundsen Sea (170-250°) region for any season and EOF1.

INTRODUCTION

The Antarctic continent is increasingly recognized as an important and dynamic component of the Earth's climate system, due to the critical role the region plays in coupling several climate subsystems (atmosphere, cryosphere, hydrosphere, and biosphere). Understanding interannual climatic variability in the Antarctic region takes on considerable importance when potential regional- to hemispheric-scale interactions are considered, acting both on and from the continent. For example, changes in Southern Hemisphere albedo (through ice sheet and sea-ice extent) can potentially alter equator-to-

pole temperature gradients, and hence influence atmospheric and ocean dynamics. The unique geography of the high-latitude Southern Hemisphere allows transport of ocean temperature and salinity anomalies between the three major oceans (Atlantic, Pacific, and Indian), in addition to potential impacts on ocean basin conditions through deep water formation. Finally, heat transport between the ocean and atmosphere, particularly near the sea-ice margin, can have a significant impact on atmospheric and oceanic circulation.

The Antarctic Circumpolar Wave (ACW) in sea-ice extent, sea-surface temperature, surface wind speed, and sea-level pressure (White and Peterson, 1996), which propagates around the continent with a period of 4-5 years is an important example of the significant interannual variability that exists in the southern polar region. Based on the frequency of ACW variability and correlation of several other Antarctic instrumental records (such as temperature and precipitation), a potential link exists between interannual Antarctic variability and the El Nino-Southern Oscillation (ENSO) (Smith and Stearns, 1993; Cullather et al., 1996; White and Peterson, 1996). Mechanisms to explain the propagation of tropical signals to higher latitudes through both the ocean and atmosphere have been proposed, and mainly focus on the strength of the split polar jet (Chen et al., 1996; Cullather et al., 1996), Although the exact dynamics of this teleconnection are not yet fully understood, such mechanisms likely exist and need to be understood both in a local and regional context.

West Antarctica and the offshore Bellingshausen, Amundsen, and Ross Sea region (hereafter referred to as WBAR) exhibit the greatest degree of interannual climatic variability in Antarctica (Bromwich, 1988; Cullather et al., 1996). Cyclonic depressions that affect weather over West Antarctica come from middle and even subtropical latitudes in the eastern Indian Ocean and western Pacific (Schwerdtfeger, 1984). The belt of westerlies in the high-latitude Southern Hemisphere includes traveling wave cyclones, which originate in the lower middle latitudes, move poleward and intensify, and then stagnate along the coast of Antarctica in four general locations (Amundsen Sea, Weddell Sea, South-East and South-West Indian Ocean; Carleton, 1989). These wave cyclones carry heat and moisture poleward, contributing to heat redistribution in the Southern Hemisphere (Rogers, 1983). Climatological charts of monthly mean sea-level pressure resolve four quasi-stationary lows which are always lower than 988 mbar around the continent. One of these low pressure cells, the Amundsen Sea Low (ASL), is known to play a large role in the interannual climatic variability observed in the WBAR region (Cullather et al., 1996). Cyclonic systems generated in this oceanic sector are of particular importance to the Antarctic continent, supplying ~40% of the moisture flux to the entire continent through West Antarctica (Bromwich, 1990). Advection of warm, moist air from the WBAR region

through West Antarctica has been noted in Automatic Weather Station (AWS) and other regional weather data (Hogan, 1997). In addition, sea-ice extent in the WBAR region displays significant interannual variability over the instrumental period (1973-present; Jacobs and Cosimo, 1997).

While meteorological and sea-ice studies have made significant progress in describing interannual variability in the WBAR region and potential teleconnections with lower latitudes, they are limited to the short length of the instrumental record in Antarctica (~40 years). Modeling efforts are making progress in simulating several climatic parameters in the high southern latitudes; they, too, however, are limited in terms of validation by the short instrumental record. High-resolution proxy records offer the potential to estimate and extend observational data prior to station or instrument installation. Correlations between ice core stable isotope and station temperature records from the Antarctic peninsula suggest that calibrated temperature proxy records can be derived in Antarctica (Peel, 1992). Ice core glaciochemical records provide proxy information on the general atmospheric circulation (e.g., Mayewski et al., 1997), recording the transport and deposition of species derived from a number of diverse source areas (Legrand and Mayewski, 1997). Here we present a new high-resolution ice core glaciochemical record from West Antarctica which can be used in conjunction with available instrumental data to investigate interannual variability in the climatologically dynamic West Antarctic region.

Glaciochemical variability, notably in seasalt species, in a Siple Dome ice core (Figure VI.1) was previously linked to the overall intensity of atmospheric circulation in the WBAR region (Kreutz et al., 1997), and documents, for example, the onset of Little Ice Age conditions in the region. Here we use numerical operational analyses, a record of meridional sea-ice extent, and instrumental (station pressure) data to investigate the influence of interannual climatic conditions in the WBAR region on glaciochemical concentrations at Siple Dome. Three overall challenges undertaken in our study are to: 1) identify the main source area(s) and transport pathway(s) for marine aerosol species to Siple Dome; 2) estimate the input timing of marine aerosol species to Siple Dome, so that the time-series ice core record can be compared to meteorological records; and 3) use high-resolution time-series of marine aerosol transport and deposition to Siple Dome to derive a proxy record of interannual climate variability in the WBAR region over the past century.

DATA

We focus here on a 150 m core recovered from Siple Dome, West Antarctica (81.65°S, 148.81°W; Fig. VI.1) during the 1994 field season (Mayewski et al., 1995). The upper 24

m of firn were processed at 2 cm intervals by removing all exposed surfaces via scraping with pre-cleaned stainless-steel blades. Sample blanks (frozen ultra-pure deionized water) were included in processing every meter to verify contamination-free procedures. Samples were melted at room temperature in sealed plastic (polyethylene) containers immediately prior to analysis. Anion (Cl, NO_3, and SO_4) and cation (Na, Ca, K, Mg, NH_4) analyses were performed via suppressed ion chromatography. Cations were analyzed with a CS12 column, 125 μL loop, and 20 mM MSA eluent. Anions were analyzed with a AS11 column, 75 μL loop, and 6 mM NaOH. Dating of the core was accomplished using annual signals preserved in several chemical species, β-activity profiles, and volcanic horizons (Kreutz et al., 1997). The resulting depth/age scale indicates an age of 1890 A.D. at 24 m, yielding a resolution of 6-12 samples/year for the past 110 years.

Empirical orthogonal function (EOF) analysis is applied to the multivariate Siple Dome glaciochemical record to examine chemical covariance through time (Kreutz and Mayewski, in review). Results indicate that the first EOF (EOF1) explains a considerable (~50%) portion of the overall chemical variance, and is loaded primarily by the major components of seasalt aerosols (Na, Cl, and Mg). Given the position and elevation (621 m) of Siple Dome, it appears that the site is heavily influenced by marine air masses advected inland from the WBAR region, and is therefore sensitive to changing coastal climatic conditions. The EOF1 time-series has no significant relationship with accumulation rate at Siple Dome (KJK, 1998), and therefore provides information on the transport and deposition of marine aerosols that is independent of moisture flux. We interpret the EOF1 time-series as a record of marine aerosol production, transport and deposition to Siple Dome, and therefore seek to quantify these processes using modeled and instrumental meteorological data. As such, we expect the relevant climatic parameters to be sea-level pressure (SLP), meridional (v) and zonal (u) wind strength, and sea-ice extent.

Numerical analyses have played an important role in a variety of atmospheric studies in high southern latitudes (e.g., Trenberth and Solomon, 1994; Bromwich et al., 1995; Budd et al., 1995). Validation studies of such analyses produced by the European Center for Medium-Range Weather Forecasting (ECMWF), the National Center for Environmental Prediction (NCEP) and the Australian Bureau of Meteorology found that the ECMWF analyses were superior in comparisons with rawinsonde and glaciological data (Bromwich et al., 1995). The ECMWF analyses are generally found to offer a reasonable depiction of the broadscale atmospheric circulation, pressure level fields, and surface winds when compared to Antarctic AWS units and ship observations (Cullather et al., 1997). The ECMWF archive we employ here was obtained from the National Center for Atmospheric Research (NCAR). The dataset contains monthly averaged analyses (reported at 0000 and

1200 UTC) on a 2.5° latitude-longitude grid, at 14 standard pressure levels as well as surface and boundary level variables for the period 1985-1995.

Instrumental data used to further investigate the link between climatic conditions in the WBAR region and EOF1 include time-series of sea-ice extent and station pressure data. The sea-ice extent data we use covers 1973-1995, and represents one of the longest Southern Hemisphere sea-ice datasets available. The monthly data (averaged over each 10° of longitude) on the latitude of the sea-ice edge is derived from the U.S. Navy-NOAA Joint Ice Facility weekly maps in the compilations of Jacka (1983) and Simmonds and Jacka (1995). Although there are several Automatic Weather Stations in the vicinity of Siple Dome, the short record length (1-5 years) and substantial data gaps make the records unsuitable for use in this study. Continuous monthly sea-level pressure (SLP) data was obtained from two stations in the Southern Ocean thought to reflect conditions in the WBAR region: Chatham Island (45°58'S, 189°29'E) and Isle de Pascua (67°10'S, 250°34'E) (Figure VI.1).

RESULTS

Investigation of Siple Dome EOF1 Time-Series Using ECMWF Analyses (1985-1994)

To begin to investigate the relationship between SLP in the WBAR region and EOF1 at Siple Dome, we define years of high and low marine aerosol transport as being at least $\pm 1\sigma$ from the 1985-1994 EOF1 mean. Accordingly, low years are 1994 and 1991, and high years are 1992 and 1989. Subtracting low year mean annual SLP fields (derived from the ECMWF dataset) from high year fields results in the spatial patterns presented in Figure VI.2. The influence of SLP conditions in the Amundsen and Bellingshausen Seas on aerosol transport to Siple Dome is apparent, with the highest negative difference occurring at ~225-270°W. The significant negative difference suggests that, at least on an annual basis, when transport of marine aerosol to Siple Dome is enhanced WBAR SLP is relatively low (~8 mbar anomaly).

The mean SLP difference field presented in Figure VI.2 resolves the Amundsen Sea Low (ASL), which is a climatological feature associated with cyclonic activity propagating into the WBAR region. Variability in both the position and intensity of the ASL is known to occur on interannual timescales, with shifts in mean annual position occurring between the Ross Sea and close to the Antarctic Peninsula (Cullather et al., 1996). Modeled moisture flux into the WBAR region clearly demonstrates the influence of the ASL, with normal net precipitation conditions occurring when the ASL occupies a position near the

eastern Ross Ice Shelf (Cullather et al., 1996). Under these conditions, moisture flux into the WBAR region (and likely to Siple Dome) occurs from almost due north. Under low net precipitation conditions, the ASL is significantly farther east and closer to the Antarctic Peninsula. Fluctuations in modeled moisture flux into the WBAR region, and hence the position of the ASL, have been linked to ENSO warm events (i.e., low precipitation and the ASL positioned near the Antarctic Peninsula during 1982 and 1987; Cullather et al., 1996).

Previous studies suggest that the majority of seasalt deposition occurs at Siple Dome in winter (Kreutz et al., in press). These results are based on linear interpolation of the depth/age scale between known summer peaks in other chemical species. In an attempt to better define seasalt input timing, as well as investigate the influence of the ASL on EOF1, we correlate monthly SLP values with mean annual EOF1 values. By doing so, we avoid any assumption regarding chemical input timing on a seasonal basis. The spatial distribution of the correlation coefficients was examined for each month. We sought correlations significant over large areas which persisted through at least two months, indicating a dominant dynamical process which may be linked to Siple Dome EOF1. Results of these monthly correlations reveal significant correlation in the Amundsen and Bellingshausen Seas during the months of September, October, and November (SON; Fig.VI.3). Correlations are negative during these months, consistent with our finding of decreased WBAR SLP and increased EOF1. SLP difference analysis (Fig. VI.4), using only the SON pressure fields, indicates a similar region of SLP influence (~235-260°) as in the annual analysis (Figure VI.2). Therefore, we suggest that SON is the season of maximum seasalt input.

Previous glaciochemical investigations have explained increased seasalt loadings as mainly being a result of increased zonal and meridional wind stress (e.g., Mayewski et al., 1993; Mayewski et al., 1997, O'Brien et al., 1995). The ECMWF dataset allows for an examination of the u and v (at 10 m) wind components and Siple Dome EOF1. Difference fields for both u and v wind components in SON indicate increased zonal (westerly) and meridional (northerly) wind strength during high EOF1 years that are consistent with increased ASL intensity. Correlations bewteen monthly u and v wind stress and annual EOF1 values reveal similar wind strength patterns (suggesting increased ASL intensity) mainly during SON.

Sea-Ice Extent/Glaciochemical Relationships 1973-1994

The influence of sea-ice extent and concentration on determining seasalt production and transport to a given core site has been addressed by several authors (e.g., Peel and

Mulvaney, 1992; Mayewski et al., 1994; Wagenbach, 1996). Two views are: 1) 'source argument'- decreased sea ice extent and increased open lead areas result in increased seasalt production, and hence increased ice core seasalt concentration, and 2) 'circulation strength argument'- seasalt aerosol and snow concentrations display maxima during cold periods of enhanced meridional flow (i.e., winter, Little Ice Age, Last Glacial Maximum), which are also the times of maximum sea-ice extent. These two views need not be mutually exclusive, and if so it may be difficult to separate their individual effect on an ice core record.

EOF analysis of the entire sea-ice anomaly dataset (thirty-six 10° longitude bands x 288 months) partitions the 170-250° region on the first EOF, suggesting that this region exhibits the greatest degree of variability in the circumpolar region. Comparison of seasonal (DJF, MAM, JJA, and SON) mean sea-ice extent time-series for this region with Siple Dome EOF1 reveals no significant correlations. A comparison of mean SON sea-ice anomalies during high and low EOF1 years (Fig. VI.5) suggests that a large portion of the WBAR region is out of phase with adjoining regions. These results suggest that during years of increased aerosol transport sea-ice extent in the WBAR region may be anomalously high. This would contradict source arguments, and support circulation strength arguments which indicate cold periods are times of increased seasalt flux (Mayewski et al., 1994; O'Brien et al., 1995). To further investigate the sea-ice/EOF1 relationship, monthly time-series of sea-ice extent in each 10°-wide longitude slice was correlated with the EOF1 mean annual time-series for 1973-1994 (Fig. VI.6). Results indicate significant correlations only in three months (January, April, and November), and in no more than two 10°- wide regions. If a strong physical link exists between sea-ice extent and aerosol transport to Siple Dome, we would expect to see significant correlations over a larger region and in consecutive months.

Extending EOF1/Synoptic Meteorological Comparisons Through Time Using Station Meteorological Data

Although results presented above are encouraging, we acknowledge that 10 years of correlation is insufficient to establish the EOF1 record as a robust proxy of the ASL prior to 1985. Given our goal of estimating climatic variability in the WBAR region over the past century using EOF1 time-series, we now seek to extend the EOF1/instrumental calibration prior to the ten years represented by ECMWF data. Differences in SLP between pairs of stations have traditionally been used as indices of the large-scale atmospheric circulation, particularly where station density is sparse (e.g., Trenberth, 1976; Lamb, 1977). Previous work has defined the Trans-Polar Index [TPI; the difference in SLP between Hobart,

Tasmania (43°S, 147°E) and Stanley, South Atlantic Ocean (52°S 58°W)] to measure the eccentricity of the polar vortex around the South Pole (Pittock, 1980).

Although the TPI has proven very diagnostic in analyzing circum-Antarctic pressure fluctuations (Villalba et al., 1997), we are interested here mainly in pressure fluctuations in the WBAR region. Therefore, we define a Trans-ASL Index (TASL) as the normalized pressure difference between Chatham Island and Isle de Pascua stations (Fig. VI.1). Selection of these stations for the TASL index is based on two criteria: 1) continuous station SLP data for at least 30 years, and 2) station location. We assume the TASL index is sensitive to ASL pressure fluctuations and location. Because the Siple Dome EOF1 record is thought to be mainly recording spring (SON) seasalt input, we further refine the TASL by focusing only on SLP differences in SON to create the spring TASL (STASL). Based on results presented in Figure VI.4, positive STASL values suggest intensification of the ASL and formation of a positive pressure anomaly near New Zealand, while negative STASL values reflect opposite conditions. Examination of mean SON pressure anomalies in the WBAR region indicates this pattern is consistent through 1985-1995. Therefore, we interpret positive STASL values as indicating increased cyclogenesis in the Amundsen Sea, and associated deeper low pressure in the ASL. While the TPI primarily represents an index of SLP wavenumber one, the STASL likely represents more regional influences. The STASL and EOF1 are significantly correlated ($r=0.40$, $p<0.02$) for the period 1958-1991 (Fig. VI.7), which further supports using EOF1 as a proxy record of SLP variability in the WBAR region. We note, however, that the correlation statistics, while significant, highlight the fact that the Siple Dome EOF1 record does not provide an absolute estimate of ASL fluctuations on an annual basis. A qualitative visual comparison of the two records suggests that EOF1 records periods of more intense ASL conditions (high STASL) more accurately (i.e., late 1970s). The overall trend in both series (using a 3 year running mean) is well correlated ($r=0.7$, $p<0.001$), and at this resolution the EOF1 series accounts for ~50% of the STASL variance (Fig. VI.7). This finding suggests that EOF1 is an accurate proxy record of interannual ASL changes. Future modeling efforts may elucidate a quantitative estimate of the amount of ASL variance recorded in a EOF1 time-series from Siple Dome. In the remainder of this study, we assume the EOF1 record to be a proxy for the overall intensity of the ASL system on interannual timescales (Fig. VI.8).

DISCUSSION

Unlike several other regions in Antarctica, there are no coastal stations in the WBAR region at which aerosol measurements are available for comparison with the Siple Dome EOF1 results. An analysis of back trajectories to South Pole (SP) for the period 1985-1989 suggests, however, that a majority of the marine aerosol that reached SP is advected through West Antarctica and originates in the WBAR region (Harris, 1992). Most input of particle-laden air to the South Pole region occurs as discrete cyclonic events resulting in widespread warming (Hogan, 1997). Aerosol measurements made during these warmings indicate the predominance of seasalt species (Parungo et al., 1979; Bodhaine et al., 1986). The annual cycle in seasalt aerosol at SP, estimated from nephelometer aerosol scattering extinction coefficients, shows a peak in SON (Bodhaine et al., 1986). Timing of this peak is consistent with the yearly breakdown of the Antarctic vortex (decline of inland high pressure systems), and associated increase in vertical mixing (Hogan and Gow, 1993). In a study of seasonal changes in surface pressure using ECMWF data, Parish and Bromwich (1997) found that the most pronounced changes occur during transitional periods (SON) when thermal adjustment in the lower atmosphere alters the vertical distribution of pressure. Rogers (1983) noted the relationship between higher spring temperature variability and increased meridional circulation in Antarctic station data. While our SON seasalt input estimate from Siple Dome is consistent with SP measurements, airmasses reaching SP across the West Antarctic polar plateau likely do not affect Siple Dome directly. Therefore, we also compare our results to those from the Ross Ice Shelf (Warburton et al., 1981; Herron and Langway, 1978). Based on chemical measurements in snowpit and core samples from this area, peaks in seasalt chemistry appear to be related to spring conditions. Thus, seasalt deposition at Siple Dome during SON appears to be consistent with regions both to the east and west, and with other chemical, isotopic, and stratigraphic measurements at Siple Dome (KJK, 1998).

Because we cannot identify a quantitative relationship between sea-ice extent and EOF1, transport of marine aerosols during SON is thought to be primarily driven by SLP changes and enhanced air mass advection. In a detailed study of the Amundsen and Bellingshausen Sea regions, Jacobs and Comiso (1996) noted significant interannual variability in sea-ice extent over the past two decades, with an overall 20% decline during that period. The decrease in sea-ice extent was negatively correlated with surface air temperatures on the west side of the Antarctic Peninsula, which has increased ~0.5° per decade since the mid-40s. No relationship was found, however, between mean wind stress or direction during the same interval. Carleton (1989) investigated relationships between the TPI and sea-ice

extent in the Ross Sea, and found that stronger mid-latitude westerlies were associated with more extensive sea-ice coverage in the region, consistent with observations by Streten and Pike (1980) and a modeling study by Mitchell and Hills (1986). SON is the period of maximum sea ice extent, which perhaps explains in part the insensitivity of the Siple Dome EOF1 record to interannual changes in sea-ice extent.

Previous comparisons of SLP and glaciochemical concentrations on the Antarctic Peninsula (Peel and Mulvaney, 1992) have suggested that seasalt concentrations in the core record are also primarily a result of SLP fluctuations and not necessarily sea-ice conditions. Major Cl peaks tend to occur when the Orcadas-Halley pressure index is low, suggesting the circumpolar trough is shifted northward. Under these conditions, cyclones will track more frequently across open ocean areas to the north of the ice edge, which favors the generation and inclusion of seasalt aerosols (Peel and Mulvaney, 1992). Although not commented upon, the Dolleman Island Cl record from 1900-1983 appears to be positively correlated with sea-ice duration in the South Orkneys (Peel and Mulvaney, 1992). In addition, mean annual Cl values at Dolleman Island are negatively correlated with air temperatures at Faraday Station (Peel et al., 1996). King (1994) demonstrated a strong correlation between annual mean temperatures in the Peninsula and index of meridional circulation (South Orkney Islands minus Faraday, MSLP), suggesting that high Cl values at Dolleman are related to enhanced southerly flow. It therefore appears that transport of Cl to Dolleman Island, as at Siple Dome, is primarily a function of SLP variations and cyclonic tracks, and not necessarily sea-ice extent. We again note the lack of correlation found between EOF1 and sea-ice extent in both the SON and prior JJA seasons, and suggest that other proxy records of sea-ice extent in the WBAR region (e.g., methanesulfonic acid; Welch et al., 1993) should be sought.

ASL Variability, ENSO, and the ACW

Studies relating ENSO to the high southern latitudes have increased recently, despite the relatively short record of conventional Antarctic meteorological data. In particular, variations in SLP and height field anomalies for the Southern Hemisphere, including Antarctica and vicinity, have been examined by van Loon and Shea (1987) and Karoly (1989) using analyzed fields. As the number of these studies grows, identification of the mechanisms involved in propagation of the ENSO signal has evolved. Newall et al. (1981) speculated that possible high-latitude forcing of the Southern Oscillation could be achieved by atmospheric forcing of the Antarctic Circumpolar current and subsequent sea surface temperature propagation northward via the Peru Current. More recent articles, however, have focused on the role of the South Pacific atmospheric double jet variability in the

southward propagation of the ENSO signal (Smith and Bromwich, 1994; Smith et al., 1995; Chen et al., 1996). Tracks of cyclones and anticyclones in this region have been found to be strongly influenced by the double jet (Sinclair, 1996). Variability in the relative strength of the two components of the double jet have been shown to vary in conjunction with the SOI (Chen et al., 1996). Although the nature and role of the double jet oscillation is not well understood, it may be responsible for at least part of the observed variability in both the position and intensity of the ASL (Cullather et al., 1996). Cullather et al. (1996) have noted that moisture flux into West Antarctica is strongly controlled by the position of the ASL, which was shown to migrate ~1400 km between years of high and low (1982-82 and 1987) precipitation. Therefore, while the link has still yet to fully quantified, it does appear that the ASL and SO have some physical connection.

Relationship Between Regional Climatic Variability and the ASL Over the Past Century

Estimates of ASL variability based on the Siple Dome EOF1 record (Figure VI.8) can be compared to other proxy records of the high latitude Southern Hemisphere over the last century. The only other investigation of SLP variations in the high-latitude Southern Hemisphere was done using tree-ring chronologies from Tierra Del Fuego and New Zealand (Villalba et al.; 1997). Summer (Nov.-Feb.) SLP conditions in the two regions, as well as long-term trans-polar teleconnections, were reconstructed for the period 1750-1985 A.D. The Siple Dome EOF1 record provides complementary information, recording SLP variability in a region between the two tree-ring locations. Comparison of the EOF1 record and TPI reconstructions from Villalba et al. (1997) suggest several periods in the 20th century where the two records are correlated. In particular, the largest positive anomaly in the 230-year reconstructed TPI record occurs during the 1930-1935 period. This period corresponds to the largest positive anomaly in the annual EOF1 record (Figure VI.8), suggesting that the TPI is recording changes in the overall atmospheric circulation of the circumpolar vortex (Carleton, 1989). High pressure blocking systems off New Zealand are known to have a large influence on steering the westerly system and cyclogenesis towards the Amundsen Sea (Sinclair, 1996). Likewise, a broad increase in the TPI occurs from ~1952-1960, which corresponds to a similar increase in EOF1.

CONCLUSIONS

In summary, results presented here represent the first instrumentally-calibrated ice core proxy record from West Antarctica, and provide a means for reconstructing SLP in the

WBAR region prior to instrumental coverage. The significant correlations found between EOF1, SLP and wind stress, but not sea-ice extent, highlights the complex interaction of various climate components in the region. As there is no apparent connection between the Siple Dome EOF1 record and sea-ice extent, other chemical records (e.g., MSA) should be investigated for possible relationships with sea-ice extent. The Siple Dome EOF1 record likely records a combination of the overall strength (as evidenced by correlation with TASL) and position of the ASL. Because Cullather et al. (1996) have demonstrated that moisture flux into WBAR region is related to ASL position, developing an additional ASL proxy from accumulation rate records could improve reconstructions of SLP in the WBAR region. The use of a number of ice core records from the WBAR region (developed in the ITASE program) will improve the reconstruction presented here, which eventually can be extended back in time once high-resolution records are available for the Holocene from Siple Dome.

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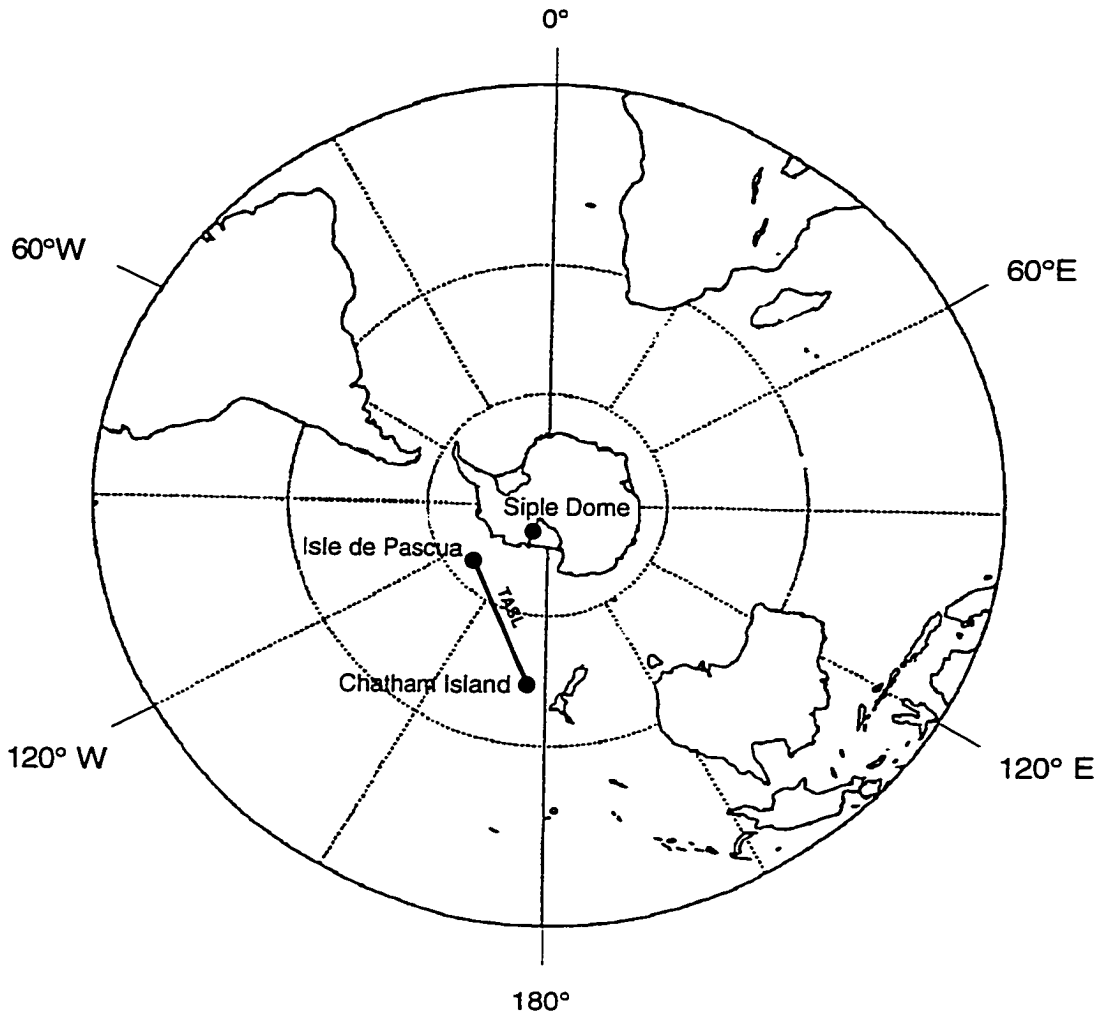

Figure VI.1. Location map for Southern Hemisphere sites. TASL represents the Trans-Amundsen Sea Low index.

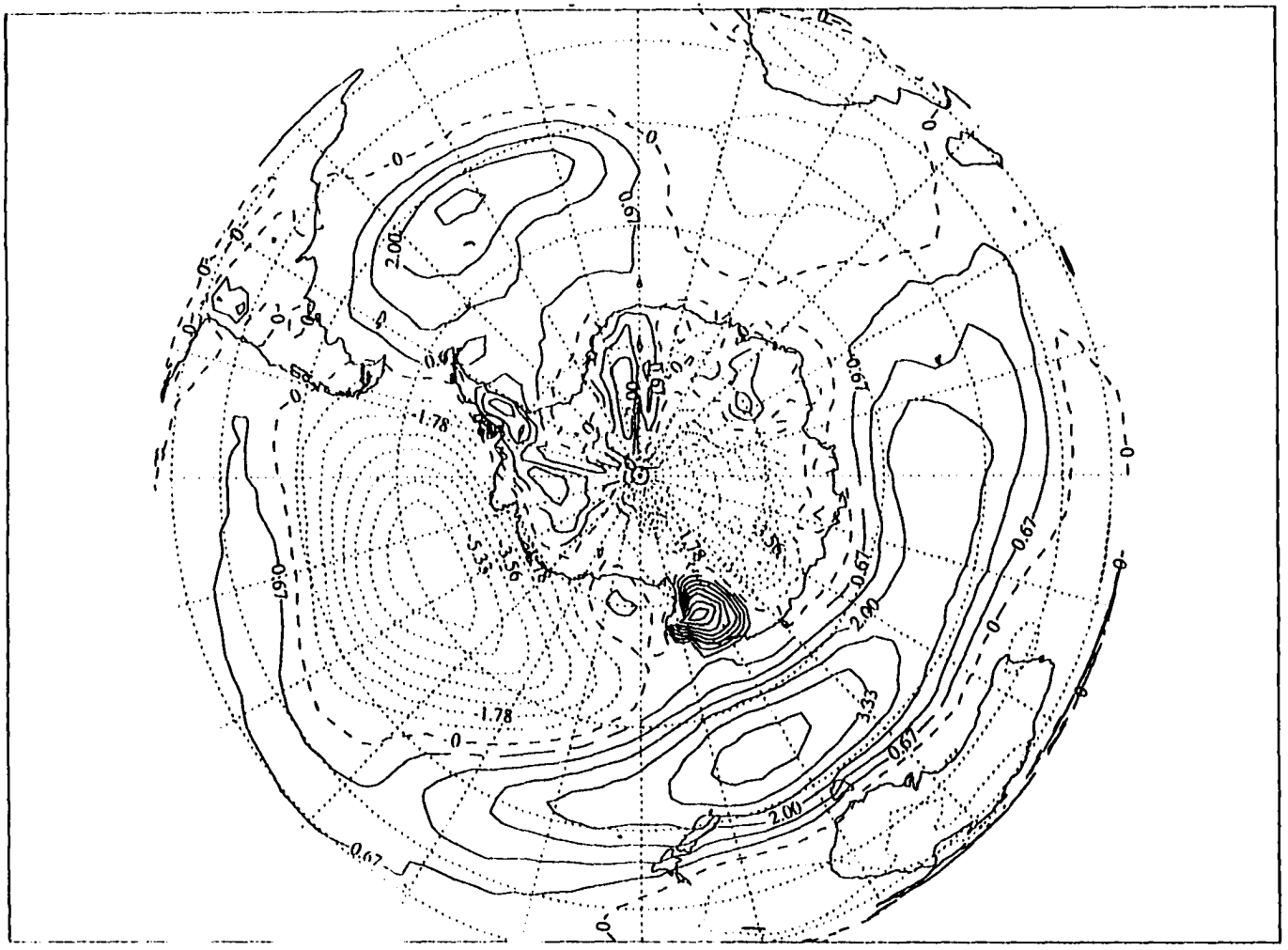

Figure VI.2. Mean annual sea-level pressure (SLP) differences dervied from ECMWF numerical analyses. Method used to select years based on Siple Dome EOF1 record is described in the text.

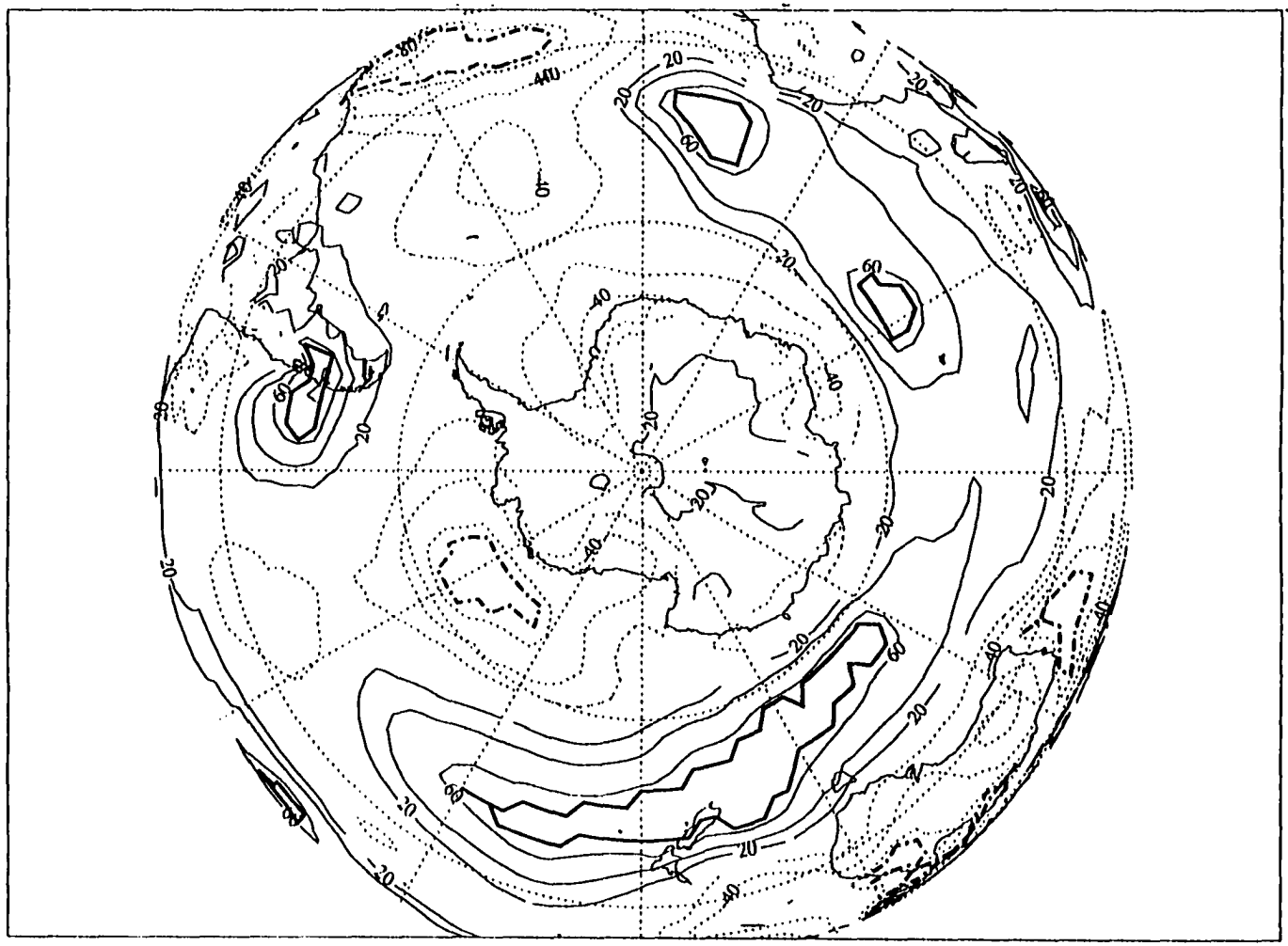

Figure VI.3. Spatial correlation patterns for the period 1985-1994 between monthly SLP and the mean annual EOF1 record for November. Bold broken lines indicate significant (95% c.l.) negative correlations, and bold solid lines represent significant positive correlations.

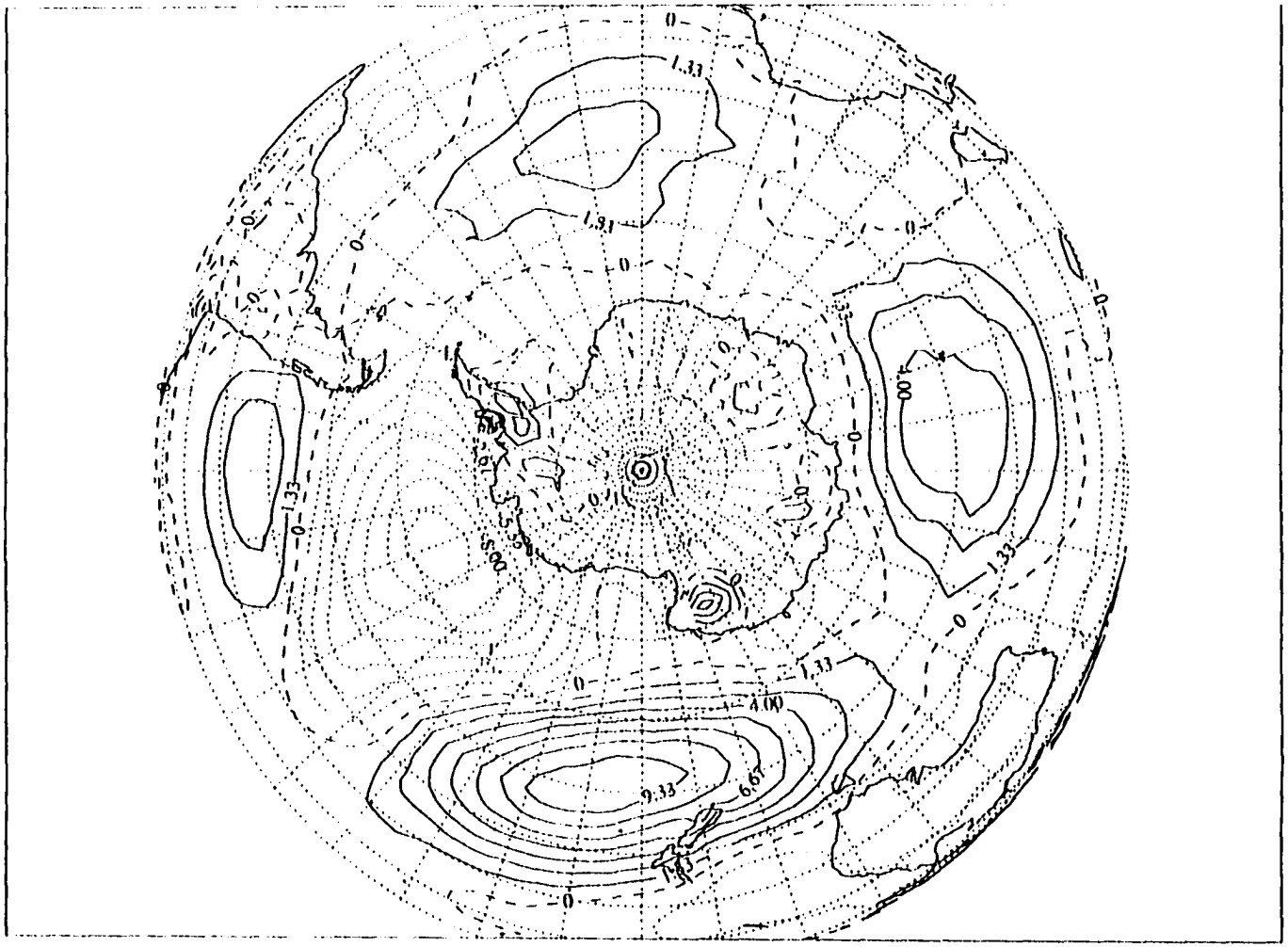

Figure VI.4. Mean SON SLP differences derived from ECMWF numerical analyses. Years used to determine SLP differences are the same as in Figure 1.

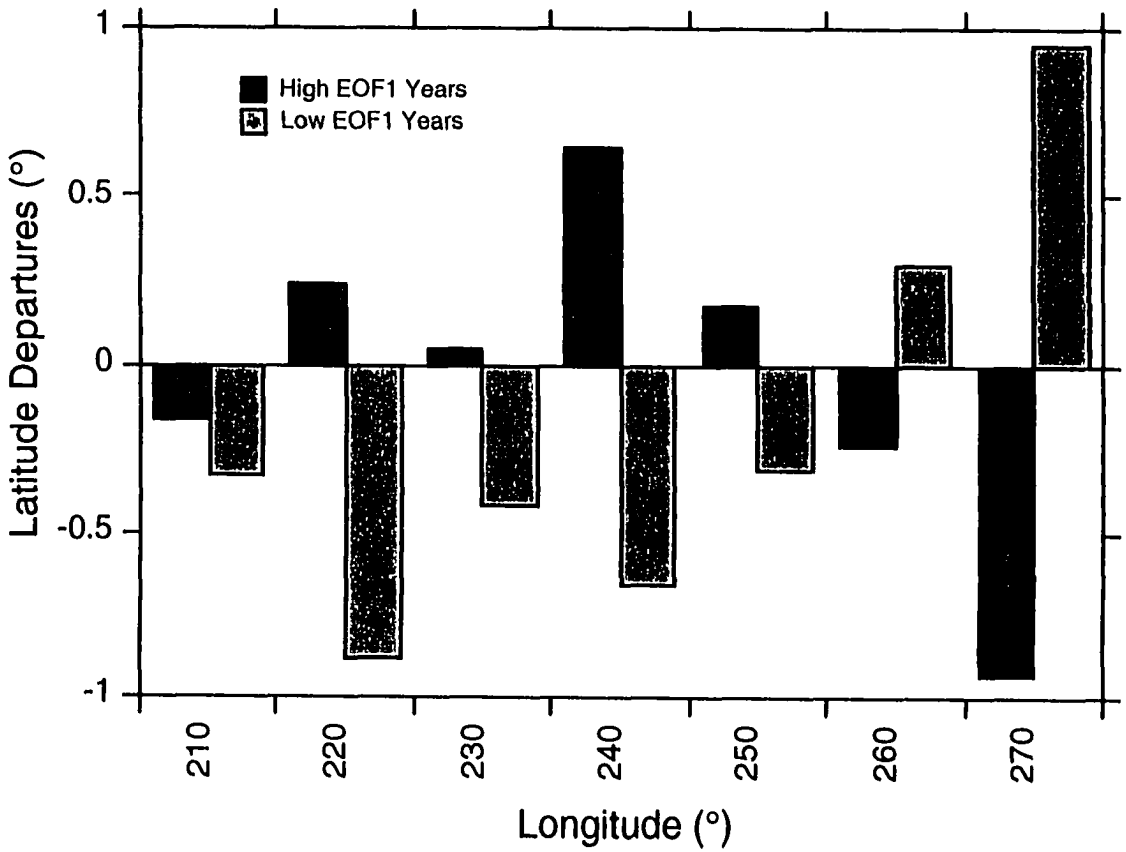

Figure VI.5. Average sea-ice extent anomalies for September-November during years of high and low EOF1.

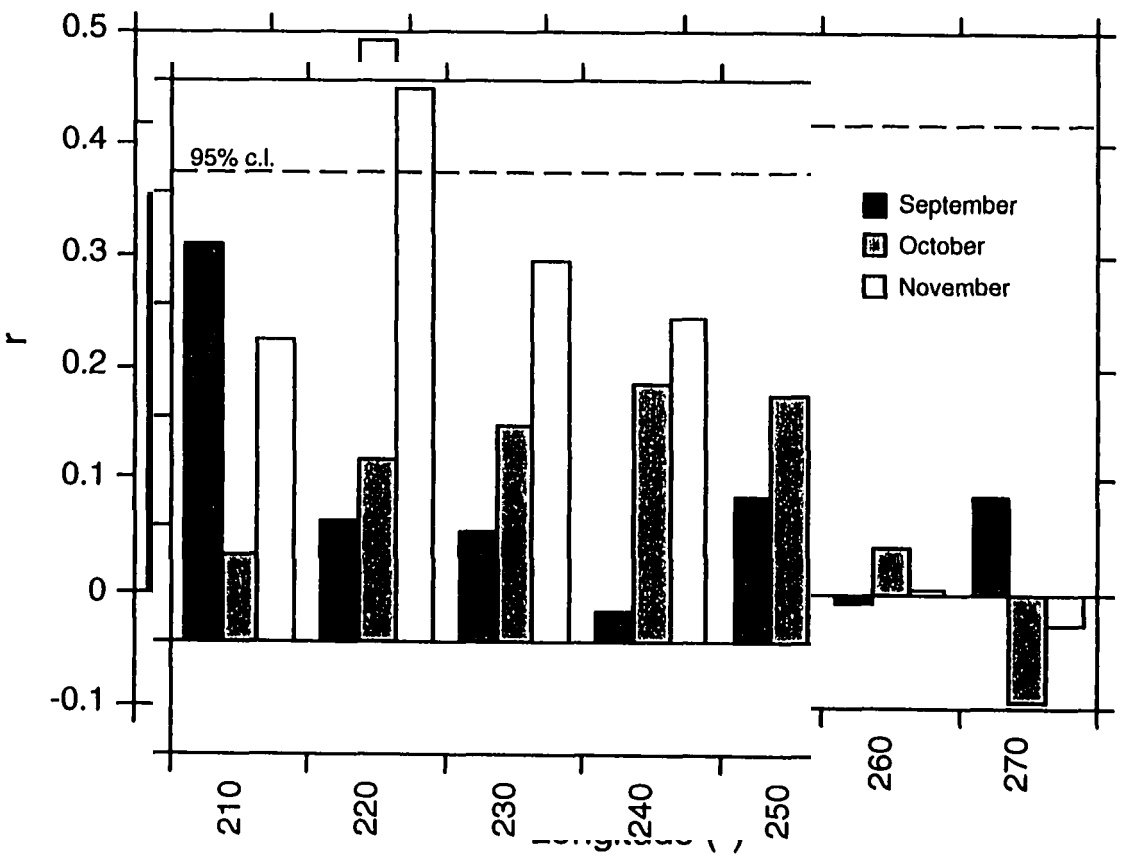

Figure VI.6. Correlation of monthly sea-ice extent (September-November) and annual EOF1 values for the period 1973-1994. Sea-ice extent data is averaged over each 10°-wide longitude slice.

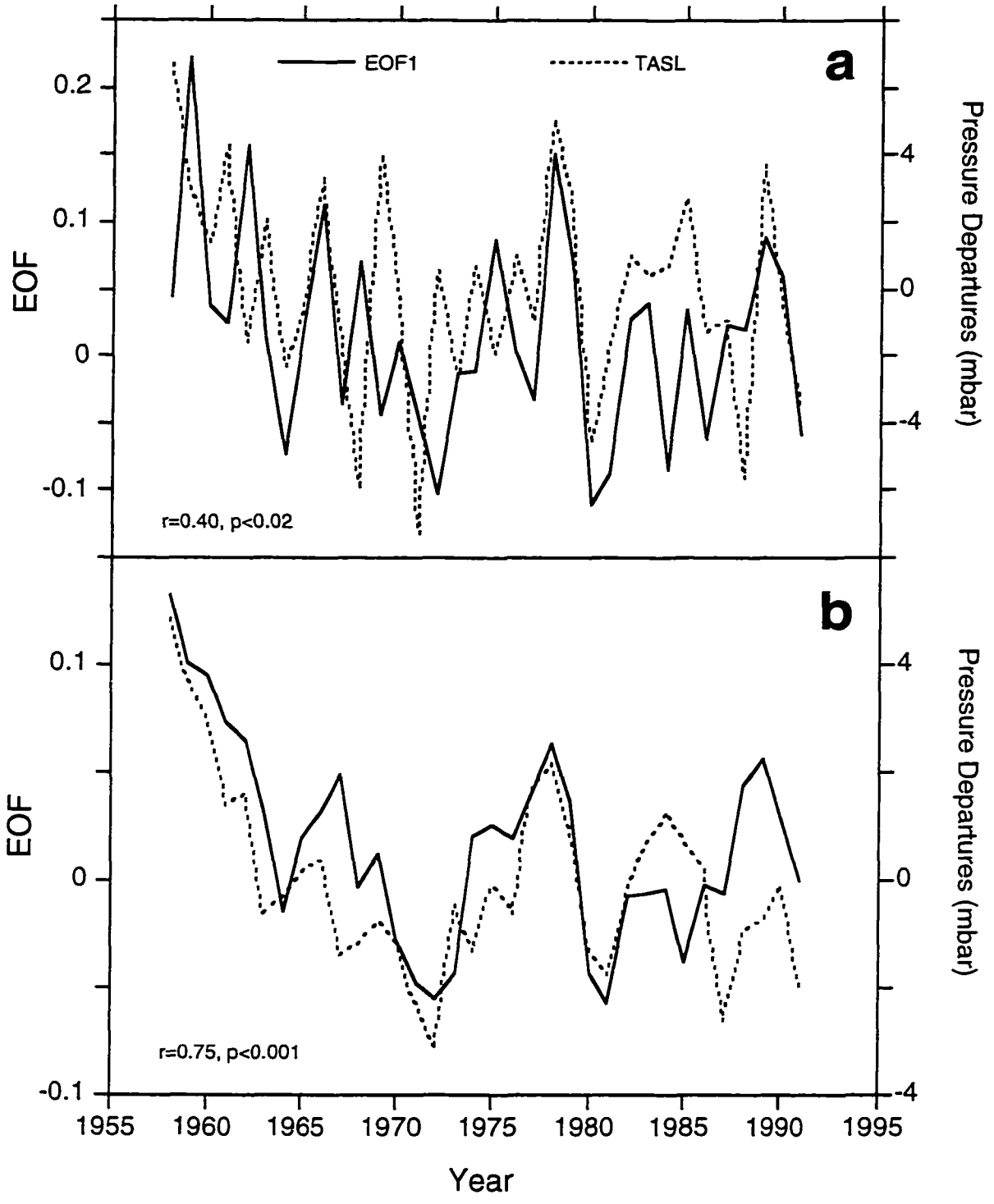

Figure VI.7. Correlation of a) annual mean and b) 3-year running mean Siple Dome EOF1 and spring Trans-Amundsen Sea Low (STASL) index records for the period 1958-1994.

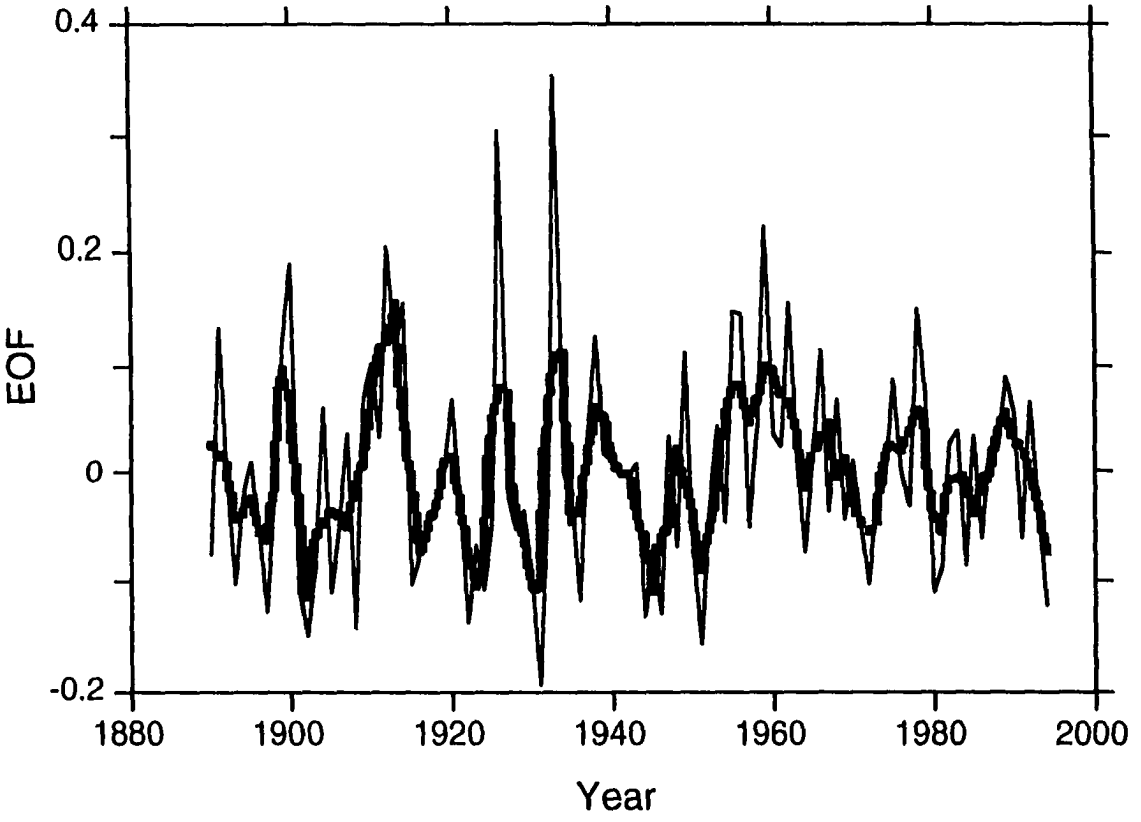

Figure VI.8. Siple Dome EOF1 record for the period 1890-1994. The light line represents annual mean values, and the heavy solid line represents a 3-year running mean.

VII. COMPARISON OF WEST ANTARCTIC AND GREENLAND CLIMATE OVER THE LAST MILLENIUM

Section VII is published in Science
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VII. COMPARISON OF WEST ANTARCTIC AND GREENLAND CLIMATE OVER THE LAST MILLENIUM

ABSTRACT

Annually-dated ice cores from central Greenland and Siple Dome, West Antarctica indicate that meridional atmospheric circulation intensity increased in both polar hemispheres at the beginning (1400 AD) of the most recent Holocene rapid climate change event, the Little Ice Age (LIA). As deduced from chemical concentrations at these core sites, the LIA was characterised by significant variability in the strength of meridional circulation, and this variability persists today. Thus, increased late-20th century storm variability may be in part a result of the continuation of these climatic fluctuations.

INTRODUCTION

The Little Ice Age (LIA; nominally ~1400-1900 AD) is recorded in several Northern Hemisphere and equatorial paleoclimatic records and was a period of cold, dry conditions and increased atmospheric circulation (Lamb, 1977; Grove, 1988). It now appears that several LIA-type events have occurred throughout the Holocene (Mayewski et al., 1993; O'Brien et al., 1995), and that relatively minor forcings may be responsible for these events (Denton and Karlen, 1973; Alley et al., 1997).

Although it was a globally distributed event, the LIA was not a 500-year period of global cooling. High-resolution tree ring records from several areas (Bradley and Jones, 1992) have suggested that although there is significant decadal-scale variability related to temperature changes over the last 2000 years, no distinct LIA signal is recorded. Indeed, it is possible that the LIA was not simply a cooling everywhere, but instead a period of both warm and cold anomalies that varied in importance geographically (Bradley and Jones, 1993). Such patterns can be attributed to changes in atmospheric circulation strength (Lamb, 1984). While instrumental records of atmospheric circulation strength do not encompass the entire LIA period, ice core glaciochemical records can provide a proxy for this climate parameter (e.g., O'Brien et al., 1995). Here we present results from an ice core recovered from Siple Dome (Fig. VII.1), Antarctica, which provides a multivariate chemical record at annual resolution to study both regional and bipolar (through comparison with the Greenland Ice Sheet Project Two [GISP2; Fig. VII.1] ice core record) atmospheric circulation conditions during the LIA.

METHODS

Siple Dome (81.654°S, 148.808°W; Fig. VII.1) is sensitive to changing coastal meteorological conditions due to its low elevation (621m) and because many cyclones pass across the relatively flat Ross Ice Shelf to the site (Mayewski et al., 1995; Kreutz and Mayewski, in review). In 1994, a 150 m ice core was collected 5 km north of the Siple Dome summit[1]. Annual-layers are evident in the core, and ice with an age of 1150 years BP (before present [2000 AD]) is present at a depth of 150m (dating error estimated to be ~1%). The average accumulation rate is ~11 cm ice equivalent/yr.

RESULTS AND DISCUSSION

The concentrations of seasalt species (viz., Na^+, Cl^-, Mg^{2+}, K^+) in Antarctic and Greenland surface snow decreases exponentially with both distance inland and elevation because coarse mode seasalt aerosols fall out of air during transport (Mulvaney and Wolff, 1994; Yang et al., 1995). Therefore, changes in the concentration of these species in the ice core imply fluctuations in the frequency and intensity of tropospheric aerosol transport to a particular site. Seasalt deposition occurs at Siple Dome primarily during the austral winter/spring when cyclonic frequency is at a maximum (Schwedtfeger, 1984). Fluctuations in the position and intensity of the Amundsen Sea Low (ASL) in response to atmospheric heating over the Pacific Ocean (Cullather et al., 1996) are likely linked to Siple Dome glaciochemistry on interannual time scales. On longer time scales (decades to centuries), overall expansion (deepening) of the ASL associated with changes in the latitude of the Antarctic low pressure belt, and hence the southern circumpolar vortex extent (Schwedtfeger, 1984), is most likely responsible for increased aerosol transport. Similarly, in central Greenland most seasalt is deposited in boreal winter when meridional air flow is intensified and the northern polar vortex is expanded (Mayewski et al., 1990; Whitlow et al., 1992). Enhanced regional winter-like meteorological conditions therefore appear consistent with increased seasalt concentrations at both of these sites. Na^+ is the most conservative seasalt species in the Siple Dome and GISP2 records[2], and therefore provides the best single-species representation of changing seasalt aerosol concentration.

The onset of LIA conditions in the GISP2 Na^+ record at ~1400 AD is abrupt (within ~20 years; O'Brien et al., 1995; Fig. VII.2). The record implies that this was the most dramatic change in atmospheric circulation (O'Brien et al., 1995) and surface temperature conditions (Stuiver et al., 1995) in the last 4000 years. Siple Dome Na^+ values also began

to increase above the 1150-year mean at ~1400 AD[3]. It appears (Fig. VII.2) that LIA conditions began ~28 years earlier at Siple Dome than at GISP2[3]. This offset is close to the combined dating error of the two records at that depth (estimated to be 12-20 years). Therefore, while it is possible that the diffference is real, we conclude that changes in atmospheric circulation occured abruptly and synchronously in both polar hemispheres at ~1400 AD.

Both the Siple Dome and GISP2 Na^+ records contain significant decadal scale variability during the LIA. It appears that regional atmospheric circulation fluctuations were of similar magnitude and timing in both polar hemispheres[3]. In particular, from 1680-1730 AD Na^+ concentrations are high in both records. During this period summer temperatures were the lowest of the last 500 years in both the Northern and Southern Hemispheres (1579-1730 AD; Bradley and Jones, 1993), and GISP2 biannual summer and winter $\delta^{18}O$ records are the most negative (Stuiver et al., 1995). In addition, during this period vertical mixing in the oceans increased and sea surface temperatures decreased (Druffel, 1982). Instrumental records from England and Switzerland, however, indicate that temperatures were warmer in the early 1700's (Bradley and Jones, 1992). These records highlight that spatially variable temperature estimates are related to increased atmospheric circulation. The period 1680-1730 AD corresponds to the Maunder sunspot minimum (Fig. VII.2; Stuiver and Brazinus, 1989). The similarity in timing between significant events in each record is intriguing, however a mechanism linking them is unclear.

Further evidence that the ASL was a deep low during the LIA comes from an Antarctic Peninsula (Palmer Deep; 64°52'S, 64°13'W) magnetic susceptibility record (Leventer et al., 1996), which shows that ocean mixing depths increased and productivity decreased. Both are related to increased wind speeds beginning at ~1400 AD (Leventer et al., 1996). The marine core site is within the band of westerlies associated with the ASL (Cullather et al., 1996). In addition, an Antarctic Peninsula (Siple Station; 75°55'S, 84°15'W) ice core record indicates decreased microparticle concentrations during the LIA (Mosley-Thompson et al., 1990). Precipitation removes dust, therefore during times of stronger cyclonic activity, particle concentrations may decrease (Mosley-Thompson et al., 1990). Westerlies bring most of the air to Siple Station, thus the microparticle record is likely recording increased ASL strength during the LIA.

Ice core $\delta^{18}O$ records have been used to imply that during the LIA West Antarctica was warm while East Antarctica was cold (Mosley-Thompson, 1992). Analysis of modern meteorological conditions indicates that surface temperature anomalies are inverse between South Pole and Siple Station during times when atmospheric circulation increases (Rogers, 1983). Storm activity at a particular site is generally associated with warmer temperature,

so that during times of increased cyclonic activity tempearture (and $\delta^{18}O$ values) may increase at sites heavily influenced by marine air masses such as the Antarctic Peninsula and portions of West Antarctica (Mosley-Thompson et al., 1990).

Enhanced zonal and meridional circulation in the polar regions during the LIA may also have impacted mid- and low- latitude circulation. Stine (1994) provided evidence that precipitation increased (vegetation submergence) at ~1400 AD in California and Patagonia, possibly caused by shifts in the latitude belt of the westerlies. African lake level and diatom records (Stager et al., 1997) and equatorial ice core dust records (Thompson et al., 1986) suggest that aridity and wind speeds increased there during the LIA, related to increased zonal circulation. Changes in Sargasso Sea surface temperatures, salinity, and nutrient pumping have been linked to stronger westerlies and south-westward shifts in storm tracks during the LIA (Keigwin, 1996).

In searching for the cause of the LIA, we see no direct connection between LIA atmospheric circulation and insolation at this time. Insolation (Berger, 1978) at site latitudes is opposite in trend over the past 1200 years, and changes occurring just before and during the LIA are small. The LIA contains the most recent period of low solar output (Maunder, Sporer, and Wolf solar activity minima triple event [T_4]; Stuiver and Brazinus, 1989; Fig. VII.2). T_4, however, began at ~1300 AD, ~100 years before the onset of LIA conditions in our Na^+ records. CO_2 decreased 6 ppb in the Law Dome, Antarctica, ice core between 1550 and 1800 AD (Fig. VII.2), which, based on modeling results, would produce a global cooling of 0.13-0.21°C (Sytkus et al., 1994; Etheridge et al., 1996). Estimates of LIA cooling (Grove, 1988) are an order of magnitude greater (1-2°C), and the LIA started ~150 years earlier (Fig. VII.2). Major volcanic activity evidently did not increase in the last 600 years (Zielinski et al., 1994; Langway et al., 1995). Only two major volcanic events are recorded in the Siple Dome and GISP2 $xsSO_4^{2-}$ records, the 1815 AD Tambora and 1259 AD eruptions (Fig. VII.2). Thus, no single factor appears to be responsible for bipolar changes during the LIA. Therefore it likely involved complicated and non-linear interactions of a number of forcing mechanisms acting together.

CONCLUSIONS

While the gradual atmospheric warming during the 20th century (~0.5°C) is almost certainly linked to anthropogenic activity (Hansen and Lebedeff, 1988; Santer et al., 1996) and provides a definite end to LIA cooling (Grove, 1988), other components of the climate system may still be responding to LIA perturbations. As evidence, Sargasso Sea and Santa Barbara Basin surface temperatures have not fully recovered from LIA minima (Kennet and

Ingram, 1995; Keigwin, 1996). In our records, Na^+ levels in modern (20th century) sections of each core are within the range of variability observed during the LIA[4] (Fig. VII.2) Regardless of the date chosen for its termination, the LIA is one of the shortest cold intervals of the last 110,000 years (Yang et al., 1997), and significantly shorter than some other major Holocene rapid climate change events (O'Brien et al., 1995). We suggest it is possible that, in terms of polar atmospheric circulation, conditions common during the LIA may have persisted into the 20th century and may still persist.

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CHAPTER NOTES

[1]High-resolution (2cm intervals for the upper 24m of core [~8-10 samples/year]; 25cm intervals for 25-150m core depth [~0.5 samples/year]) core samples were processed using contamination-free techniques, and analyzed for major ion content (Na^+, Mg^{2+}, K^+, Ca^{2+}, NH_4^+, Cl^-, NO_3^-, SO_4^{2-}, and methanesulfonic acid [MSA]) by ion chromatography similar to procedures described in Buck et al. (1992). Annual layer counting of the Siple Dome core was accomplished using a combination of discrete and continuous (Cl^-, NO_3^-, and liquid conductivity) chemical measurements, stratigraphic layer analysis, and marker horizons (radioactive bomb layers and volcanic events).

[2]We employ an iterative process model to determine the most conservative (limiting) species (O'Brien et al., 1995). The limiting ion is then used to derive estimated seasalt and nonseasalt concentrations for each seasalt species. The model assumes no chemical fractionation occurred during seasalt aerosol formation and transport (e.g., E.J. Hoffman et al., 1977), so that, if anything, this model underestimates the seasalt contribution. Estimated marine source species confirm that the majority of Na^+ in the GISP2 (>70%; O'Brien et al., 1995) and Siple Dome (>85%) records is derived from seasalt.

[3]To investigate the increasing trend through the entire 1150-year Siple Dome Na^+ record, we used 5 and 10-bit moving step-wise linear regression trend analyses. The largest change in slope occurs at 1389 AD, which we interpret as significant changes in atmospheric circulation associated with the onset of the LIA. Likewise, the largest change in slope in the GISP2 Na^+ record occurs at 1408 AD. The first 2σ increase in Na^+ above the Siple Dome 1150-year mean and GISP2 1200- year mean occurs at 1399 AD and 1427 AD, respectively. Na^+ coefficient of variation estimates for the LIA period (1400 AD-present) are 0.17 (Siple Dome) and 0.21 (GISP2).

[4]Average surface snow Na^+ values (covering 1990-1995) from 5 Siple Dome snowpits range from 103.27-163.3 ppb (Kreutz and Mayewski, in press), or ~40% above pre-LIA values. Analysis of the high-resolution Siple Dome upper core (~5-10 samples/year) reveals no distinct trend in atmospheric circulation over the past 110 years (Kreutz and Mayewski, in press). Modern GISP2 Na^+ concentrations are also significantly (at least a factor of 2) greater than pre-LIA values (O'Brien et al., 1995; Mayewski et al., 1990).

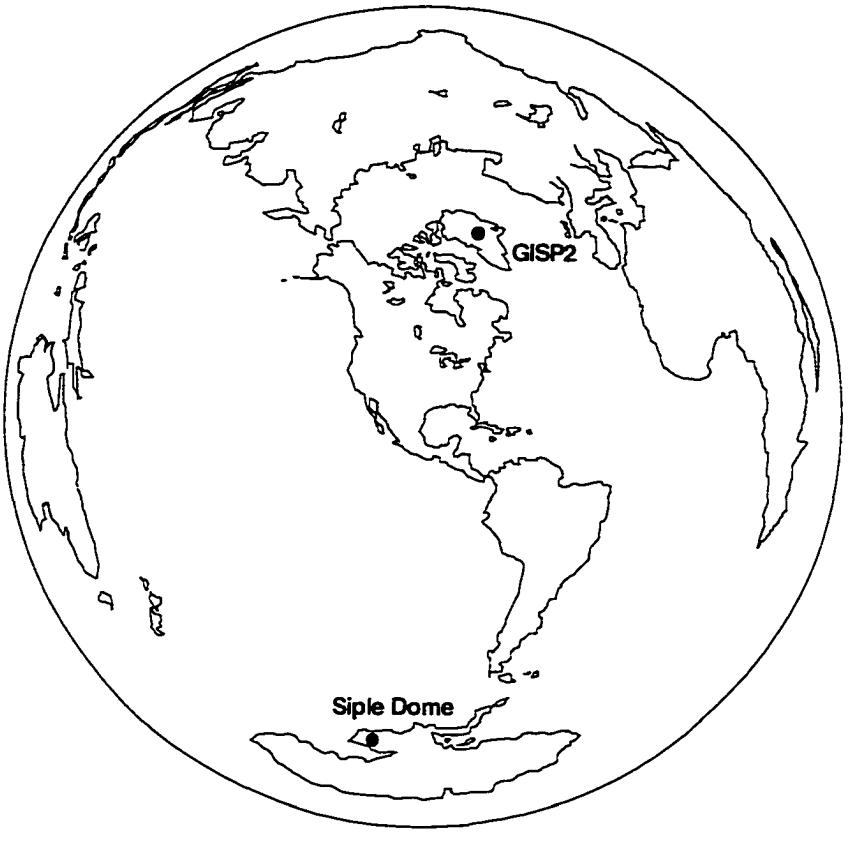

Figure VII.1. Location map for Siple Dome (Antarctica) and GISP2 (Greenland) ice cores.

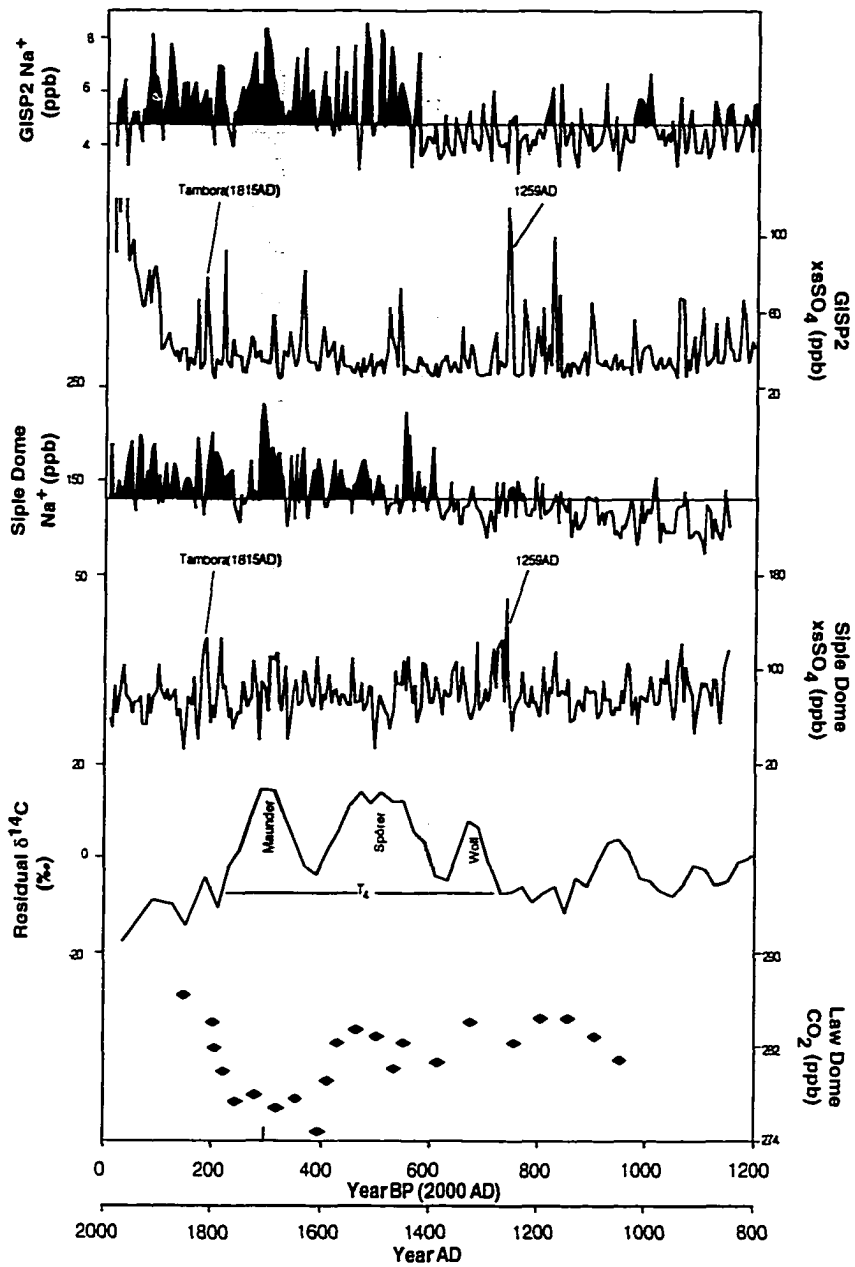

Figure VII.2. Comparison of GISP2 (Greenland) and Siple Dome (West Antarctica) ice core records with climate forcing factors. The GISP2 (Zielinski et al., 1994; O'Brien et al., 1995) and Siple Dome Na^+ and $xsSO_4^{2-}$ (in parts per billion) are in 5-year intervals. Two time periods are highlighted: 1680-1730 A.D. (period of coeval increase in Siple Dome and GISP2 records) and 1399 to 1427 A.D. (onset of Little Ice Age conditions). Two prominent volcanic events (as indicated by increased $xsSO_4^{2-}$ deposition) at 1815 A.D. (Tambora) and 1259 A.D. are used to confirm annual dating in both cores. The obvious $xsSO_4^{2-}$ increase during the last century in the GISP2 record, attributed to anthropogenic emissions, is notably absent from the Siple Dome $xsSO_4^{2-}$ record.

VIII. CONCLUDING REMARKS

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The research and results presented in this dissertation represent the first calibrated ice core glaciochemical proxy record of atmospheric circulation from Antarctica, and more specifically provide the first high-resolution documentation of Late Holocene climatic variability in West Antarctica. As such, this dissertation makes a significant contribution to the stated goal of the International Geosphere-Biosphere Program (IGBP) to understand the last 2000 years of climatic history. The most recent Holocene rapid climate change event, the Little Ice Age (LIA), is for the first time shown to exist in the high-latitude Southern Hemisphere, at least in terms of atmospheric circulation. A comparison with a record of polar North Atlantic atmospheric circulation conditions suggests a synchronous onset of LIA conditions in the two regions. Examination of potential climate forcing factors reveals no single cause which would explain the observed atmospheric changes, and instead suggests that a more complex interaction of several factors is likely involved. This finding highlights the need for a vastly improved spatial coverage of high-resolution records from the Southern Hemisphere.

While results from Siple Dome can be correlated to changes in the Amundsen Sea Low (ASL), and likely are recording conditions in an area broader than just Siple Dome itself, it is unclear how broad this region is. Indeed, even with the results presented here from Siple Dome and Inland West Antarctic snowpits and cores, our understanding of glaciochemical variability in both a spatial and temporal sense in West Antarctica is limited. This sparse data coverage provides much of the impetus for the U.S. component of the International Trans-Antarctic Scientific Expedition (ITASE). The ITASE program will collect ~40 new high-resolution ice core records from West Antarctica during ground-based sampling in 1999-2001. These 200-year long records will add substantial data and knowledge to West Antarctic research. The results presented here contribute significantly to the goals of ITASE. First, a major objective of the ITASE program is to link remote sensing information with ground-based observations. This dissertation contains two examples of such comparisons in West Antarctica, namely between isotopic composition and surface brightness temperature and between glaciochemical concentrations and sea-ice extent. Second, meteorological observations from AWS stations, satellite observations, and forecast models, will play an important role in investigating mesoscale processes in West Antarctica. By the end of the ITASE sample collection, processing, and analysis, the

observational record in West Antarctica will span ~25 years. While this period is still short relative to other regions in the Northern hemisphere, the number, length, and quality of records available will be much greater than what is available at this time. As the ultimate goal of ITASE is to calibrate ice core records to observational data so that climate processes of the last 200 years can be reconstructed in great detail, the methods developed in this dissertation provide an initial road map for achieving this goal.

While the ITASE program seeks an improved spatial understanding of the last 200 years of environmental change in West Antarctica, the U.S. WAISCORES program aims to investigate climatic change in West Antarctica over the last ~150,000 years. On a global scale, a second goal of the WAISCORES program is to produce ice core records of similar length and quality to those recovered from Summit, Greenland, in hopes of determining the global existence, timing, and phasing of rapid climate change events. As with the ITASE program, the results of this dissertation contribute significantly to the WAISCORES program. At Siple Dome (the site of the first WAISCORES deep core, drilling scheduled to be completed during the 1998/99 field season), a major concern is dating accuracy for larger comparisons. Conditions at Siple Dome (relatively high mean annual temperatures and low accumulation rate) lead to ambiguous dating results based on 'classic' isotopic and stratigraphic techniques. This study demonstrates, however, that glaciochemical signals can be used to accurately identify annual layering at Siple Dome. Therefore, the basis for high-resolution environmental interpretations at Siple Dome may be dependent upon depth/age scales derived mainly from glaciochemical measurements. It is possible that annual layers may be able to be resolved over the entire Holocene from the Siple Dome deep core. If so, periods of Holocene rapid climate change events noted in the Northern Hemisphere (O'Brien et al., 1995) can be investigated with dating confidence in the Southern Hemisphere. This examination of LIA conditions in West Antarctica and Greenland presented in this dissertation provides the first example of such comparisons. Site selection for deep drilling in Inland West Antarctica is underway, and glaciochemical results from the three IWA core presented here can help in the selection. Based on glaciochemical concentrations and accumulation rate estimates, there are steep gradients in moisture transport into and through Marie Byrd Land. A long-term record of this moisture flux into West Antarctica (and the rest of the continent), as well as changing conditions in the Amundsen and Bellingshausen Seas, will complement the deep core record from Siple Dome. In addition, results presented here suggest that the inland deep core will add crucial information about upper atmospheric processes (due to the higher elevation of the Inland site) over the past ~150,000 years.

Although the results of this dissertation contribute to the ITASE and WAISCORES programs, much can be learned from further investigation of the existing Siple Dome and IWA datasets. In particular, the high-resolution ice core data is particularly well-suited for time-series analysis, which can be used to investigate periodic climate forcing factors in the region (see Appendix A). New high-resolution ice core records from South Pole (Meyerson et al., in prep.), Central West Antarctica (Reusch et al., in review), and Taylor Dome (e.g., Mayewski et al., 1996) can be compared to Siple Dome and IWA records to investigate Late Holocene climate variability on a regional scale in Antarctica. In addition, development of proxy records using other chemical species holds promise. MSA concentrations in snow and firn from Newall Glacier, Antarctica, have been linked to sea-ice extent (Welch et al., 1993). Although MSA is shown here to migrate in West Antarctic cores, the records may still be used to reconstruct sea-ice extent changes on a interannual basis. While much work is yet to be done before ice core NO_3 concentrations can be used to accurately reconstruct atmospheric NO_y concentrations (Dibb et al., 1998), existing data NO_3 data presented here can be used to investigate longer-term changes in the N cycle in West Antarctica. Finally, a detailed chronology of volcanic SO_4 deposition in West Antarctica can be derived from these records. Such a chronology would not only add to the understanding of past volcanic impacts on climate, aerosol optical depth, and spatial gradients in SO_4 flux, but also provide known stratigraphic horizons for dating purposes.

In summary, this dissertation demonstrates that through extensive reconnaissance, high-resolution sampling and analysis, and the use of the entire suite of observational data, calibrated ice core glaciochemical records can be used to reconstruct past atmospheric circulation conditions in West Antarctica. Such reconstructions have demonstrated the existence of the latest Holocene rapid climate change event, the LIA, in West Antarctica, and highlight the need to consider all aspects of the climate system (i.e., temperature, precipitation, and atmospheric circulation) when interpreting past environmental change. Further, comparison of West Antarctic and Greenland records suggests that atmospheric circulation conditions common during the LIA may have persisted into the 20th century, despite an obvious end to the LIA in terms of temperature. This finding has several potential implications: 1) increased atmospheric circulation, storminess, and precipitation observed in mid- and high latitudes of the Northern and Southern Hemispheres during the last ~40 years may be due in part to natural climatic fluctuations; 2) incorporating the relative magnitudes and spatial and temporal evolution of different natural forcings (particularly indirect aerosol effects) remains a challenge for climate modelers, and will be even more difficult if atmospheric circulation variability associated with the LIA has to be considered; and 3) if LIA-type circulation conditions do persist, then it is all the more likely

that anthropogenically-induced greenhouse warming during the 20th century has artificially ended LIA-cooling, and may in fact be underestimated. Therefore, decadal-scale atmospheric circulation variability suggested by these records could potentially be detracting from or reinforcing anthropogenic effects during this century, and may serve to amplify future forcings in unforeseen ways. Therefore, the results of this study reinforce the basis for undertaking any paleoclimatic investigation: To fully understand climatic change, the influence of human activity, and to predict future climate, investigation of both modern and past climate is essential.

COMPLETE LIST OF REFERENCES

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APPENDIX A

PERIODIC COMPONENTS OF SIPLE DOME AND RIDSA GLACIOCHEMICAL RECORDS OVER THE LAST 500 YEARS: PALEOCLIMATIC IMPLICATIONS

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INTRODUCTION

Glaciochemical signals deposited on polar ice sheets are a result of a series of production, transport, deposition, and post-depositional processes. These processes are all subject to the complex response of the Earth's non-linearly coupled climate subsystems (atmosphere, lithosphere, cryosphere, hydrosphere, and biosphere) to stationary, non-stationary, and random processes.

In addition to periodic components related to primary driving forces, glaciochemical records may describe almost periodic behavior on a variety of timescales, temporal variations in stochastic processes, and long-term unpredictability (Meeker et al., 1995). Therefore, statistical dissection and description of glaciochemical records can be used to investigate the contribution of various periodic forcings to the overall variance of the record. Such time-series analyses on the GISP2 glaciochemical dataset have documented periodic behavior of both the atmosphere and biosphere (Mayewski et al., 1997; Meeker et al., 1997).

Several processes acting in the high latitude Southern Hemisphere are known to affect components of the climate system on interannual to decadal scales. A signal of the largest global source of interannual climate variability, the El-Nino Southern Oscillation (ENSO), has recently been found in Antarctic meteorological records (Smith and Streams, 1993). As noted in Chapter VI, a link has also been proposed between ENSO and the Amundsen Sea Low (ASL; Cullather et al., 1996). This link has been shown to affect the transport of moisture into West Antarctica on interannual timescales (Cullather et al., 1996). In addition, periodic structure on ENSO timescales (4-5 years) has also been noted in sea-level pressure, sea-surface temperature, sea ice extent, and meridional wind stress (the Antarctic Circumpolar Wave [ACW] of White and Petersen, 1996). On longer timescales, accumulation rate variability from several Antarctic locations (South Pole, Dome C, Wilkes and South Ice Point) has been linked to sea-level pressure (SLP) variability in the 40-50°S latitudinal zone (Enomoto, 1991). Long-term SLP fluctuations in this zone are likely

related to zonal fluctuations with wave number zero structure. The temporal scales for these SLP fluctuations were found to be 20-30 years and 40-60 years, which was correlated to similar periodicities found in the accumulation rate records.

The new, high-resolution ice core glaciochemical records presented in this dissertation offer the possibility to extend estimates of these periodic forcings prior to the instrumental coverage. EOF1 and accumulation rate records from Siple Dome have been linked to SLP conditions in the Amundsen Sea (Chapter VI) and moisture flux into the region (Chapter IV). EOF1 and accumulation rate records from RIDSA are likely affected by similar processes, and therefore may be expected to provide complementary information on the periodic processes acting in West Antarctica. Therefore, this appendix contains preliminary analyses of EOF1 and accumulation rate records from Siple Dome and RIDSA. The EOF1 record is analyzed in two ways, based on sample resolution: 1) Annual EOF1 records spanning the past 110 years at Siple Dome and 160 years at RIDSA; and 2) Biannual EOF1 records at both sites spanning the past 500 years (the period of common overlap in both records). Annual accumulation rate records of the past 500 years are analyzed from both sites.

SPECTRAL PROPERTIES OF SIPLE DOME AND RIDSA EOF1 RECORDS

To establish dominant periods in which variance occurs over the past century in the Siple Dome annual EOF1 record, we employ spectral analyses using modified discrete Daniel smoothing (Meeker *et al.*, 1995). The 95% and 99% red noise critical values are estimated by 15 simulation runs of a Markov process with lag-1 autocorrelation of the time-series. Figure A.1a and Table A.1 show the power spectrum for the Siple Dome EOF1 record. A large portion of the variance is concentrated at higher frequencies. Peaks that exceed the 95% confidence limit occur at 3.4 and 7.0 years. Because these periods are less than 10 times the sample interval, we tested for significance using a Fisher's test of the un-padded spectrum. Again, peaks at 3.3 and 7.0 years are significant at least the 95% confidence level. As a further test, identical analyses were performed on 12 sample/yr resampled EOF1 series (close to the resolution of the original raw series) and yielded the same 3.3- and 7.0-year components. As the both these peaks are known periodicities in the Southern Oscillation Index (SOI), cross-spectral analysis of EOF1 and the SOI during the interval 1890-1994 was performed. Results show coherent peaks at 4-5 and 14-15 years.

Figure A.1b and Table A.1 show the dominant periodicities in the RIDSA annual EOF1 record. As in the Siple Dome EOF1 record, significant periodicities are present in the 3-7

year range, suggesting the possible influence of the Antarctic Circumpolar Wave (and possibly ENSO) on the transport of seasalt aerosols into both regions of West Antarctica. This may provide further support for a physical mechanism linking the ASL to interannual variability in lower latitudes (Chen et al., 1996; Cullather et al., 1996). The RIDSA annual EOF1 record contains a strong component at ~11 years. While this might suggest a possible association with the known 11-year sunspot cycles, a physical explanation to connect aerosol transport and the sunspot cycle remains to be explored. Somewhat weaker periodicities occur in the RIDSA annual EOF1 record at ~19, 29, and 42 years. Possible explanations include decadal-scale variability associated with ENSO (Mann and Park, 1994), and SLP variability noted by Enomoto (1991).

Spectral analysis of biannual EOF1 records from Siple Dome and RIDSA are presented in Figure A.2 and Table A.1. Common periodicities are confined to the 40-60 year interval, again suggesting an association with SLP fluctuations noted by Enomoto (1991). Variability in the range is particularly strong in the RIDSA record.

SPECTRAL PROPERTIES OF SIPLE DOME AND RIDSA ANNUAL ACCUMULATION RATE RECORDS

Spectral analysis of annual accumulation rate records from Siple Dome and RIDSA are presented in Figure A.3 and Table A.1. Variability in the Siple Dome record appears to be confined to a periodicity of ~5 years. This may be due in part to the relatively low accumulation rate at Siple Dome, but is consistent with interannual control on moisture flux to Siple Dome by changes in the strength and position of the ASL (Chapter IV). In contrast, the RIDSA record contains significant variability over a much larger periodic range. As in the Siple Dome record, the RIDSA record contains significant periodicities in the 3-7 year range, again suggesting the possible influence of ACW and ENSO forcings. The RIDSA record also contains significant periodicities in the 20-30 and 40-60 year range, and suggests the influence of SLP variability in the 40-50°S latitude range noted by Enomoto (1991).

SUMMARY

A preliminary assessment of the periodic components of the Siple Dome and RIDSA EOF1 and accumulation rate records suggests associations between periodic variability in the records and known climatic forcing mechanisms. In particular, interannual variability in the EOF1 and accumulation rate records suggests that the ACW and possibly ENSO

systems may have an influence on aerosol transport and moisture flux into both regions. Lower frequency periodicities (20-60 years) in the records may be related to SLP variability in higher latitudes (40-50°S). To investigate these relationships further, the various periodic components will be extracted from the EOF1 and accumulation rate records, and compared to the periodic structure of the Southern Oscillation Index, SLP records from mid-latitude stations (i.e., New Zealand and Hobart), and records used to define the ACW (SLP, SST, sea-ice extent, and meridional wind stress).

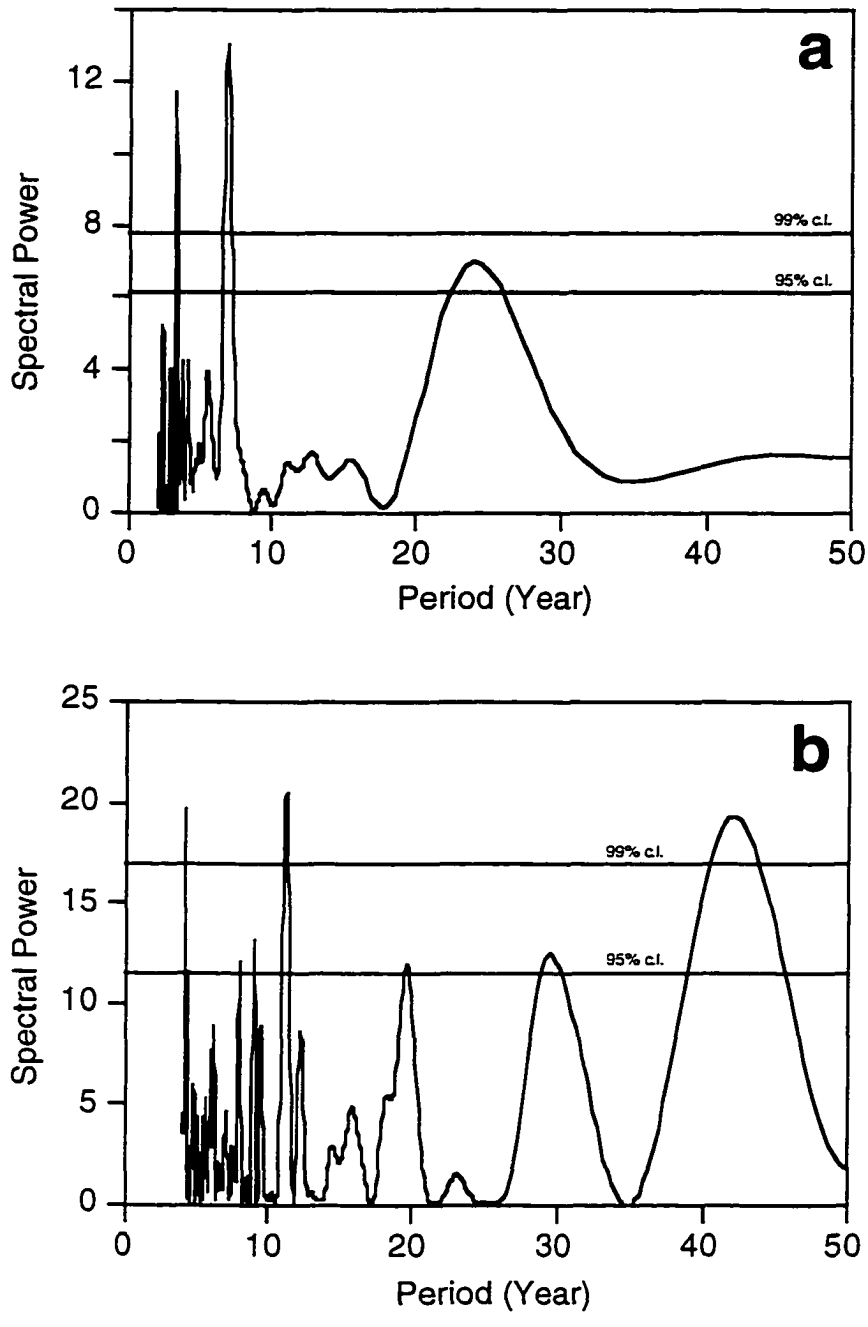


Figure A.1. Estimated spectra of the mean annual EOF1 records from (a) Siple Dome (1890-1994) and (b) RIDSA (1829-1995) cores.

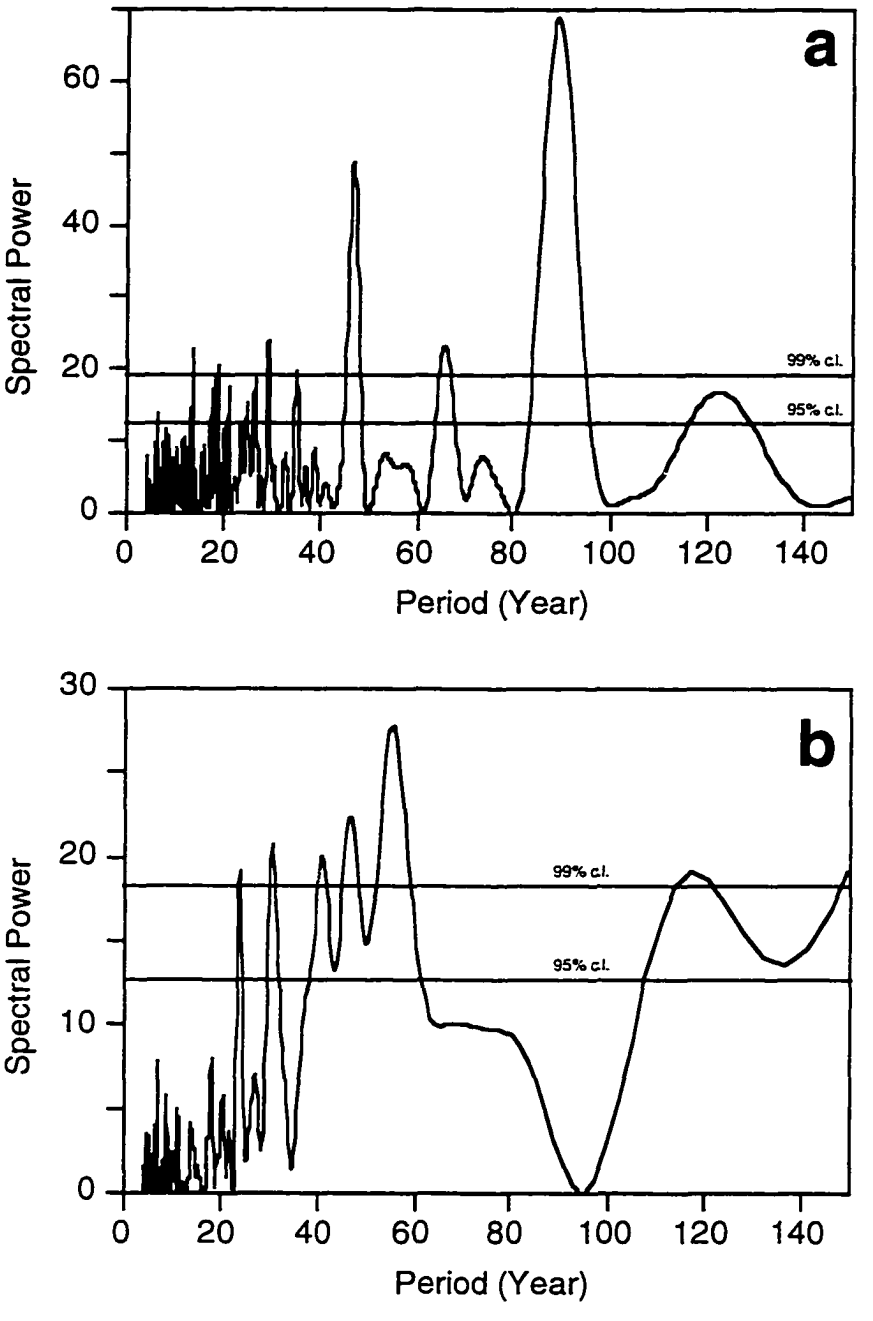


Figure A.2. Estimated spectra of biannual (500 year) EOF1 records from (a) Siple Dome and (b) RIDSA cores.

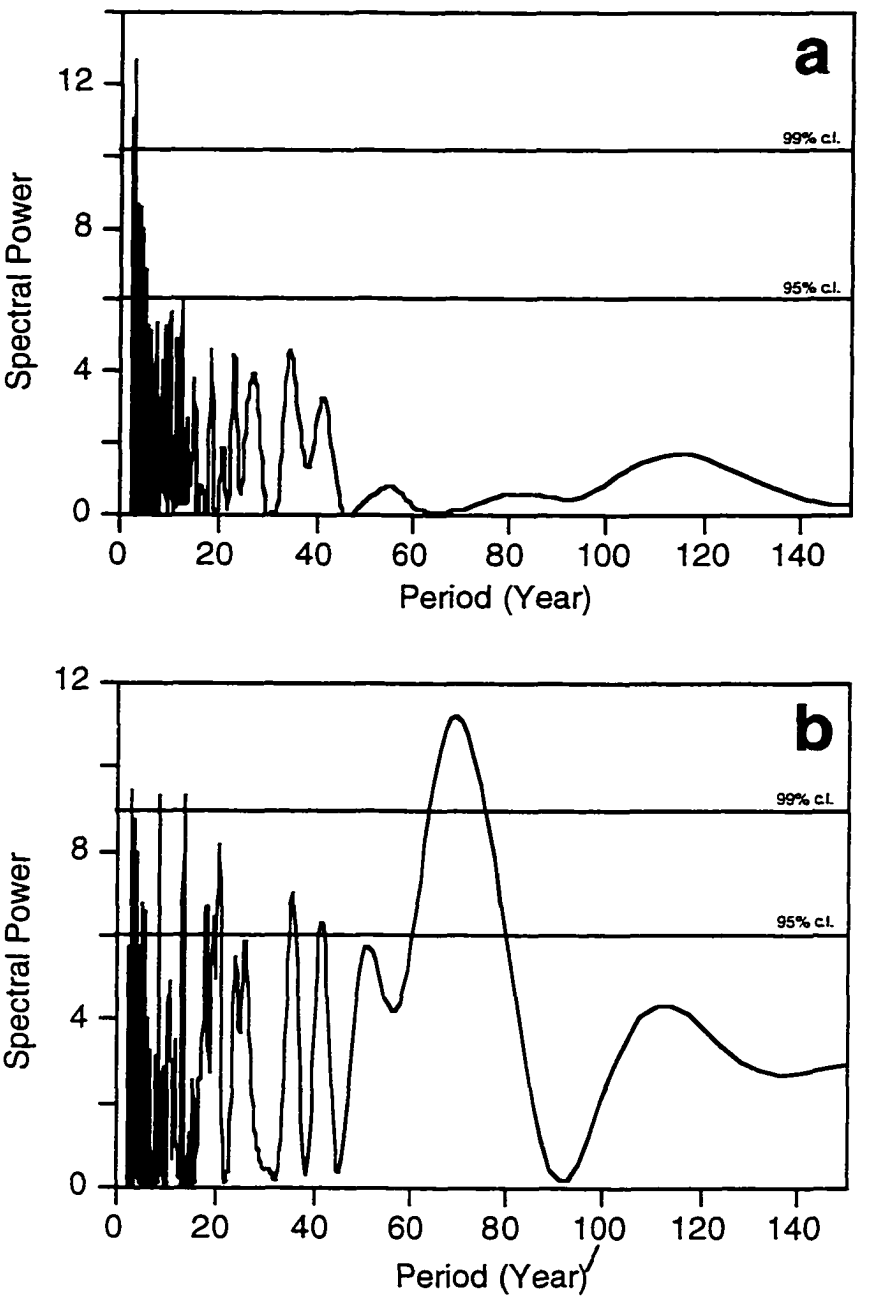


Figure A.3. Estimated spectra of annual accumulation rate records (500 years) from (a) Siple Dome and (b) RIDSA cores.

EOF1 (Summary of seasalt species variance)

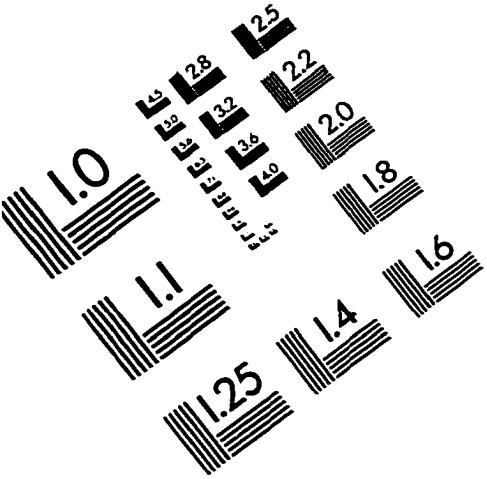
Siple Dome		*RIDSA*	
Annual (110 Years)	Biannual (500 Years)	Annual (160 Years)	Biannual (500 Years)
24	89	43	116
7	65	29	55
3.4	47	19	46
	35	10	41
	29	5.6	30
	26	4.5	24
	24	4	
	20		
	18		
	17		
	13		
	6		

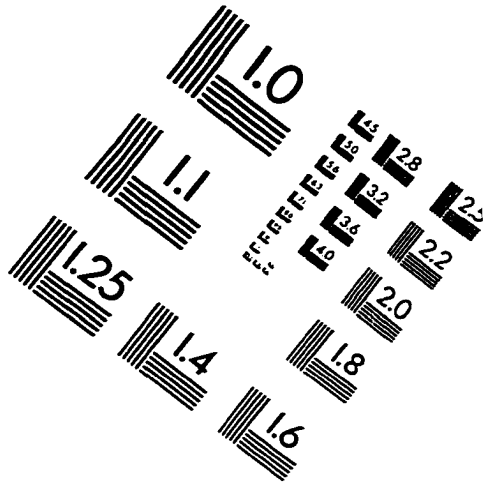
Accumulation Rate

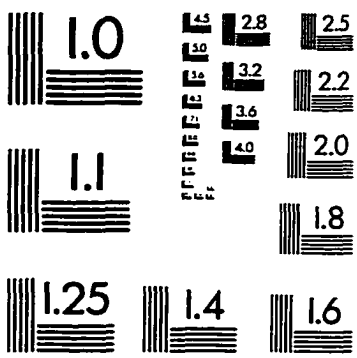
Siple Dome	*RIDSA*
Annual (500 Years)	Annual (500 Years)
12	69
5.32	41
	35
	20
	14
	8
	5.5
	3.7

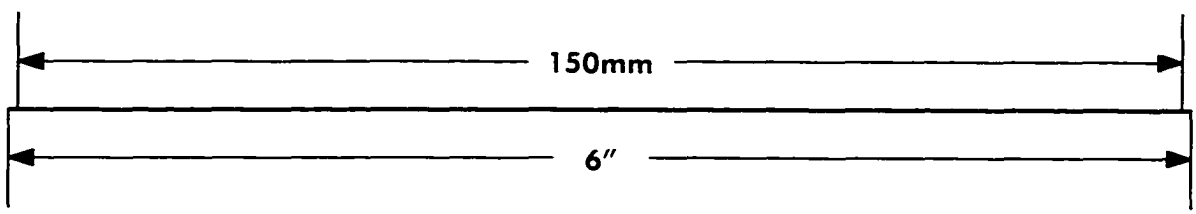
Table A.1. Summary of periodic components (in years) above the 95% c.l. in the Siple Dome and RIDSA cores. Annual EOF1 series are dervived from high-resolution (8-10 samples/year) data.

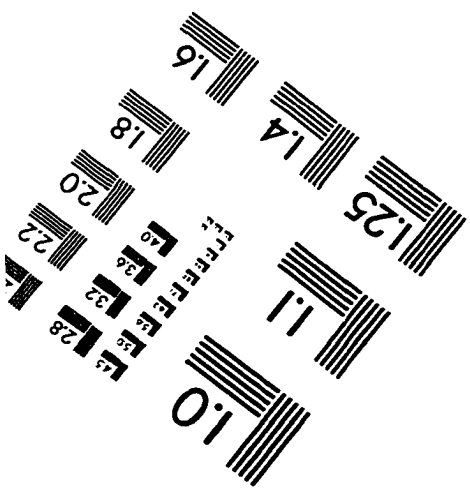
IMAGE EVALUATION TEST TARGET (QA-3)

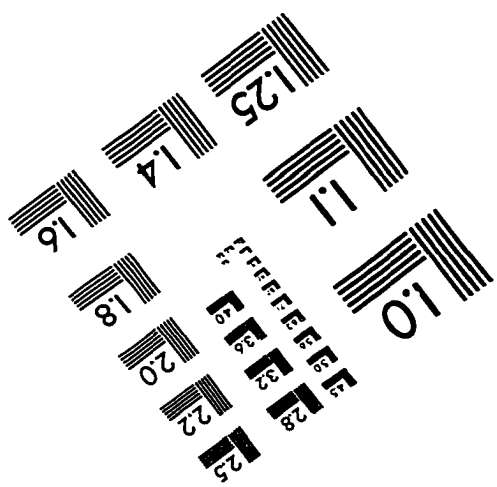












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