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STABLE SULFUR ISOTOPE RATIOS ($\delta^{34}S$) FROM WEST ANTARCTICA AND THE TIEN SHAN MOUNTAINS: SULFUR CYCLE CHARACTERISTICS FROM TWO ENVIRONMENTALLY DISTINCT AREAS

By

Lee Pruett

B.A. University of Chicago, 1999

A THESIS

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Advisory Committee:

Karl Kreutz, Assistant Professor of Geological Sciences and Quaternary and Climate Studies, Advisor

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STABLE SULFUR ISOTOPE RATIOS ($\delta^{34}S$) FROM WEST ANTARCTICA AND THE TIEN SHAN MOUNTAINS: SULFUR CYCLE CHARACTERISTICS FROM TWO ENVIRONMENTALLY DISTINCT AREAS

By Lee Pruett

Thesis Advisor: Dr. Karl J. Kreutz

An Abstract of the Thesis Presented
in Partial Fulfillment of the Requirements for the
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Continuous snow pit and ice core samples from two distinct environments (West Antarctica and the Tien Shan mountains in central Asia) were analyzed for $\delta^{34}S$ and used to assess different regional sulfur cycle characteristics. In West Antarctica, 18 continuous samples were obtained from the RIDSA ice core (78.73°S, 116.33°W, 1740 m asl), covering the years 1935 to 1976. Each sample represents from 2 to 3 years of snow deposition, and the combination of summer and winter seasons varies by sample. $\delta^{34}S$ values range from 3.1‰ to 9.9‰, and reflect the overall isotopic composition of precipitation in West Antarctica during non-eruptive times as well as global volcanic events. There is no apparent change in $\delta^{34}S$ due to the sulfate (SO_4^{2-}) from a global volcanic event (1963 Agung eruption), indicating that the $\delta^{34}S$ is independent of SO_4^{2-} concentration and may not be perturbed by all large eruptions. The $\delta^{34}S$ value of each sample represents a combination of SO_4^{2-} with sources including marine biogenic (18 to 20‰), sea salt (21‰), and volcanic (~0‰). Given the relatively large input of marine

aerosols at RIDSA (determined from Na^+ data and the seasonal SO_4^{2-} cycle), there is a large marine biogenic SO_4^{2-} influence. Because the $\delta^{34}S$ values from the RIDSA dataset are all well below those predicted for SO_4^{2-} with a purely marine biogenic source, another SO_4^{2-} source with low (<0‰) must be involved.

In Central Asia, continuous samples from a 2 m deep snow pit were collected from the Inilchek Glacier, Kyrgyzstan (42.16° N 80.25° E, 5100 m asl). Based on the snow pit $\delta^{18}O$ profile, these samples represent only the summer or possibly the spring/summer 1999 season. There is a good correlation (r=0.87) between concentration and $\delta^{34}S$, with $\delta^{34}S$ values ranging from 19.4‰ during times of high SO_4^{2-} concentration (>26 μeq/L) to 0.4‰ during times of low SO_4^{2-} deposition (<1 μeq/L). This relationship illustrates the influence of both dust storms (caused by an increase in vertical convective transport) and anthropogenic inputs on the regional sulfur cycle. Anthropogenic emissions are the source of the background SO_4^{2-}, with changes in isotopic signature occurring with dust deposition. Overall, anthropogenic emissions contributed 43% of the SO_4^{2-} while dust sources contributed 57%.

These two datasets provide insight into the strengths and limitations of applying sulfur isotopes to ice core studies. $\delta^{34}S$ measurements can be used to partition and estimate relative SO_4^{2-} source contributions in individual samples, and thus provide better estimates of the impact of the sulfur cycle on climate and ecosystems. The isotope ratio mass spectrometer (IRMS) techniques used in this study require large sample volumes (100 μg of S) and thus limit the sample resolution possible in typical ice core locations. New methods of $\delta^{34}S$ analysis via inductively coupled plasma mass spectrometry (ICP-MS) show promise, with high (0.09 RSD) precision $\delta^{34}S$ analysis with sample concentrations of SO_4^{2-} as low as 1 ppb. ICP-MS analysis may allow high-resolution (sub seasonal) $\delta^{34}S$ ice core data to be routinely produced from remote polar and alpine regions.

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1. INTRODUCTION

The sulfur cycle has a critical impact on many earth systems. Sulfur is an important component of plants because it is necessary to synthesize proteins (Noggle, 1980). Sulfur exists primarily as sulfate (SO_4^{2-}) in rivers, oceans and the atmosphere and is the major cause of acidity in both natural and polluted environments (Charlson *et al.*, 2000). The weathering of rocks responds to changes in the sulfur cycle, as do cloud properties. Sulfate is the dominant component of cloud condensation nuclei (Bigg *et al.*, 1984). Perhaps the most important impact of SO_4^{2-} on the climate system is the interaction with clouds and the hydrologic cycle (Ramanathan *et al.*, 2001). The sulfur cycle is the major elemental cycle most altered by human activity, and therefore is an important area of study (Charlson *et al.*, 2000). Studying the atmospheric component of the sulfur cycle can yield much information about background SO_4^{2-} conditions as well as the extent of the anthropogenic influence. This information can then be used to assess the climatic effects of atmospheric SO_4^{2-}.

The Earth's climate is controlled in part through atmospheric chemistry, with SO_4^{2-} playing a major role in the aerosol effect on climate (Warneck, 1988). Aerosol particles in the air scatter atmospheric radiation. Aerosols affect Earth's climate through both direct and indirect methods (Charlson, 2000). As suspended particles, aerosols participate in direct radiative forcing by reflecting incoming radiation. Aerosols indirectly affect radiative properties by interfering with the formation mechanisms and precipitation efficiency of clouds. Because the aerosol is not directly interfering with incoming radiation, but rather affecting properties of clouds (which in turn affect incoming radiation), this effect is considered secondary. Perhaps the most important factor governing the climatic effect of the SO_4^{2-} aerosol is the way in which it formed.

Sulfate aerosols are classified as either primary or secondary aerosols depending on whether or not any transformation occurs after emission (Prospero *et al.,* 1983). Primary aerosols are those that are emitted and undergo no chemical transformation. These aerosols remain in the same form (SO_4^{2-}) throughout their lifetime and include, for example, sea salt and evaporite gypsum ($CaSO_4 \bullet 2H_2O$) dust. Secondary SO_4^{2-} aerosols are formed from precursor gases that interact with other atmospheric constituents to form particles. Volcanic sulfur emissions are normally as SO_2 and undergo oxidation only after ejection into the atmosphere (Stoiber *et al.*, 1987). Primary aerosols are generally coarse particles (>1µm), whereas finer particles (<1µm) are normally secondary aerosols. If this transformation occurs in an aqueous phase, or heterogeneous oxidation, then the SO_4^{2-} aerosol forms on a pre-existing particle and normally does not add to the total number of aerosols, but instead to the aerosol mass (McMurry and Friedlander, 1979). Gas-phase, or homogeneous production, of SO_4^{2-} aerosols results in the formation of new aerosol particles that contribute to the total aerosol concentration.

The distribution of aerosol mass relative to aerosol size determines the extent to which pollution effects occur (Schwartz, 1996). Aerosols in the accumulation mode (dry diameters between 0.1 and 1 µm) are the most important to radiative forcing because they can hydrate to between 0.1 and 2 µm, which is the range where aerosols scatter the most light per unit mass. The effect that secondary aerosols have on climate also varies depending on concentration, vertical distribution, and transport. The major contributors to secondary atmospheric SO_4^{2-} aerosols include volcanic emissions, H_2S from anoxic bottom waters, H_2S from sea marshes and intertidal flats, terrestrial biogenic emissions, marine biogenic emissions, and anthropogenic emissions (in various forms such as native sulfur, sulfide ores, coal and petroleum) (Nielsen, 1974).

The rate at which secondary SO_4^{2-} particles are formed depends in part on air temperature. For example, samples from Hubbard Brook Experimental Forest in New Hampshire were collected from July to December, 1980 and analyzed for concentrations of SO_4^{2-}, SO_2, and $\delta^{34}S$ (Saltzman *et al.,* 1983). Late summer-early fall samples had low SO_2 and high SO_4^{2-} concentrations, while late fall-early winter samples had high SO_2 and low SO_4^{2-} concentrations. These data indicate a seasonal trend with faster oxidation of SO_2 and consequently a higher concentration of SO_4^{2-} during warmer months. The lifetime of secondary aerosols is dependent on the time necessary for the aerosol to form, and the time for atmospheric transport and deposition of the aerosol. The atmospheric lifetime after aerosol formation is contingent on where the aerosol is traveling in the atmosphere and the rate of deposition. Tropospheric aerosols have a shorter lifetime than stratospheric aerosols because of continuous dry and wet deposition (Charlson *et al.*, 1992). Thus, the source greatly influences the atmospheric position and lifetime of SO_4^{2-} aerosols.

The extent to which the source strength and transformation mechanisms are known varies greatly, and therefore limits our understanding of climatic effects of SO_4^{2-}. The transformation from the precursor gas to SO_4^{2-} aerosols introduces uncertainty when estimating the amount of anthropogenic emissions (Graf *et al.,* 1998). Sulfur gas that is emitted from anthropogenic sources is released close to the ground and scavenged by rain and dry deposition before it is oxidized to the SO_4^{2-} aerosol, thereby eliminating its climatic effect (Charlson and Wigley, 1994). Volcanic emissions, though only one-fifth the volume of anthropogenic SO_4^{2-} emissions, are thought to have as powerful a radiative effect in the troposphere (Graf *et al.*, 1997). In addition, once in the stratosphere, little is lost to deposition and therefore the residence time of the aerosol is longer in stratospheric conditions.

An assessment of the climatic effect of SO_4^{2-} is hindered by several factors. For primary aerosols, the main limitation is knowing how much a source emits. Studies have been conducted to measure the emissions of sea salt particles in study areas around the world (O'Dowd and Smith, 1993; Quinn *et al.*, 1996; Murphy *et al.*, 1998). However, extrapolating this information to other regions is difficult due in part to the dependence of sea salt aerosol on wind speed, which is highly variable. Secondary aerosol effects are also difficult to assess due to uncertainties in source emissions. Additional uncertainties, which are as large as a factor of 2, arise when assessing the conversion of the precursor gas to SO_4^{2-} (Nyenzi and Prospero, 2002). The assessment of both primary and secondary aerosol effects is hampered by an insufficient understanding of the physical properties that are relevant to radiative forcing. With so many unknowns, the sulfur cycle is an important area of study. To better understand the relationship between the sulfur cycle and climate, it is essential to study the source strengths and temporal variations.

Stable sulfur isotopes ($\delta^{34}S$) have been used to investigate sulfur biogeochemistry (Patris *et al.*, 2000; Saltzman *et al.*, 1983; Castleman *et al.*, 1973). There are four stable isotopes of sulfur in nature (^{32}S, ^{33}S, ^{34}S, ^{36}S). ^{32}S is the most abundant, accounting for 95% of the sulfur isotopes found in nature. ^{34}S is the second most abundant, accounting for 4.2% (Thode, 1991). The most widely studied ratio is $^{34}S/^{32}S$ because it measures the two most abundant and thus easily measured isotopes. Isotope ratios are measured as $^{34}S/^{32}S$ in the sample relative to an international standard. This per mil value is represented as:

$$\delta^{34}S(‰)=\{[(^{34}S/^{32}S)_{sample}/(^{34}S/^{32}S)_{standard})]-1\}*1000$$

The standard is troilite from the Canyon Diablo meteorite (CDT), which is isotopically uniform.

Sulfur isotope fractionation occurs via two systems—equilibrium and kinetic (Faure, 1986). In systems in equilibrium, isotope exchange processes cause fractionation. In this system reactions proceeds in forward and backward directions to achieve equilibrium. These reactions generally have ^{34}S concentrating in the more oxidized species (Thode, 1991). Exchange processes are measured by evaluating the extent to which the equilibrium constant, K, differs from unity (1). When a system proceeds unidirectionally, it can undergo kinetic isotope effects. Fractionation in this system is due to reaction rate differences of the isotopes (^{32}S and ^{34}S). If the reaction is of first order and therefore undergoes only one transformation, then the fractionation factor is the ratio of rate constants. Generally, fractionation occurs only in this first step. Kinetic fractionation produces larger fractionation and is associated with biologically mediated processes. Dissimilatory reduction of SO_4^{2-} by bacteria strongly fractionates sulfur isotopes.

Natural variations in sulfur isotope abundances due to either equilibrium or kinetic fractionation are the basis for sulfur isotope studies. Ninety-eight percent of all samples analyzed for $\delta^{34}S$ fall within the range of –40 to 40‰ (Thode, 1991). Igneous rocks, granitic intrusions, meteorites and basic sills have $\delta^{34}S$ values around 0‰. Atmospheric sulfur has a variable concentration and isotopic composition of sulfur due to the differences between sources contributing to atmospheric sulfur. Sea salt SO_4^{2-}, for example, has a well-constrained present day $\delta^{34}S$ of 21‰ (Rees *et al.*, 1978). Coal emissions generally have $\delta^{34}S$ values between 0 and 5‰ (Krouse and Grinenko, 1991). Differences are due to incorporation in the biological sulfur cycle.

Sulfur isotopes were originally used to fingerprint SO_4^{2-} pollution sources (Pichlmayer *et al.,* 1998; Wadleigh *et al.,* 1996), monitor changes in the $\delta^{34}S$ of stratospheric air after a volcanic eruption (Castleman *et al.,* 1973), and identify possible contributors to SO_4^{2-} in precipitation (Patris *et al.,* 2000). After an eruption powerful enough to penetrate the stratosphere, the $\delta^{34}S$ of stratospheric air decreased from a positive value (~10‰) to as low as -28‰ (Castleman *et al.,* 1973). When sulfur isotopes were used in conjunction with back trajectories of air masses, slight variations in the isotopic composition of pollution source regions were identified (Pichlmayer *et al.,* 1998). These studies were useful because they illuminated transformation processes and source dispersal—two areas of uncertainty in assessing the sulfur cycle. Most studies are limited, however, in that they convey information only about the present conditions in specific regions. Other records are necessary in order to investigate the sulfur cycle over time.

Ice cores provide a unique archive with which to investigate past changes in the chemistry of the atmosphere (Legrand and Mayewski, 1997). At a given location, ice core chemistry can yield important information about regional atmospheric circulation patterns (Mayewski *et al.,* 1993; Mayewski *et al.,* 1994), globally teleconnected phenomena such as ENSO (Legrand and Feniet-Saigne, 1991; Meyerson *et al.,* 2002), and general changes in atmospheric chemistry (Mayewski *et al.,* 1986; Mayewski *et al.,* 1990), including those that have an impact on climate such as changes in the oxidative capacity of the atmosphere (Alexander *et al.,* 2002). The sulfur cycle is explored through ice cores typically by analysis of the SO_4^{2-} concentration and methanesulfonic acid (MSA) concentration (Saigne and Legrand, 1987; Legrand *et al.,* 1992; Legrand and Pasteur, 1998). This information is valuable because it reflects changes in SO_4^{2-} production and/or sulfur emissions. In general, however, there exists great uncertainty in SO_4^{2-} partitioning (Dibb and Whitlow, 1996). This is problematic because knowing the sources and emissions of SO_4^{2-} these sources produce from year to year is pertinent to paleo-climate assessment (Zielinski *et al.,* 1996).

Several methods are currently used to assess the sources of an ice core SO_4^{2-} record. The seawater ratio of a conservative sea-salt species (such as Na^+) to SO_4^{2-} ($Na^+/SO_4^{2-}= 0.251$) is used to separate sea-salt SO_4^{2-} from excess SO_4^{2-}. Statistical analysis using an empirical orthogonal function (EOF) can identify chemical associations. This method divides the time variance of the data into empirical eigenvectors. When ordered, these eigenvectors can explain the maximum amount of remaining variance in the data. When eigenvectors represent a large amount of the variance, they are thought to be physically significant and indicative of important processes (Peixoto and Oort, 1992). Another method, the R value (the ratio of MSA to excess (xs) SO_4^{2-}) is used in aerosol studies and ice cores as a tool for determining the biogenic component of total SO_4^{2-} (Arimoto *et al.,* 2001; Prospero *et al.,* 1991). In general, however uncertainty exists in SO_4^{2-} partitioning, especially in areas where little is known about the sulfur cycle, such as the high latitude Southern hemisphere.

Recent studies of sulfur isotopes in ice cores have provided useful information about the SO_4^{2-} production over time, thereby enhancing current paleo-climate understanding. $\delta^{34}S$ studies in Greenland (Patris *et al.*, 2002) and East Antarctica (Patris *et al.*, 2000) have attempted to quantify SO_4^{2-} sources in those regions. In the Antarctic, SO_4^{2-} production was dominated by marine biogenic emissions except during periods of global volcanism (Pszenny *et al.*, 1989; Legrand *et al.*, 1991; Minikin *et al.*, 1998). The sulfur cycle in Greenland has undergone changes since the industrial revolution, with anthropogenic emissions adding to the pre-existing marine and continental sources of SO_4^{2-} (Mayewski *et al.*, 1993). These two sites, however, do not provide information on the sulfur cycle for all ice core locations.

This thesis used sulfur isotopes to interpret SO_4^{2-} sources in two environmentally distinct regions and provided additional information about the applicability of sulfur isotopes to ice core studies. $\delta^{34}S$ measurements made on 19 meters of a West Antarctic ice core (RIDSA) provide continuous data spanning from 1935-1976. The other $\delta^{34}S$ data presented in this thesis from Central Asian ice cores and provide high-resolution data of SO_4^{2-} deposition during the summer season. These data sets are useful for reconstructing SO_4^{2-} emissions over time (for West Antarctica) and provide a detailed record of SO_4^{2-} emissions over one season (for Asia).

2. SULFUR ISOTOPIC MEASUREMENTS FROM A WEST ANTARCTIC ICE CORE: IMPLICATIONS FOR SO_4^{2-} SOURCE AND TRANSPORT

Chapter 2 has been submitted to the Annals of Glaciology (June 2003) for publication (Full citation appears in the References)

2.1 Abstract

Measurements of $\delta^{34}S$ covering the years 1935-1976 and including the 1963 Agung eruption were made on a West Antarctic firn core (RIDSA, 78.73°S, 116.33°W, 1740 m). Results are used to unravel potential source functions in the sulfur cycle over West Antarctica. The $\delta^{34}S$ values of excess SO_4^{2-} range from -0.7‰ to 6.8‰. These values are lower than those reported for East Antarctica, from near South Pole station, of 9.3‰ to 18.1‰ (Patris *et al.,* 2000). While the Agung period is isotopically distinct at the South Pole, it is not in the RIDSA dataset, suggesting differences in the source associations for the sulfur cycle between these two regions. Given the relatively large input of marine aerosols at RIDSA (determined from Na^+ data and the seasonal SO_4^{2-} cycle), there is likely a large marine biogenic SO_4^{2-} influence. The $\delta^{34}S$ values indicate, however, that this marine biogenic SO_4^{2-}, with a well-established $\delta^{34}S$ of 18‰, is mixing with SO_4^{2-} that has extremely negative $\delta^{34}S$ values to produce the measured isotope values in the RIDSA core. The transport and deposition of stratospheric SO_4^{2-} in West Antarctica and local volcanic input seem to account for the variance in $\delta^{34}S$ values.

2.2 Introduction

Deconvoluting the biogeochemical cycling of atmospheric sulfur is important to understanding climate change. Sulfate (SO_4^{2-}) aerosols play a key role in moderating the Earth's climate. They function as cloud condensation nuclei (CCN) and can enhance the lifetime of clouds and their ability to reflect incoming solar radiation. Additional aerosol mass in the atmosphere results in an increase in optical thickness and cloud albedo (Anderson *et al.,* 1995). This effect could in turn cause a change in oceanic productivity (which is a source of SO_4^{2-} aerosols), thereby creating a climate feedback loop that is susceptible to climate change (Charlson *et al.,* 1987; Bates *et al.,* 1987). Sulfate aerosols also contribute to the formation of SO_4^{2-} haze. The size of SO_4^{2-} particles determines their effect on climate. Sulfate derived from sea-salt particles are generally < 1 μm in diameter and play an important role in the marine boundary layer (Murphy *et al.,* 1998). The smaller of these sea-salt particles can be augmented through the contribution of mass from excess (xs) SO_4^{2-} (i.e., SO_4^{2-} that is not from sea-salt), thereby increasing their effectiveness as CCN. Sulfate aerosols play various other roles in atmospheric chemistry that could be affected by or affect climate change, including an alteration of oxidation processes in the marine boundary layer (Andreae and Crutzen, 1997).

The Antarctic displays high sensitivity to climate change and in turn greatly impacts the climate of low latitudes (Bromwich and Parish, 1998). One of the limitations to understanding the sulfur cycle is the assessment of how much each potential SO_4^{2-} source contributes and the accompanying effect on atmospheric processes and climate. There are three recognized sources of SO_4^{2-} in Antarctica: sea-salt, marine biogenic, and volcanic (Delmas, 1982; Legrand, 1997). Anthropogenic source contributions to

Antarctica are believed to be negligible (Dixon *et al.,* in review; Legrand and Mayewski, 1997; Shaw, 1982). Unlike ice core records from Greenland, which clearly show an increase in background SO_4^{2-} concentration since the industrial revolution (Mayewski *et al.,* 1993), Antarctica shows no increase in total SO_4^{2-} concentration with time (Legrand and Mayewski, 1997; Legrand, 1997). The relatively few sources of SO_4^{2-}, when compared to Greenland, make Antarctica a useful environment to observe the natural sulfur cycle.

Estimates of the Antarctic SO_4^{2-} budget are based on aerosol measurements, analysis of snow and ice samples, and an understanding of volcanism and meteorology of the region. Aerosol studies indicate that background xs SO_4^{2-} in the Antarctic comes primarily from marine biogenic sources (Minikin *et al.,* 1998; Pszenny *et al.,* 1989). Mt. Erebus, the only active volcano on the continent, contributes to the Antarctic sulfur cycle, but the strength of this source varies temporally depending on the size of the lava lake (Kyle and Meeker, 1990).

Ice core records provide an historical record of atmospheric chemistry, including SO_4^{2-} deposition (Delmas and Boutron, 1977; Delmas, 1982; Legrand *et al.,* 1991; Legrand, 1997) and have been used to assess the sulfur cycle in Antarctica (Delmas and Boutron, 1980; Legrand and Feniet-Saigne, 1991; Meyerson *et al.,* 2003). Snow pits and ice cores demonstrate that the SO_4^{2-} production operates seasonally, with concentration minima in the winter and maxima in the summer (Legrand and Pasteur, 1998; Minikin *et al.,* 1998). Excess SO_4^{2-} concentrations are independent of accumulation rate and elevation (Mulvaney and Wolff, 1994; Kreutz and Mayewski, 1999). Distance inland correlates to a decrease in the concentration of xs SO_4^{2-}, which may be due to the portion of SO_4^{2-} that is derived from marine productivity. The 1998 Italian ITASE traverse in East Antarctica demonstrated that the decrease inland of xs SO_4^{2-} extended only 250 km and then SO_4^{2-} increased in concentration from 250 to 770 km (Proposito *et al.,* 2002). In surface snow measurements, there is a negative correlation between both distance inland and elevation and methanesulfonic acid (MSA) concentration. As with xs SO_4^{2-}, accumulation rate does not affect MSA concentration (Legrand *et al.,* 1992). A seasonal variation of MSA occurs in several cores. The presence of the seasonal signal depends on location, with only an interannual signal at the South Pole and a stronger signal in coastal areas (Legrand *et al.,* 1992; Meyerson *et al.,* 2003). In other Antarctic studies there is no seasonal variation, unlike both sea-salt SO_4^{2-} and xs SO_4^{2-} (Ivey *et al.,* 1986). Recent aerosol studies indicate that MSA and xs SO_4^{2-} correlate on a seasonal basis, with summer peaks and winter lows (Arimoto *et al.,* 2001).

The SO_4^{2-} sources and emission rates are important indicators of the vertical distribution of SO_4^{2-} aerosols over Antarctica and therefore the radiative effects. The easiest source to factor out of total SO_4^{2-} concentration is sea-salt. The seawater weight ratio of a conservative sea-salt species (such as Na^+) to SO_4^{2-} ($Na^+/ SO_4^{2-} = 0.251$) is used to separate sea-salt SO_4^{2-} from xs SO_4^{2-} (Wilson, 1975). Statistical analysis using an empirical orthogonal function (EOF) performed on West Antarctic cores partitions sea-salt SO_4^{2-} into the first mode of the EOF analysis along with Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^- (Kreutz and Mayewski, 1999; Reusch *et al.,* 1999). This chemical association, identified through the EOF, suggests the ocean as the major source region. The marine biogenic portion of total sulfur comes from the oxidation of atmospheric dimethylsulfide (DMS) to MSA and SO_2 (Hatakeyama, 1982). The ratio of MSA to xs SO_4^{2-} (R value) is used in aerosol studies and ice cores as a tool for determining the biogenic component of total SO_4^{2-} (Arimoto *et al.*, 2001; Prospero *et al.*, 1991). The pathways of MSA and SO_4^{2-} formation from DMS are not completely understood, however, requiring caution when interpreting R values (Dibb and Whitlow, 1996). Attempts to partition marine biogenic and volcanic SO_4^{2-} with the EOF technique have been made (Zielinski *et al.*, 1996). In fact, the EOF partitioning for SO_4^{2-} from volcanic events is well defined and based on calibration with historic events, but it is the background volcanic SO_4^{2-} which is more elusive. In general, there still exists great uncertainty in SO_4^{2-} partitioning, especially in areas where little is known about the sulfur cycle.

Stable sulfur isotopes provide another tool for estimating SO_4^{2-} sources in ice cores. This technique has previously been used to determine the source of SO_4^{2-} in precipitation and aerosol studies (Wadleigh *et al.*, 1996; Nriagu *et al.*, 1987; Calhoun *et al.*, 1991). Sulfur isotopes are useful in studying atmospheric transport mechanisms and chemistry during volcanic eruptions (Castleman *et al.*, 1973) and during anthropogenic emissions (Newman *et al.*, 1975). Differences in chemical reaction rates can cause isotope fractionation, resulting in an isotopic "signature" that can be used to identify the chemical process (such as incorporation into a biologic system) or source of the atmospheric SO_4^{2-}. The isotopic signature of sulfur can be used to indicate the source of the SO_4^{2-} if there are a few sources with distinct signatures, as is the case in Antarctica (Nielsen, 1974; McArdle and Liss, 1995). The resulting $\delta^{34}S$ can be deconstructed through a mixing equation. The more that is understood about the sources of atmospheric sulfur in a region, the easier it becomes to use sulfur isotopes to quantify SO_4^{2-} sources.

Recently, sulfur isotopes were used in an ice core study in East Antarctica (Patris *et al.,* 2000). A quantitative assessment of SO_4^{2-} at South Pole was made based on sulfur isotopic measurements on sections of a firn core. Patris *et al.* (2000) determined that marine biogenic emissions are the dominant background source of SO_4^{2-}. Sulfur isotopes in a Greenland ice core were also used to examine the Arctic sulfur cycle during both pre-industrial and industrial times (Patris *et al.,* 2002). Applying sulfur isotope studies to ice core records can greatly improve the understanding of the sulfur cycle over long periods of time by providing evidence for SO_4^{2-} source regions and transport.

The $\delta^{34}S$ measurements presented here are the first sulfur isotopic measurements from the West Antarctic ice sheet and are used to estimate the relative contributions of each of the three SO_4^{2-} sources (marine biogenic, sea-salt and volcanic) to the West Antarctic SO_4^{2-} budget.

2.3 Methods

2.3.1 Core Processing

The 147 m RIDS A ice core (78.73°S 116.33°W, 1740 m asl (Fig. 1)) was retrieved in West Antarctica in 1995 (Kreutz and Mayewski, 1999). Core processing was performed in clean conditions, with samples collected into pre-cleaned containers and stored below –15°C until melting and analysis. Processing and chemical analysis were done at 3 cm intervals down to 60 m, yielding high- resolution (sub-annual) chemical data. One meter sections of core from 10 to 26 m were used for sulfur isotopic analysis, covering the period 1935 to 1976. The time covered by individual samples in this data set (RIDSA(2001)) was between 2 and 3 years, depending on accumulation rate.

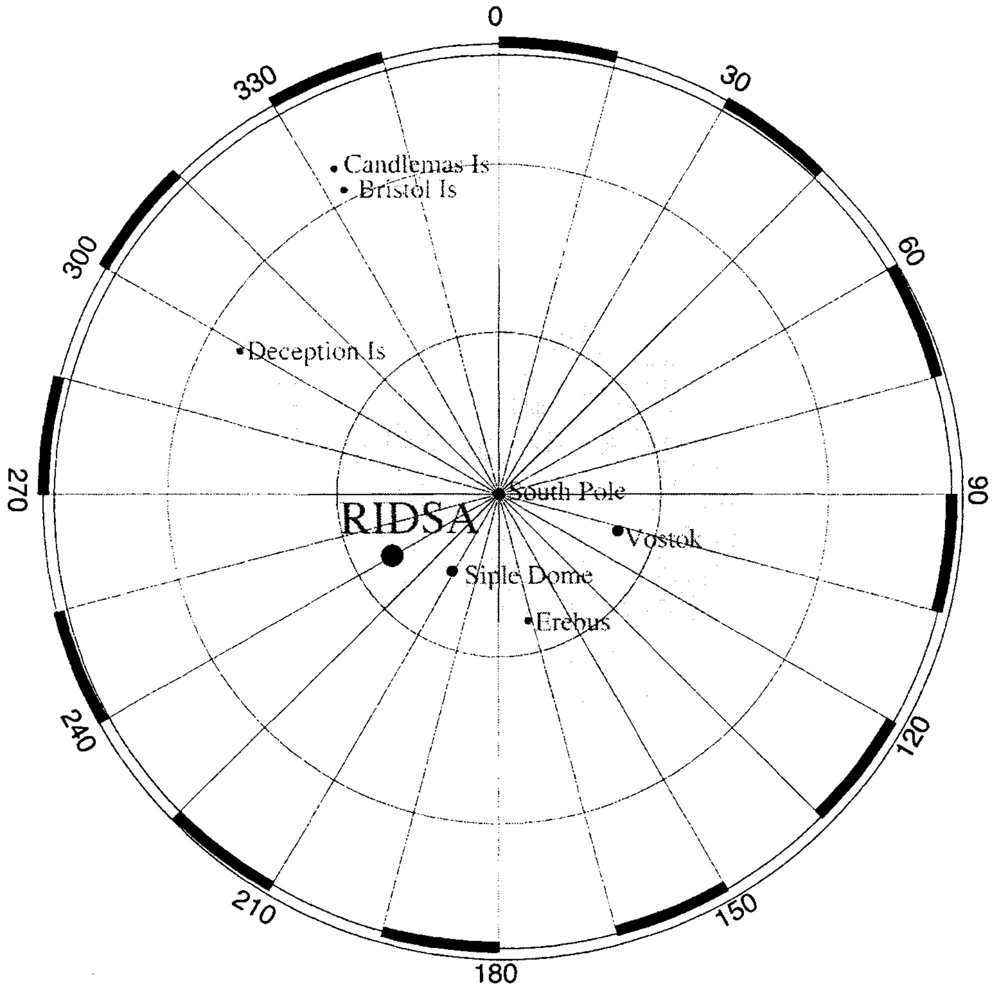


Figure 1. RIDSA location map. Several other long ice core records are denoted by the black dots. Volcanoes that are known to have been active during the time period covered by isotopic measurements presented in this paper are represented as gray dots.

Sections of the RIDSA core from 67.2 to 69.6 m, covering the years 1796-1805 and 13.8-15.9 m covering the years 1961-1967 were used for isotopic method development. These samples are designated as RIDSA(2000).

2.3.2 Ion Analysis

Major ions (Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, SO_4^{2-}) and MS (measured as methanesulfonic acid or MSA) measurements were made by ion chromatography at the (parts per billion) ppb level. Anions were analyzed on a Dionex DX-500 ion chromatograph with an AS-11 column using 6 mM NaOH eluent. Cations were analyzed on a Dionex DX-500 ion chromatograph with a CS-12A column using 25 mM MSA eluent. A β-activity profile was made using 20 cm samples (Kreutz *et al.,* 2000). The β-activity maximum is assumed to indicate the austral summer 1964/65, based on the global peak from the Atmospheric Test Ban Treaty (1963) and the transport lag to Antarctica (Picciotto and Wilgain, 1963). These dating techniques show that the entire core covers the time period 1506 to1995.

The excess SO_4^{2-} is calculated from the Na^+ concentration of the samples using the following equation:

$$SO_4^{2-}{}_{excess} = [SO_4^{2-}] - k[Na^+] \qquad (1)$$

Where k is equal to the seawater (SO_4^{2-} / Na^+) mass ratio, 0.251.

2.3.3 Isotopic Analysis

One hundred micrograms of SO_4^{2-} is necessary for isotopic analysis, making high-resolution analysis difficult in Antarctic cores due to low accumulation rates (Patris *et al.,* 2000). The RIDSA (2000) samples are aggregated residual from samples taken from the RIDSA core that were previously aliquoted for chemical analysis. Additional isotopic analysis was performed on 1 m sections of the RIDSA core, including the Agung period (1963 eruption). All core sections were melted in sterile conditions and then transferred to 1 L bottles for analysis.

Sample aliquots used for stable isotopic analysis were transferred to acid-washed 'snap-cap' vials. Vials were placed on a hot plate in a positive-pressure, HEPA-filtered air fume hood, and the solutions were slowly evaporated until the volume was reduced to approximately 20 mL from an initial 1 L. The concentrated sample was then used to fill 10 x 10 x 10 mm tin capsules and evaporated to dryness. The process was repeated between 2 and 5 times according to the measured SO_4^{2-} concentration in order to obtain sufficient sample for isotopic analysis. After the final evaporation the tin capsule was closed and placed in the auto-sampler of a Carlo Erba 1500 elemental analyzer interfaced by ConFlo II to a Finnigan MAT 252 stable isotope ratio mass spectrometer.

The sulfur isotopic ratio is expressed in delta notation with respect to VCDT and is represented by:

$$\delta^{34}S(‰)=\{[(^{34}S/^{32}S)_{sample}/(^{34}S/^{32}S)_{VCDT})]-1\}*1000 \qquad (2)$$

Calibration to VCDT was performed using NZ-1 and NZ-2 with reported values of –0.30 ± 0.3‰ and +21.0 ± 0.3‰ respectively. The overall error on isotopic analysis based on duplicates and internal standards is ± 0.5‰.

2.4 Results

2.4.1 Ion Data

Ion averages for each of the meters taken for isotopic analysis (10 to 26 m; RIDSA (2001)) and the RIDSA(2000) samples are presented in Table 1, along with the years covered. The two RIDSA datasets show similar concentrations.

Sodium and xs SO_4^{2-} have strong seasonal cycles, consistent with other studies in the Antarctic (Fig. 2) (Murozumi *et al.,* 1969; Herron and Langway, 1979; Hammer, 1980; Legrand *et al.,* 1992; Whitlow *et al.,* 1992; Minikin *et al.,* 1998; Kreutz and Mayewski, 1999; Reusch *et al.,* 1999).

Na^+ peaks in the winter due to increased storm activity, while xs SO_4^{2-} has a summer peak due to its marine biogenic component (Whitlow *et al.,* 1992). During the summer months sea ice retreats, leaving more open ocean in which primary productivity can thrive. One sign of increased productivity might be an increase in SO_4^{2-} concentration during local precipitation events. The MSA profile shows a subdued seasonal signal relative to the xs SO_4^{2-} signal (Fig. 2). In other glaciochemical studies done in the Antarctic, MSA has also been found to correlate with xs SO_4^{2-}, with both showing a summer maximum (Kreutz *et al.,* 1999). The xs SO_4^{2-} is a combination of primarily, or perhaps exclusively, marine biogenic and volcanic SO_4^{2-}. Table 2 gives values for all of the possible contributors to total SO_4^{2-} for the RIDSA samples.

Depth(m)	Years	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}	MSA	xs SO_4^{2-}	Cl^-/Na^+ mass ratio	R value ($MSA/xs\ SO_4^{2-}$)
RIDSA ('01)													
10-11	1976-1974	20.3	1.4	1.5	3.1	1.4	42.8	32.6	27.9	5.6	22.8	2.1	0.25
11-12	1974-1971	22.7	1.3	1.4	2.9	1.6	46.1	35.5	34.2	5.3	28.5	2.0	0.19
12-13	1971-1969	25.7	1.4	2.3	3.4	1.7	53.0	36.6	29.5	6.6	23.0	2.1	0.29
13-14	1969-1966	26.2	1.8	1.7	3.5	2.1	53.3	39.2	36.6	7.2	30.1	2.0	0.24
14-15	1966-1963	26.2	1.7	1.5	3.4	1.6	53.7	37.7	56.2	8.9	49.6	2.0	0.18
15-16	1963-1960	19.9	1.3	1.1	2.6	1.3	37.2	32.5	36.6	9.4	31.6	1.9	0.30
16-17	1960-1958	21.0	1.4	1.2	3.1	1.6	47.4	31.1	26.2	6.1	20.9	2.3	0.29
17-18	1958-1955	17.1	1.4	1.1	2.3	1.2	34.5	32.2	29.2	8.8	24.9	2.0	0.35
18-19	1955-1953	39.4	1.9	2.0	5.2	2.2	77.8	36.6	38.5	8.1	28.6	2.0	0.28
19-20	1953-1950	22.7	1.4	1.2	2.9	1.3	45.8	32.7	35.2	10.2	29.5	2.0	0.35
20-21	1950-1947	30.3	1.7	4.4	4.0	1.8	60.8	33.8	35.1	11.3	27.5	2.0	0.41
21-22	1947-1945	17.0	1.7	1.1	2.3	1.4	37.3	43.3	36.7	8.8	32.4	2.2	0.27
22-23	1945-1943	19.0	1.8	1.3	2.5	1.3	41.4	34.9	27.3	5.7	22.6	2.2	0.25
23-24	1943-1940	24.0	1.9	1.5	3.2	1.5	48.4	39.4	33.2	7.5	27.2	2.0	0.28
24-25	1940-1937	17.6	2.0	2.5	2.2	1.2	36.5	37.5	26.8	9.3	22.4	2.1	0.42
25-26	1937-1935	38.2	2.1	2.5	5.1	3.0	74.5	28.8	27.2	8.8	17.6	2.0	0.5
RIDSA ('00)													
13.8-15.9	1961-1967	25.8	1.7	1.5	3.3	1.6	50.9	37.8	42.9	9.0	36.4	2.0	0.25
67.2-69.6	1796-1805	28.6	0.9	1.6	3.7	1.3	60.0	38.3	33.1	8.1	25.9	2.1	0.31

Table 1. Ion concentrations for each RIDSA sample. Units are ng/g except for Cl/Na mass ratio and R value, which have no units.

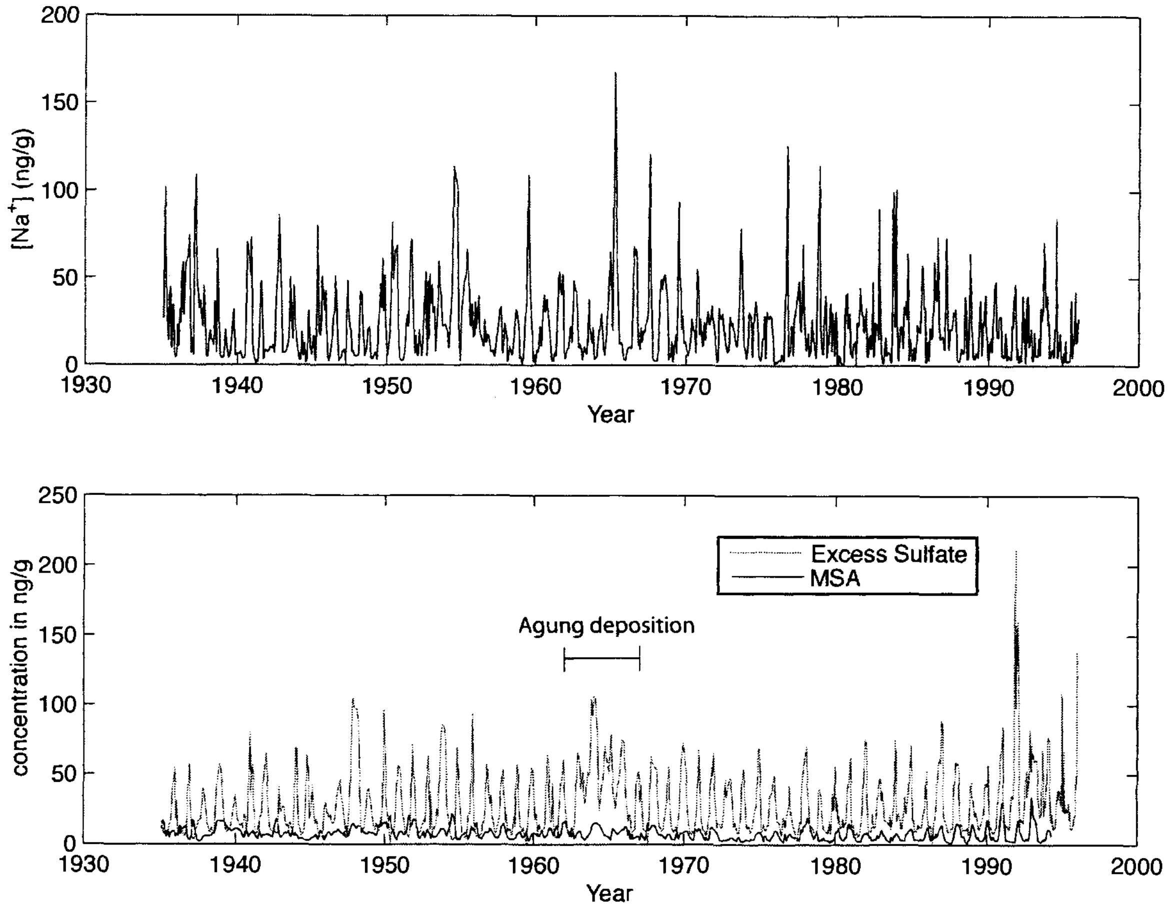


Figure 2. High resolution Na$^+$, xs SO_4^{2-} and MSA data from the RIDSA core. These data cover the portion of the core that was analyzed for sulfur isotopes (1935 to 1976) along with the top of the core (1976 to 1995).

Sample	Depth(m)	$[SO_4^{2-}]$ (ng/g)	*Contributions to total SO_4^{2-} (ng/g)*		f_{ss}	δ_{tot}(‰)	δ_{nss}(‰)
			sea salt	biogenic + volcanic			
RIDSA (2001)	10-11	27.9	5.1	22.7	0.18	4.5	0.8
RIDSA (2001)	11-12	34.2	5.7	28.4	0.17	5.5	2.4
RIDSA (2001)	12-13	29.5	6.5	22.9	0.22	5.1	0.6
RIDSA (2001)	13-14	36.6	6.6	29.8	0.18	4.8	1.3
RIDSA (2001)	14-15	56.2	6.6	49.5	0.12	5.4	3.3
RIDSA (2001)	15-16	36.6	5.0	31.5	0.14	4.2	1.5
RIDSA (2001)	16-17	26.2	5.3	20.8	0.20	5.6	1.7
RIDSA (2001)	17-18	29.2	4.3	24.8	0.15	6.7	4.2
RIDSA (2001)	18-19	38.5	9.9	28.5	0.26	5.5	0.1
RIDSA (2001)	19-20	35.2	5.7	29.4	0.16	6.0	3.1
RIDSA (2001)	20-21	35.1	7.6	27.4	0.22	9.9	6.8
RIDSA (2001)	21-22	36.7	4.3	32.3	0.12	5.9	3.9
RIDSA (2001)	22-23	27.3	4.8	22.4	0.18	3.1	-0.7
RIDSA (2001)	23-24	33.2	6.0	27.1	0.18	5.6	2.2
RIDSA (2001)	24-25	26.8	4.4	22.3	0.16	5.7	2.7
RIDSA (2001)	25-26	27.2	9.6	17.3	0.35	7.5	0.1
RIDSA (2000)	13.76-15.93	42.9	6.5	36.3	0.15	4.8	1.9
RIDSA (2000)	67.2-69.6	33.1	7.2	25.9	0.22	7.2	3.4

Table 2. SO_4^{2-} and $\delta^{34}S$ data from the RIDSA core.

The 1963 Agung eruption (March 17, 1963) is apparent in the xs SO_4^{2-} profile (Fig. 2) and can be seen as an increase in the seasonal minima of SO_4^{2-} from late 1963 to 1966 (Devine *et al.*, 1984). The eruption occurred in Indonesia and is recorded in the RIDSA core starting in late 1963, about six months after the eruption. This time difference of around six months between the eruption and its subsequent deposition in the Antarctic is due to the long distance the SO_4^{2-} load is transported. The lag time varies depending on the location of the volcano, but other work done in the Antarctic shows a similar six-month time lag for the Agung eruption (Legrand, 1997). Other Antarctic cores show volcanic peaks as a SO_4^{2-} spike above all other seasonal maxima. In the RIDSA core, however, volcanic input is typically represented by an increase in background SO_4^{2-} (Fig. 2). This may be related to seasonal changes/differences in atmospheric transport.

2.4.2 <u>Isotope Data</u>

The $\delta^{34}S$ of each meter of core analyzed is given in Table 2. The values range from 3.1‰ to 9.9‰, which is lower than those reported for East Antarctica, which range from 9.3‰ to 18.1‰ (Patris *et al.*, 2000). The measured isotopic signature is plotted against the inverse of total SO_4^{2-} concentration to highlight isotope trends with concentration (Fig. 3).

The East Antarctic data show a clear trend towards lower $\delta^{34}S$ values with increased concentration, and a linear regression (r=0.997) yields a value of 2.6‰ for the intercept, which is assumed to be predominantly volcanic SO_4^{2-}.

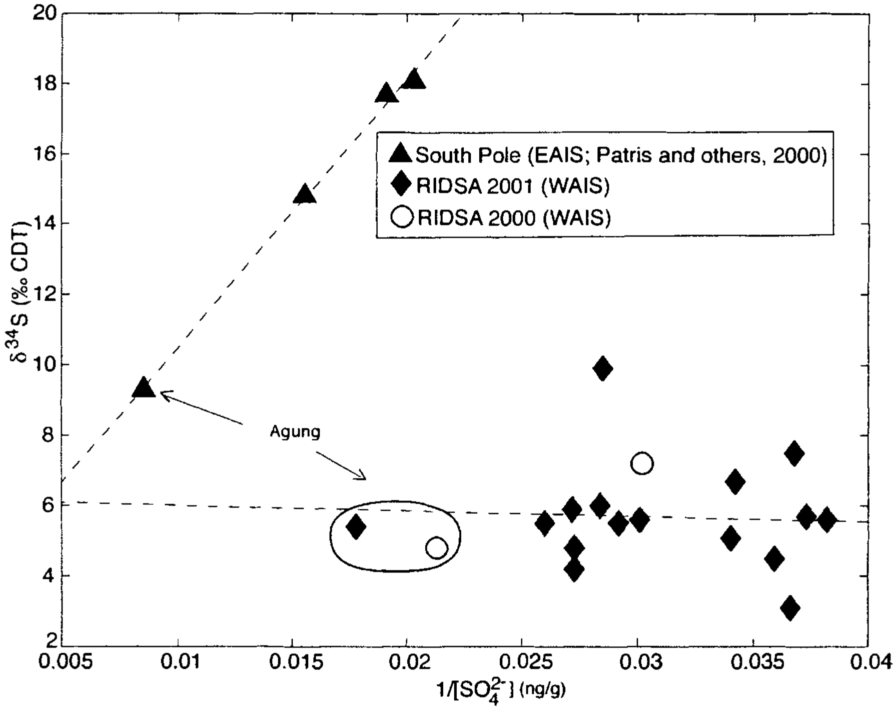


Figure 3. Sulfur isotope measurements from the RIDSA core and published data from East Antarctic cores (Patris *et al.*, 2000). The linear regression is shown for each data set. The $\delta^{34}S$ values are plotted against the inverse of the total SO_4^{2-} concentration.

In West Antarctica, there is no discernable trend with SO_4^{2-} concentration for the raw data. The Agung period, which was isotopically distinct in the East Antarctic data, is not distinct in West Antarctica. The variability, or scatter, in the RIDSA data may be due in part to the sampling technique. The core was sampled continuously at one-meter intervals. This resulted in ten samples containing two summer sections and six samples containing three summer sections.

The isotopic signature of the samples can be broken down into its components (Patris *et al.*, 2000):

$$\delta_{\mathrm{mes}}=f_{ss}\delta_{\mathrm{ss}}+f_{xs}\delta_{\mathrm{xs}}=f_{ss}\delta_{\mathrm{ss}}+f_{vol}\delta_{\mathrm{vol}}+f_{mb}\delta_{\mathrm{mb}} \qquad (3)$$

Where δ_{mes} is the measured isotopic signature as given in Table 2, δ_{ss} , δ_{vol} , δ_{mb} are the isotopic signatures of the sea-salt, volcanic and marine biogenic components of the sample, and f_{ss}, f_{xs}, f_{vol} and f_{mb} are the mass fractions of the sea-salt, excess, volcanic and marine biogenic components, respectively. f_{ss} and f_{xs} can be determined using the concentration for xs SO_4^{2-}, which was computed using the Na^+ concentration. The following equation represents the sea-salt fraction of a sample:

$$f_{ss}=([\ SO_4^{2-}] - [xs\ SO_4^{2-}])/[\ SO_4^{2-}] \qquad (4)$$

The non sea-salt fraction is $(1-f_{ss})$. The isotopic signature of sea-salt SO_4^{2-} is well constrained through field study to be 21‰ (Rees *et al.,* 1978). This reflects an enrichment in ^{34}S in ocean water compared to terrestrial sulfur. Rearranging equation 3 yields:

$$\delta_{xs}=(\delta_{mes} - f_{ss}\delta_{ss})/ f_{xs} \qquad (5)$$

Substituting the established value for δ_{ss} into the equation, along with the calculated f_{ss} and f_{xs} , yields an isotopic signature for the excess component of the samples (Table 2). These values are plotted against the inverse of the xs SO_4^{2-} concentration to yield a mixing diagram for the xs component in Fig. 4.

The xs component regression against $\delta^{34}S$ intersects at a value of 5.75‰. The correlation is insignificant (r= 0.4176).

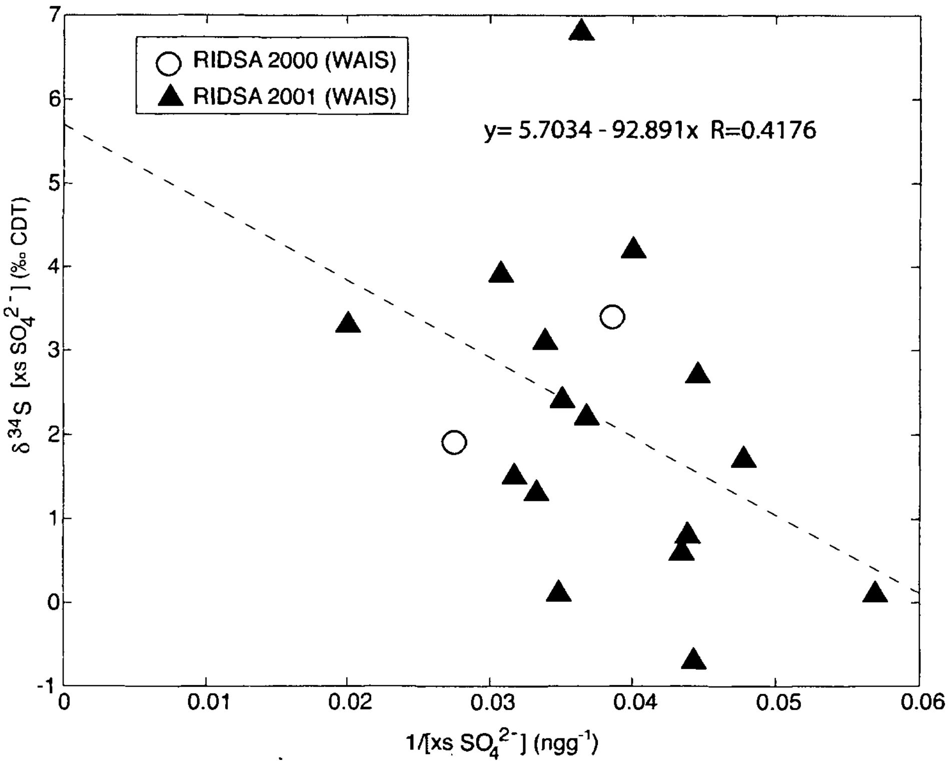


Figure 4. The $\delta^{34}S$ measurements for the xs SO_4^{2-} portion of the total SO_4^{2-} from the RIDSA core versus the inverse of the xs SO_4^{2-} concentration.

The highest $\delta^{34}S$ value (in the RIDSA time series) occurs in the sample covering the years 1947 to 1950 (Fig. 5). Mt Erebus eruptions are noted on the time series. The original xs SO_4^{2-} data was smoothed using a high-tension robust spline to produce the data in Fig. 5B. The robust spline technique differs from other statistical procedures because it is more resistant to outliers, providing a smoothing technique that yields useful information without under-estimating sporadic processes (Meeker *et al.*, 1995). The peaks in the smoothed data reflect changes in volcanic SO_4^{2-}. There appears to be a relationship between increases in background xs SO_4^{2-} and $\delta^{34}S$.

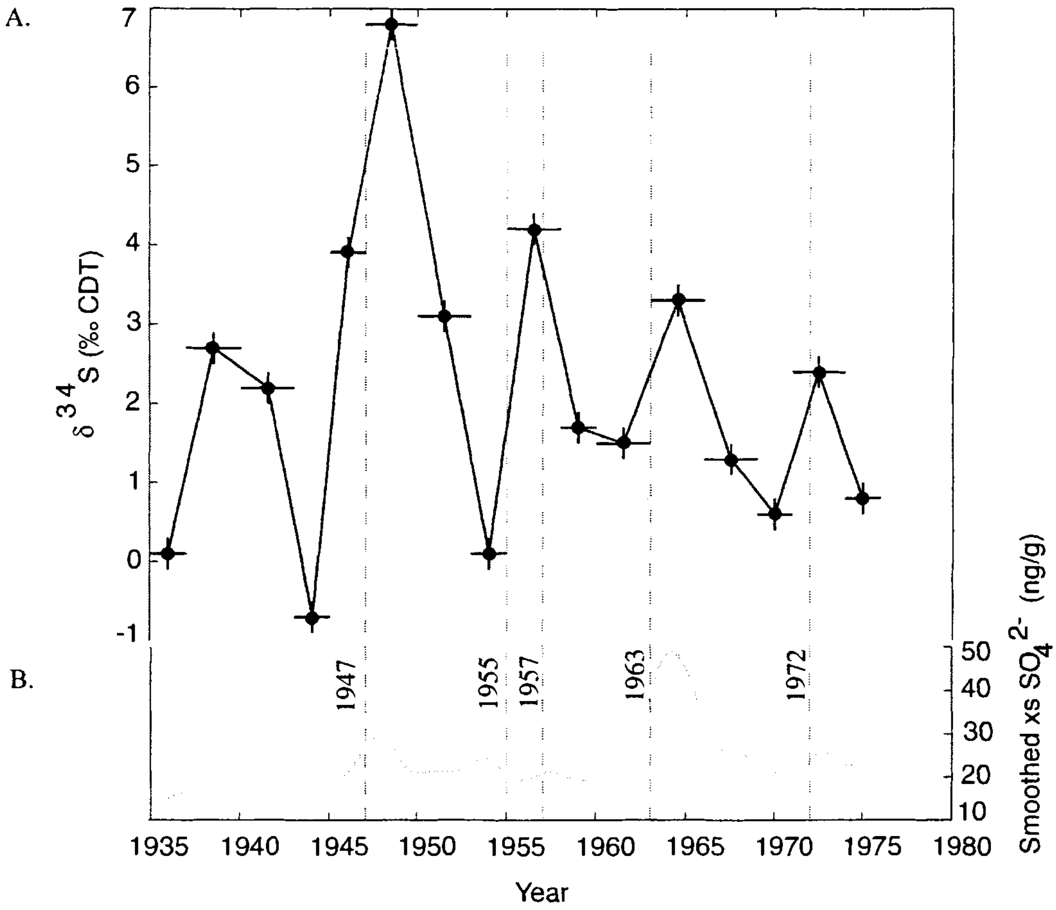


Figure 5. Time series isotope measurements from the RIDSA core along with Erebus eruptions and smoothed xs SO_4^{2-} data. Mt. Erebus eruptions are noted by dashed lines with the year. X-axis error bars depict the years that the data point represents. The variation on the y-axis represents the analytical precision of the measurement. The bottom figure is the smoothed xs SO_4^{2-} time series from the RIDSA core. Smoothing was done with a robust spline. The peaks represent increases in the background SO_4^{2-} concentration.

2.5 Discussion

The sulfur isotope ratios in the RIDSA ice core are lower than those in East Antarctica (Patris *et al.,* 2000). Caution must be used when looking at sulfur isotopic signatures as a source fingerprint because while processes such as atmospheric transport generally lead to similar trends, the $\delta^{34}S$ value can still vary greatly for any different source (Castleman *et al.,* 1973). For example, $\delta^{34}S$ values from volcanic emissions have been estimated to range from –15‰ to +25‰ (McArdle and Liss, 1999) and from –5‰ to 5‰ (Nielsen, 1974). Taking this uncertainty into account, there are several explanations for the West Antarctic sulfur isotope data.

Because the $\delta^{34}S$ values from West Antarctica fall within the range of newly erupted volcanic material, the background SO_4^{2-} source might at first appear to be entirely of volcanic origin. The $\delta^{34}S$ values of sulfur from newly erupted basalts range from 2‰ to 7‰ (DeHoog *et al.,* 2000). Studies of volcanic gas emissions show a positive $\delta^{34}S$ value (Castleman, 1974). There was active volcanism in Antarctica during the time period of the RIDSA core. The Smithsonian database of volcanic eruptions (www.volcano.si.edu/gvp/) lists Mt. Erebus, Deception Island, Candlemas, and Bristol Island as known eruptive volcanoes between 1935-1976.

It is unlikely, however, that the low $\delta^{34}S$ values can be attributed solely to local volcanism. It is clear that there is a strong marine influence on the RIDSA site. Sea-salt SO_4^{2-} makes up between 11.7% to 35.3% of the total SO_4^{2-} concentration for the samples (Table 2). The isotopic signature of SO_4^{2-} from a marine biogenic source is reasonably well constrained at ~18‰ (Calhoun *et al.,* 1991; Patris *et al.,* 2000). This value is slightly lower than that of sea-salt SO_4^{2-}, which is close to 21‰ (Rees *et al.,* 1978). The difference between these two marine constituents is the result of fractionation that occurs in the biological use of seawater SO_4^{2-}. Because there is a strong sea-salt component to the total SO_4^{2-} at the RIDSA site, it is reasonable to assume that there is a strong marine biogenic component. An isotopic study of the sulfur cycle in East Antarctica determined that the background source of sulfur was almost exclusively of marine biogenic origin (Patris *et al.,* 2000). In West Antarctica, however, the background isotopic signature is too depleted in ^{34}S to be of marine origin. The $\delta^{34}S$ values for the xs component of the RIDSA samples range from -0.7‰ to 6.8‰. Factoring out the sea-salt contribution reduces the $\delta^{34}S$ values, suggesting that the $\delta^{34}S$ values from xs SO_4^{2-} represent some combination of marine biogenic and volcanic SO_4^{2-}.

The heavier isotope (^{34}S) gets depleted faster than the lighter isotope (^{32}S) after volcanic eruptions due to changes in stratospheric chemistry and the pathway of SO_4^{2-} aerosol formation. Plume studies from anthropogenic emissions confirm this mechanism (Castleman *et al.,* 1974; Newman *et al.,* 1975). The lowest $\delta^{34}S$ values (-24.4‰) occur higher in the stratosphere (Castleman *et al.,* 1974). One possibility in West Antarctica is that a large portion of the sulfur budget comes from a marine biogenic source with a $\delta^{34}S$ value around 18‰, and that the rest of the SO_4^{2-} can be attributed to aged and fractionated stratospheric air. Stratospheric sulfur with extremely low $\delta^{34}S$ values could mix with local air masses with a relatively high $\delta^{34}S$ value to produce the intermediate values (Fig. 4). For example, using a 50/50 input from stratospherically-transported materials and marine materials (18‰), a calculation can be made from the overall xs $\delta^{34}S$ to determine the $\delta^{34}S$ of the second contributor. Using the following mixing relationship between recalculated xs $\delta^{34}S$ value and its two components

$$\delta_{\text{mes}} = f_{mb}\delta_{\text{mb}} + f_{vol}\delta_{\text{vol}} \tag{6}$$

and substituting an xs $\delta^{34}S$ value of 2‰, within the range of the recalculated xs $\delta^{34}S$ values, gives the $\delta^{34}S$ value of the unknown contributor as -14‰. If stratospheric transport and temperature affects yield $\delta^{34}S$ values that are even more negative than –14‰, then the ratio of marine biogenic to stratospheric input would be lower, indicating that stratospheric input is of greater consequence to the West Antarctic sulfur cycle than local tropospheric deposition.

The variance within the time series (-0.7‰ to 6.8‰, Fig. 5) corresponds to changes in the smoothed background SO_4^{2-} signal (Fig. 5). Increases in the $\delta^{34}S$ values over time correspond to increases in the xs SO_4^{2-} concentration over time. These xs SO_4^{2-} peaks do not appear to reflect any global volcanism. Mt. Erebus, however, is known to have erupted during the time period covered by each of the samples that has a peak in the time series. The largest xs $\delta^{34}S$ value is 6.8‰, in the sample covering the years 1947 to 1950. It coincides with the largest peak in the background xs SO_4^{2-} and a known Erebus eruption. Local volcanism would cause an increase in the $\delta^{34}S$ value because newly erupted material has a positive $\delta^{34}S$ value and is deposited relatively quickly, without the fractionation associated with transport (Castleman *et al.,* 1974). The $\delta^{34}S$ peak during the 1947 Erebus event is much larger than the peak associated with the two other local events that occurred during 1957 and 1972. The peak in xs SO_4^{2-} during the 1947 event is also much larger than the other peaks and is further evidence of the importance of local volcanism on the West Antarctic sulfur cycle (Delmas, 1982).

The $\delta^{34}S$ value during the Agung period could be expected to be very depleted in the heavier (^{34}S) isotope and show a minimum in the data set based on the assumption that stratospheric SO_4^{2-} (which is depleted in ^{34}S) is mixing with SO_4^{2-} from a marine biogenic source. It actually shows a higher value than the samples it precedes and follows. Local volcanism (Mt. Erebus) also impacted deposition during this time and may provide an explanation for this discrepancy. If the 1963 Erebus eruption caused a higher $\delta^{34}S$ in local precipitation, then the subsequent mixing with precipitation from Agung (which carries a low $\delta^{34}S$) might provide a mechanism by which the overall measured $\delta^{34}S$ in the sample might not be as strongly affected by stratospheric air as it would during periods which are free from global volcanic events, such as the data from the 1947 to 1950 sample.

2.6 Conclusions

The first sulfur isotope measurements have been made in a West Antarctic ice core and used to assess SO_4^{2-} deposition in West Antarctica from 1935-1976. The measured $\delta^{34}S$ values were recalculated to reflect only the xs component of total SO_4^{2-}, which in Antarctica includes only marine biogenic and volcanic contributions. These xs SO_4^{2-} $\delta^{34}S$ values range from -0.7‰ to 6.8‰, lower than those reported in East Antarctica (Patris *et al.*, 2000). Based on the relatively high percentage of sea-salt SO_4^{2-} in the RIDSA core, it can be assumed that there is also a substantial amount of marine biogenic SO_4^{2-} in each sample. The xs $\delta^{34}S$ values are too low to represent solely a marine biogenic influence. Volcanic plume studies have shown that volcanic emissions into the stratosphere are initially positive with respect to $\delta^{34}S$, and then become progressively lower over time due to a change in the chemical pathway of SO_4^{2-} aerosol formation. $\delta^{34}S$ values decrease with time and vertical distribution after an eruption (Castleman, 1973). Samples taken at the top of the stratosphere show more negative $\delta^{34}S$ values than those lower in the stratosphere. This stratospheric air, which is extremely depleted in ^{34}S, could be mixing with local, higher $\delta^{34}S$ air to produce the values seen in West Antarctica. Local volcanic emissions, specifically from Mt. Erebus, also play a role in the sulfur cycle in West Antarctica, based on the correlation between increased $\delta^{34}S$ values, increased background xs SO_4^{2-}, and Mt. Erebus eruptions.

Background peaks in xs SO_4^{2-} from West Antarctica can be attributed to local volcanic input. The low resolution of each sample, however, hinders this interpretation of Antarctic SO_4^{2-} production. High-resolution $\delta^{34}S$ samples are needed to dissect further the seasonality of the isotopic signature. Once this is determined it may be possible to apply the use of sulfur isotopes to ice core studies to more accurately assess the past SO_4^{2-} production.

3. ASSESSMENT OF DUST AND ANTHROPOGENIC SO_4^{2-} SOURCES IN HIGH-ELEVATION ASIAN PRECIPITATION USING STABLE SULFUR ISOTOPES ($\delta^{34}S$)

3.1 Abstract

Sulfur isotope measurements were made on samples from a 2 m snow pit (Inilchek Glacier, 42.16° N 80.25° E, 5100 m) to assess sulfate (SO_4^{2-}) source strengths in central Asia. Oxygen isotope ($\delta^{18}O$) data constrain the age of the snow pit to the summer season during which it was retrieved (1999), indicating high-resolution sub-annual measurements. Twenty $\delta^{34}S$ measurements were made at 10 cm resolution, with $\delta^{34}S$ values ranging from 0.4‰ during background, or low dust periods to 19.4‰ during a dust event. The potential SO_4^{2-} sources in this area include anthropogenic and dust emissions. Sulfur isotope studies from Russia show that anthropogenic atmospheric coal emissions to have a $\delta^{34}S$ value between 0-5‰. Asian evaporite deposits have a well-constrained $\delta^{34}S$ value of 20‰. Inilchek $\delta^{34}S$ measurements likely reflect a two end member system (anthropogenic and dust) that can be deconvoluted with a mixing equation. Anthropogenic SO_4^{2-} accounts for 57 to 98% of the SO_4^{2-} during background conditions. The SO_4^{2-} deposited during a large dust event (SO_4^{2-} concentration was 26.6 μeq/L) had only 22% of the SO_4^{2-} coming from anthropogenic sources. Overall, 57% of the SO_4^{2-} deposited during summer (1999) came from evaporite dust deposits, while 43% came from anthropogenic sources. $\delta^{34}S$ data in longer snow pit/ice core records from the Inilchek may prove useful for assessing changes in the regional SO_4^{2-} production through time.

3.2 Introduction

Studies in the Arctic, Antarctic and high-alpine sites in Austria have used sulfur isotope ratios to explore sulfur sources in those regions (Patris *et al.*, 2000; Patris *et al.*, 2002; Pichlmayer *et al.*, 1998). Sulfur species in precipitation at high elevations causes acidification of precipitation that can have adverse effects on ecosystems, influences geochemical cycling, and impacts the radiative balance of the atmosphere. Understanding the relative contribution of natural versus anthropogenic SO_4^{2-} is useful for quantifying the physical effects of the SO_4^{2-} aerosol at high latitudes. $\delta^{34}S$ measurements of air samples from high elevation alpine sites in Europe were used in combination with back trajectories to characterize anthropogenic emissions from different sources (Pichlmayer *et al.*, 1998). An ice core study in the Antarctic employed $\delta^{34}S$ measurements to determine the background source of SO_4^{2-} for a site near the South Pole (Patris *et al.*, 2000). Measurements of $\delta^{34}S$ from a Greenland ice core were used to assess the changes in SO_4^{2-} production since the industrial revolution (Patris *et al.*, 2002). Previous ice core studies of SO_4^{2-} production through $\delta^{34}S$ are useful because information about the source regions and the natural background SO_4^{2-} concentration was obtained. $\delta^{34}S$ from Asian sites are of interest because there is evidence of an anthropogenic influence on precipitation (Wake *et al.*, 1992). In order to understand the potential effect these anthropogenic SO_4^{2-} emissions have on climate, it is necessary to know how much they contribute to the natural sulfur cycle.

The Tien Shan region of central Asia is a remote region free from the influence of marine air masses with only two sources of SO_4^{2-}: anthropogenic and dust (Wake *et al.*, 1992). Previous work done in the Tien Shan region confirms the importance of dust in precipitation chemistry (Mayewski *et al.,* 1983; Mayewski *et al.,* 1984; Wake *et al.,* 1990; Wake *et al.,* 1993; Kreutz and Sholkovitz, 2000; Kreutz *et al.,* 2001). The temporal variations of major ion concentrations are greater than spatial variations for an individual precipitation event, indicating that the major control on ion concentrations is sporadic dust input (Wake *et al.,* 1992; Williams *et al.,* 1992; Kang *et al.,* 2000; Kang *et al.,* 2002). Elevated levels of SO_4^{2-} are partially accounted for by an influx of weathered soil materials. Anthropogenic emissions are a small source of SO_4^{2-} as well. A comparison of SO_4^{2-} levels from several central Asian glaciers revealed that SO_4^{2-} levels can vary greatly depending on location (from 1 to 50 μeq/L), with a general enrichment in SO_4^{2-} to the east. Areas near urban locations can have SO_4^{2-} levels that are five times as great as rural areas (Wake *et al.,* 1992). This increase is attributed to anthropogenic emissions.

A previous study of the $\delta^{34}S$ composition of central Asian precipitation found that a visible dust layer (with elevated SO_4^{2-} concentration) within an ice core had a $\delta^{34}S$ value of 15.0‰, whereas a clean layer (with lower SO_4^{2-} concentration) had a $\delta^{34}S$ value of 5.4‰ (Kreutz and Sholkovitz, 2000). The $\delta^{34}S$ value from the dust layer indicates the presence of evaporitic material, whereas the clean layer indicates SO_4^{2-} from an anthropogenic source. This study presents the first continuous $\delta^{34}S$ profile for a snow pit from Central Asia to assess the relative contribution of dust and anthropogenic sources to the regional SO_4^{2-} sources.

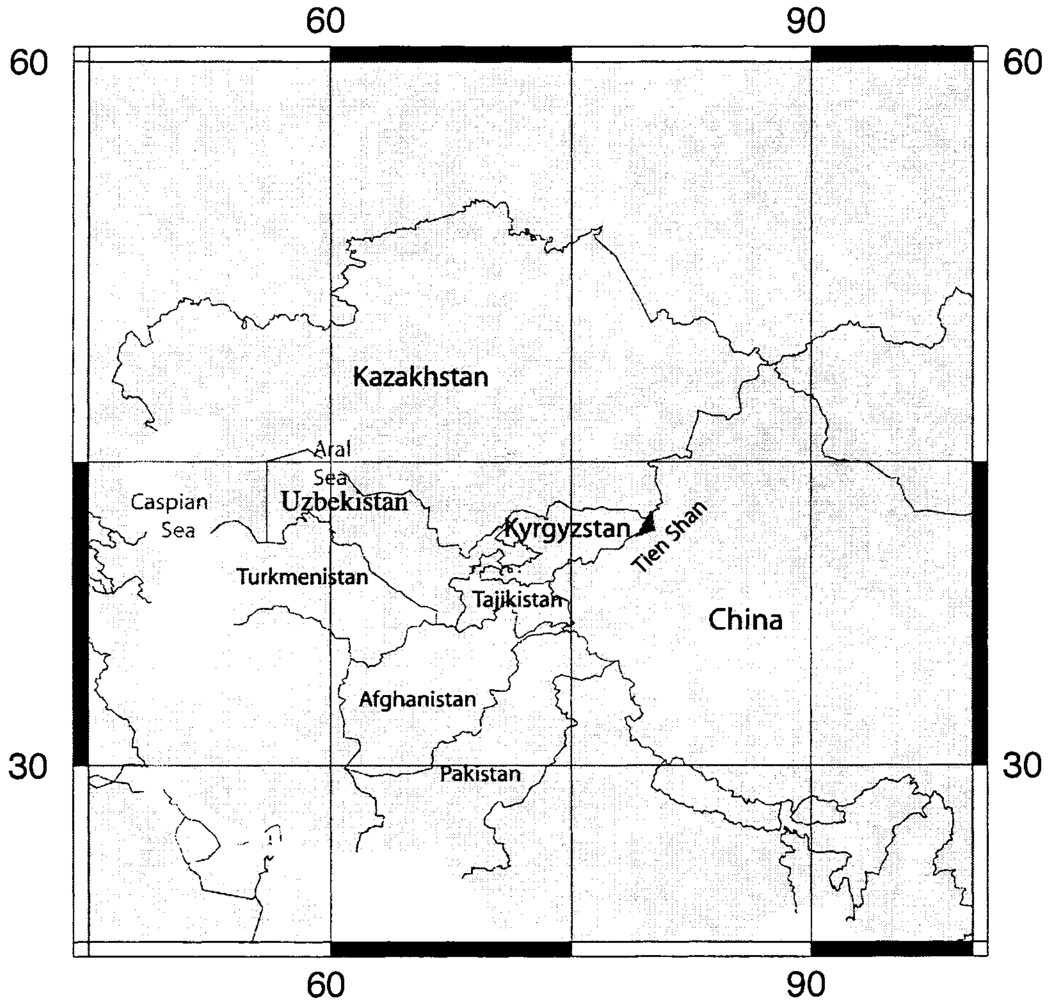


Figure 6. Location map of snow pit measured for $\delta^{34}S$. The Inilchek Glacier is located at the eastern boundary of Kyrgyzstan and denoted by the triangle.

3.3 Methods

Snow pit samples were collected from the Inilchek Glacier (5100 m; Figure 6) during the summer of 1999. The snow pit was 2 m deep and 1 liter samples were collected every 10 cm for $\delta^{34}S$ analysis. A separate depth profile was sampled at 5 cm resolution for major ion and $\delta^{18}O$ measurements. Samples were placed into pre-cleaned containers and stored below –15°C until melting and analysis. Major ions (Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, SO_4^{2-}) and MS (measured as methanesulfonic acid or MSA) measurements were made via ion chromatography at the University of Maine. Anions were analyzed on a Dionex DX-500 ion chromatograph with an AS-1 column using 6 nM NaOH eluent. Cations were analyzed on a Dionex DX-500 ion chromatograph with a CS-12A column using 25 mM MSA eluent. $\delta^{18}O$ analysis was performed at the University of Maine by the Epstein and Mayeda (1953) method. Data are reported in delta notation relative to a standard (SMOW).

Twenty samples, covering 0 to 2 m, were collected for $\delta^{34}S$ measurement at the Memorial University of Newfoundland. Sample aliquots used for sulfur isotopic analysis were transferred to acid washed 'snap-cap' vials. Vials were placed on a hot plate in a positive-pressure, HEPA-filtered air fume hood, and the solutions were slowly evaporated until the volume was reduced to approximately 20 ml. The concentrated sample was then used to fill 10 x 10 x 10 mm tin capsules and evaporated to dryness. The process was repeated between 2 and 5 times according to the measured SO_4^{2-} concentration in order to obtain sufficient sample for isotopic analysis. After the final evaporation the tin capsule was closed and placed in the auto-sampler of a Carlo Erba

1500 elemental analyzer interfaced by ConFlo II to a Finnigan MAT 252 stable isotope ratio mass spectrometer.

The sulfur isotopic ratio is expressed in delta notation with respect to VCDT and is represented by:

$$\delta^{34}S(‰)=\{[(^{34}S/^{32}S)_{sample}/(^{34}S/^{32}S)_{VCDT})]-1\}*1000 \qquad (1)$$

Calibration to the primary standard (VCDT) was performed using secondary standards (NZ-1 and NZ-2) with reported values of –0.30 ±0.3‰ and +21.0 ±0.3‰ respectively. The overall error on isotopic analysis based on duplicates and internal standards is ±0.5‰.

3.4 Results and Discussion

Ion concentrations and $\delta^{18}O$ for the samples taken at 5 cm resolution are presented in Table 3. $\delta^{18}O$ values range from –8.0‰ to –18.4‰ (Figure 7). A 14.4 m firn core previously analyzed from the Inilchek Glacier shows a clear seasonal $\delta^{18}O$ trend (Figure 7), with summer values generally higher than -20‰ and winter values reaching as low as -35‰ (Kreutz *et al.,* 2001). The 2 m snow pit samples were collected in the summer of 1999 (July-August), and the lowest $\delta^{18}O$ value is –17.8‰. Because this value is not low enough to represent snowfall from the previous winter season, the snow pit data record precipitation events that occurred only during the summer of 1999 or possibly the spring/summer season. The samples taken for sulfur isotopic analysis, therefore, provide high-resolution $\delta^{34}S$ data of the summer season.

Depth(m)	$\delta^{18}O$	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}
0.00	-12.5	1.9	4.1	0.5	0.1	0.1	2.4	1.4	0.2
0.05	-12.2	0.4	4.4	0.2	0.0	0.1	0.8	2.3	0.2
0.10	-17.7	10.3	9.0	1.4	2.4	19.0	9.1	6.9	2.7
0.15	-14.9	30.7	20.7	6.3	2.5	16.7	27.4	5.2	2.5
0.20	-11.0	1.4	3.8	0.2	0.2	0.2	1.6	2.6	0.6
0.25	-13.1	0.9	8.0	0.3	0.1	1.3	1.2	1.9	0.5
0.30	-14.3	0.8	4.4	0.2	0.0	0.1	0.9	2.2	0.3
0.35	-14.9	0.5	7.8	0.2	0.0	0.1	0.8	2.1	0.2
0.40	-8.0	5.6	16.3	0.7	3.1	26.7	7.6	7.9	3.5
0.45	-10.8	15.7	12.8	1.8	7.8	36.6	15.3	4.6	3.2
0.50	-12.9	2.9	9.0	0.4	1.6	7.9	3.1	2.2	0.7
0.55	-14.0	1.9	5.3	0.4	0.9	0.9	2.1	3.2	0.6
0.60	-9.9	22.5	12.3	2.4	8.5	54.0	24.5	5.2	4.4
0.65	-13.0	10.7	33.5	0.7	1.3	20.1	10.0	8.2	4.0
0.70	-15.1	9.8	8.2	2.1	3.1	14.8	10.4	3.9	1.0
0.75	-13.6	16.4	15.3	3.3	0.4	6.1	17.1	7.6	0.8
0.80	-12.5	0.8	8.9	0.3	0.0	0.0	0.9	1.4	0.3
0.85	-14.0	1.2	4.5	0.2	0.1	1.2	1.2	2.9	0.3
0.90	-9.9	1.5	4.0	0.3	0.4	7.2	2.2	3.5	0.4
0.95	-12.3	2.0	3.0	0.5	0.5	5.6	2.8	3.5	0.3
1.00	-16.1	2.8	11.1	0.4	0.6	0.4	3.5	2.1	0.5
1.05	-16.2	2.1	15.3	0.4	0.2	2.1	2.4	3.3	0.4
1.10	-12.2	1.3	5.6	0.4	0.1	1.8	1.8	2.0	0.4
1.15	-13.6	0.6	5.2	0.2	0.0	0.1	0.9	2.4	0.4
1.20	-13.2	10.5	4.7	0.8	5.0	29.2	9.7	3.5	2.3
1.25	-17.8	26.9	169.6	6.0	1.6	12.9	23.7	3.5	1.9
1.30	-11.4	23.4	16.4	2.9	2.8	43.3	25.1	11.3	5.8
1.35	-10.5	93.1	29.3	3.8	7.5	79.8	121.4	40.0	47.4
1.40	-11.0	6.5	1.0	0.7	2.0	21.0	6.7	4.4	1.7
1.45	-12.9	6.1	9.5	0.9	0.9	11.9	5.7	3.1	1.5
1.50	-18.4	0.9	4.6	0.3	0.1	0.1	7.7	78.9	0.8
1.55	-10.6	41.8	22.1	7.9	1.5	5.7	37.2	0.1	0.8
1.60	-13.1	0.7	6.9	0.2	0.1	0.9	0.9	2.8	0.2
1.65	-12.6	1.0	1.6	0.3	0.1	1.5	1.7	1.8	0.1
1.70	-14.0	0.4	2.2	0.1	0.0	0.1	0.7	0.6	0.1
1.75	-13.3	0.7	3.2	0.3	0.0	0.0	0.9	2.9	0.1
1.80	-10.9	9.2	9.9	1.4	2.0	15.7	8.7	4.2	1.3
1.85	-12.8	2.5	9.3	0.3	1.1	8.0	3.0	3.4	1.2
1.90	-10.6	0.9	7.0	0.3	0.2	0.4	1.2	2.4	0.2
1.95	-14.2	0.3	5.3	0.1	0.1	1.1	0.6	1.0	0.2

Table 3. $\delta^{18}O$ (‰ vs. SMOW) and ion data (μeq/L) at 5 cm resolution for the 2m snow pit taken during the summer of 1999 from the Inilchek Glacier.

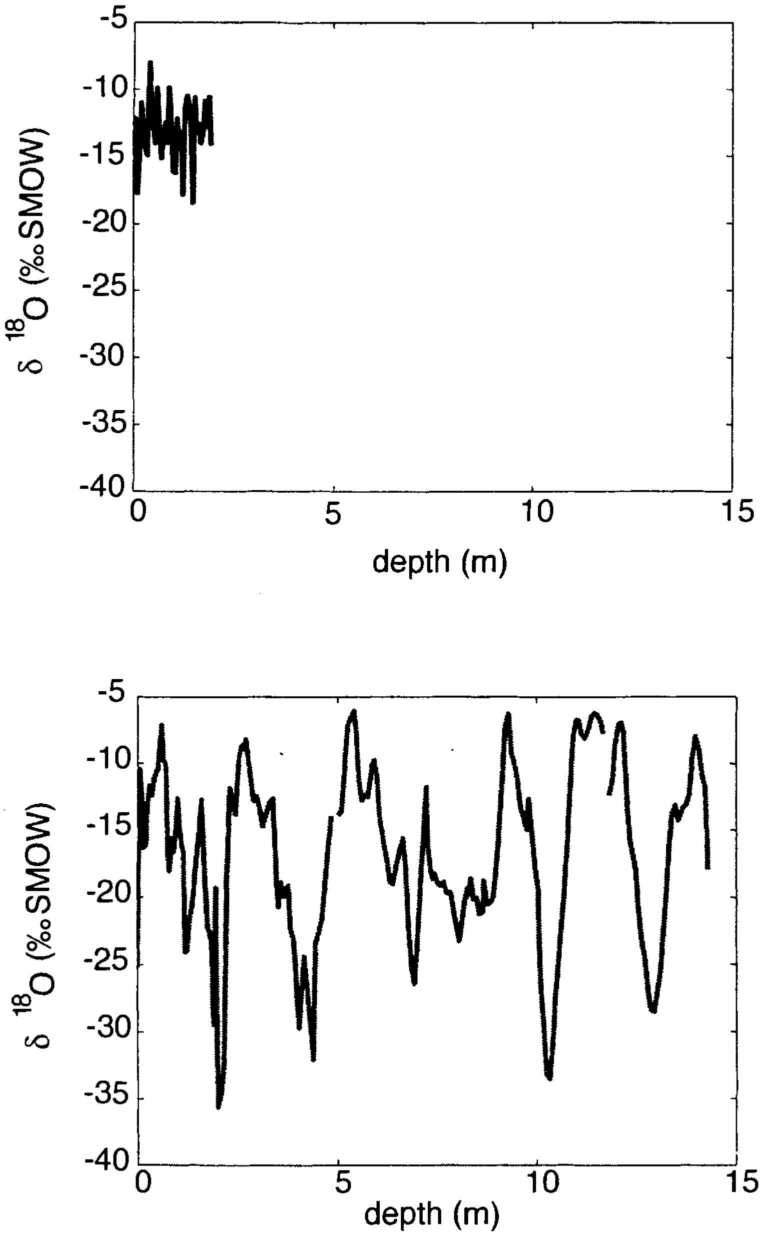


Figure 7. The $\delta^{18}O$ profile of the 2m snow pit and 15m firn core collected from the Inilchek Glacier. The top graph is the $\delta^{18}O$ profile of the 2m snow pit collected in 1999. The bottom graph is the $\delta^{18}O$ profile of the 15 m firn core collected in 1998 (Kreutz *et al.*, 2001). Both profiles are from the Inilchek Glacier.

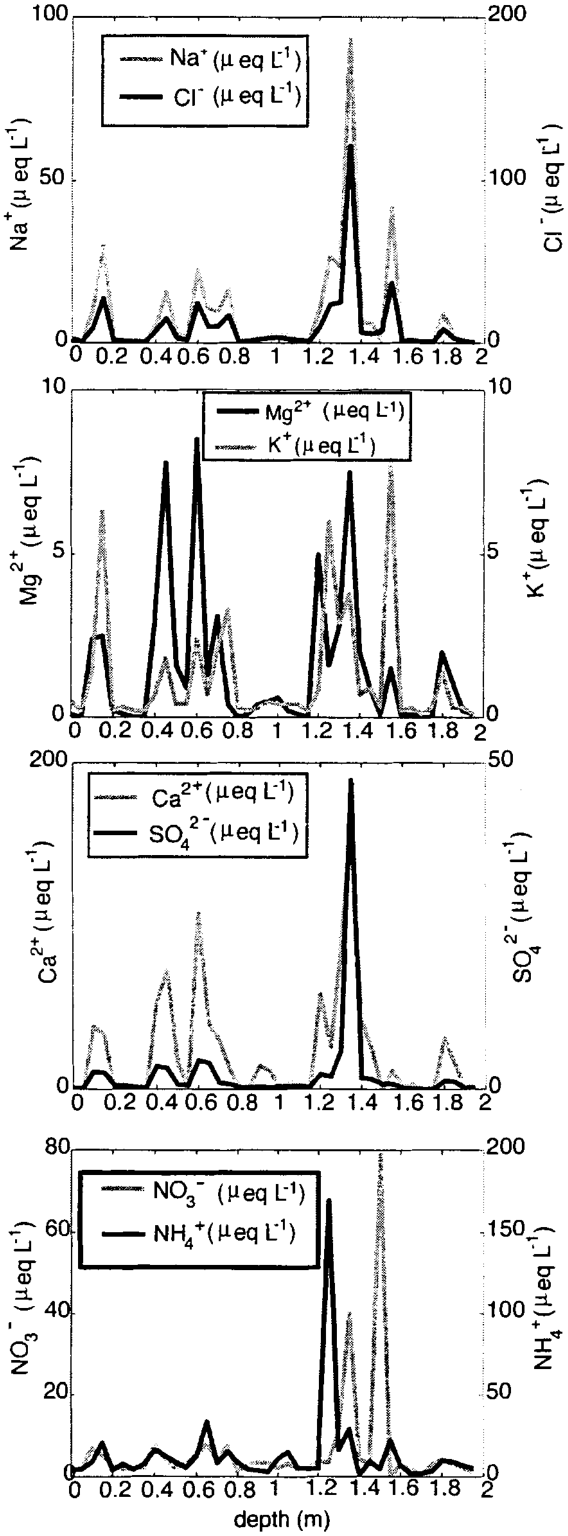


Figure 8. Ion concentrations plotted vs. depth for the 2 m Inilchek Glacier snow pit.

Major ion data are presented in Figure 8, and suggest several dust events during the 1999 summer. All ion species show similar trends, with peaks below 0 m, a peak above and below 0.5 m and a peak above 1.5 m. The concentrations of all ions except NH_4^+ and NO_3^- are below 1 μeq/L during background intervals. Wake (*et al.*, 1992) also showed low periods punctuated by abrupt increases in ion concentrations. Work done on Glacier 1 in the Tien Shan region found similar concentrations for SO_4^{2-}, Cl^-, K^+, and higher concentrations of Na^+, Ca^{2+} and Mg^{2+}. Nitrate and NH_4^+ were in lower concentrations in Glacier 1 than in this study (Wake *et al.,* 1992). A comparison of aerosol measurements with snow samples at Glacier 1 found that the snow chemistry was a good reflection of air chemistry because ion concentrations from aerosol measurements were similar in proportion to Glacier 1 precipitation data (Sun *et al.,* 1998). The absence of a marine source for precipitation in this region was confirmed by other work in this region (Wake *et al.,* 1990; Wake *et al.,* 1992; Kreutz *et al.,* 2001). The distance from a marine source and meteorology also do not support a marine influence. Though there is no modern marine source of SO_4^{2-} in precipitation, the presence of SO_4^{2-} from evaporitic dust constitutes a paleo-marine source.

The $\delta^{34}S$ data are plotted in Figure 9 along with the average SO_4^{2-} concentration for each sample. There is a good correlation (r=0.87) between SO_4^{2-} concentration and $\delta^{34}S$. Other studies in the area have suggested that anthropogenic activity is a source of SO_4^{2-} when SO_4^{2-} concentrations are below 5 μeq/L (Wake *et al.,* 1990). Anthropogenic SO_4^{2-} generally has a $\delta^{34}S$ range of 0 to 5‰ (Nielsen, 1974). The other source of SO_4^{2-} in this region is dust (Wake *et al.,* 1992).

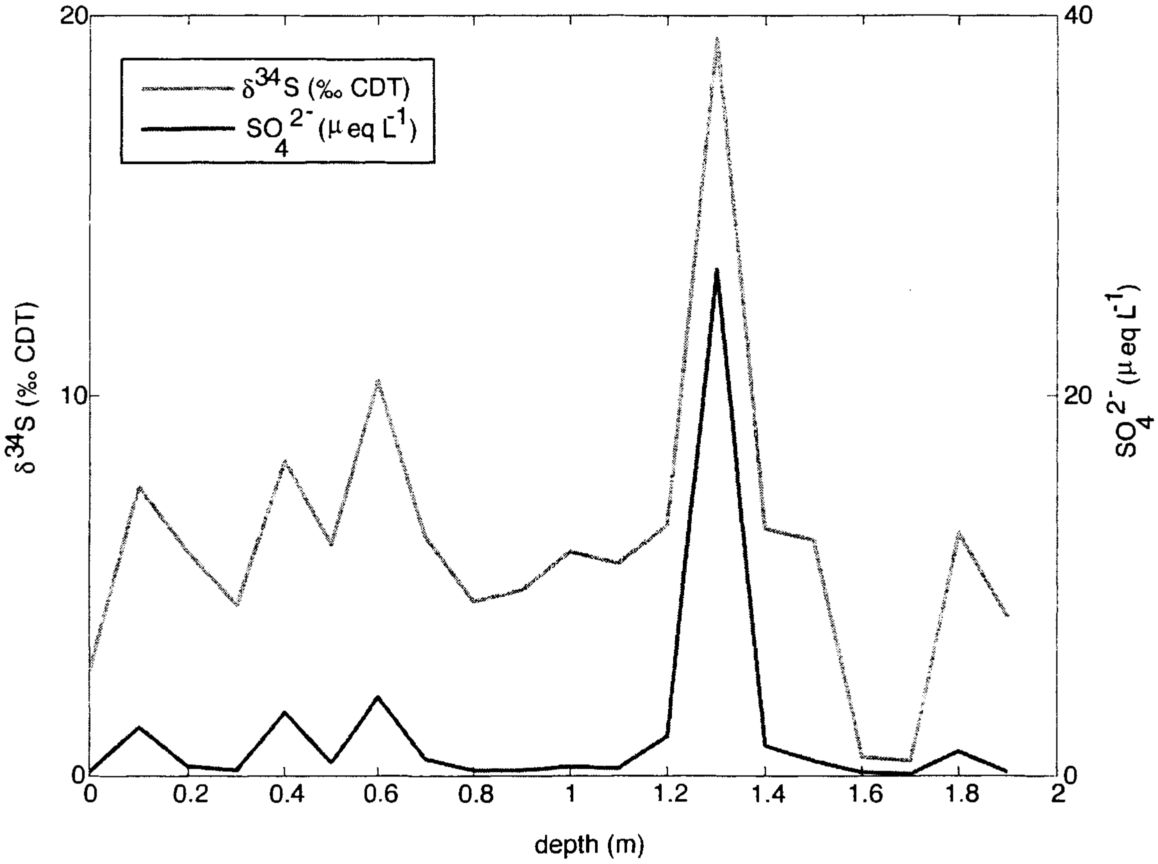


Figure 9. SO_4^{2-} concentration and $\delta^{34}S$ plotted against depth. SO_4^{2-} concentration data is available at 5 cm resolution. Because $\delta^{34}S$ was only measured at 10 cm resolution, the average of the two SO_4^{2-} concentrations representing each isotope sample was graphed.

Gypsum ($CaSO_4 \bullet 2H_2O$) is likely a major source of sulfur-rich dust in the Inilchek glacier (Kreutz and Sholkovitz, 2000). Soil modeling indicates that the largest source of soil gypsum in the world is to the west of the Inilchek Glacier (Claquin *et al.*, 1999). Magnesium sulfate ($MgSO_4$) is another evaporite source of SO_4^{2-} and could also be a source in the Tien Shan Mountains. Not all of the measured Ca^{2+} is associated with SO_4^{2-}, as some comes from $CaCO_3$ deposits. The composition of the dust deposited in Central Asia can vary through time, though the SO_4^{2-} will always be from evaporitic deposits. Modern day seawater has a well-constrained $\delta^{34}S$ of 21‰ (Rees *et al.,* 1978). Evaporite deposits have $\delta^{34}S$ ranges around the value of seawater (Krouse and Grinenko, 1991). The temporal variability indicates possible changes in atmospheric transport and deposition.

The measured $\delta^{34}S$ for SO_4^{2-} in this region can be resolved in the following way:

$$\delta_{meas.} = f_{dust}\delta_{dust} + f_{anth.}\delta_{anth} \qquad (2)$$

δ_{dust} is from a well-constrained source: evaporites (20‰). The linear regression further narrowed the δ_{anth} value (5‰). Thus, it is possible to partition the SO_4^{2-} concentration for each of the 20 samples into two parts. If f_{dust} is equal to x and f_{anth} is therefore 1-x, then (2) can be rewritten as:

$$(\delta_{meas} - 5)/15 = x \qquad (3)$$

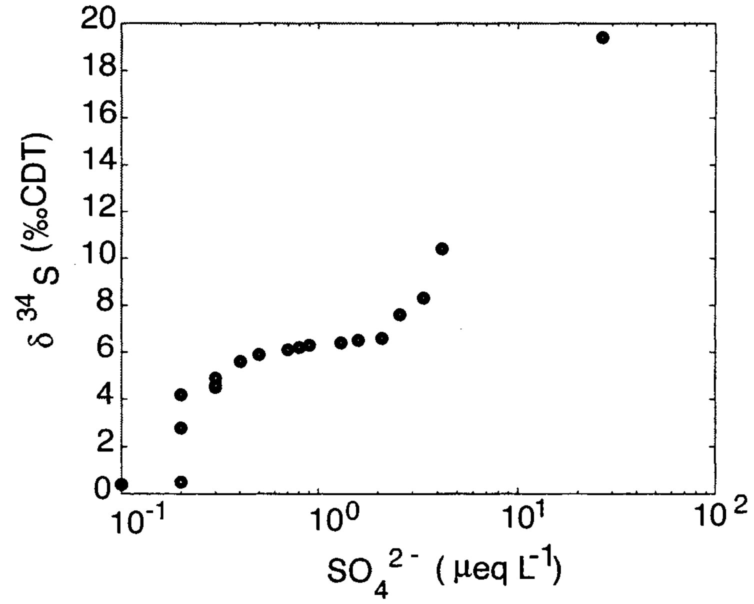
Once this has been calculated for each sample, it is possible to look at changes in the SO_4^{2-} source over time (Figure 11).

In Asia, the average $\delta^{34}S$ for evaporite deposits is 20.6‰. Increases in ion concentrations are likely the result of dust storms. These dust storms deposit SO_4^{2-} with a high (20‰) $\delta^{34}S$. Background conditions are dominated by anthropogenic emissions with a low (around 5‰) $\delta^{34}S$.

$\delta^{34}S$ values are plotted versus the SO_4^{2-} concentration to evaluate the relationship between SO_4^{2-} and $\delta^{34}S$ (Figure 10). Because there are two distinct end members (evaporitic dust and anthropogenic input) and only one is well constrained (evaporitic input is 21‰), a linear regression is used to further constrain the anthropogenic $\delta^{34}S$ signature. The linear regression yields a y-intercept of 4.77‰, which is well within the average range for anthropogenic emissions (Krouse and Grinenko, 1991).

For the sample representing high dust input, the quantity of anthropogenic SO_4^{2-} also increases. Work done in the Swiss Alps can be used to infer that anthropogenic emissions are strongly seasonal, with increased concentrations in precipitation in the summer due to an increase in vertical convective transport in the atmosphere (Doscher *et al.,* 1996). Wagenbach et al. (1988) noticed a relationship between a summer SO_4^{2-} peak and high $\delta^{18}O$ values in a shallow snow pit in the Swiss Alps, which was also attributed to vertical convection. Increased convective transport could be the mechanism by which more SO_4^{2-} is deposited during storm events. The percentage of anthropogenic SO_4^{2-}, however, remains similar to the percentage of dust input during anthropogenically dominated (background) periods (Figure 12). During times of negligible dust deposition (for example 0.3 m depth) the quantity of anthropogenic deposition is low but accounts for nearly all (83%) of the SO_4^{2-}. The high dust period is characterized by a dominance of evaporitic material (78% of the SO_4^{2-}) as well as an increase in the anthropogenic SO_4^{2-} concentration.

a



b

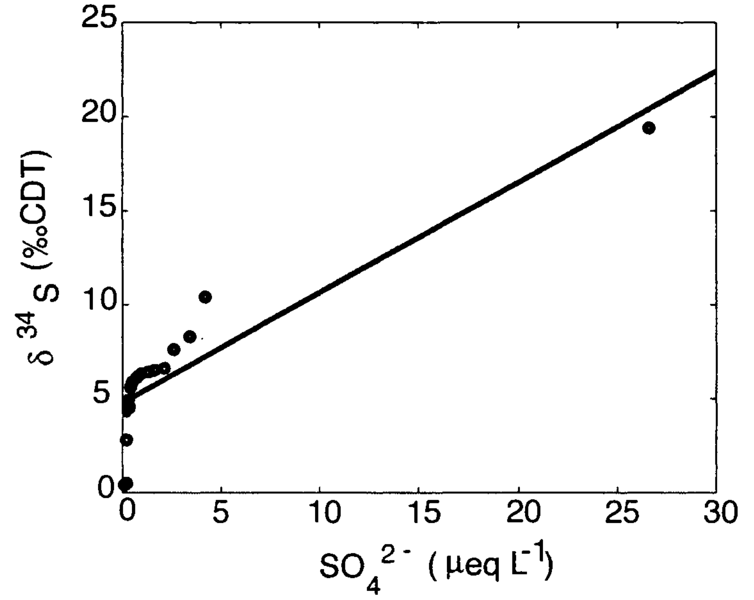


Figure 10. $\delta^{34}S$ versus SO_4^{2-} (μeq/L). a. $\delta^{34}S$ versus the log of SO_4^{2-} (μeq/L). b. without the log values.

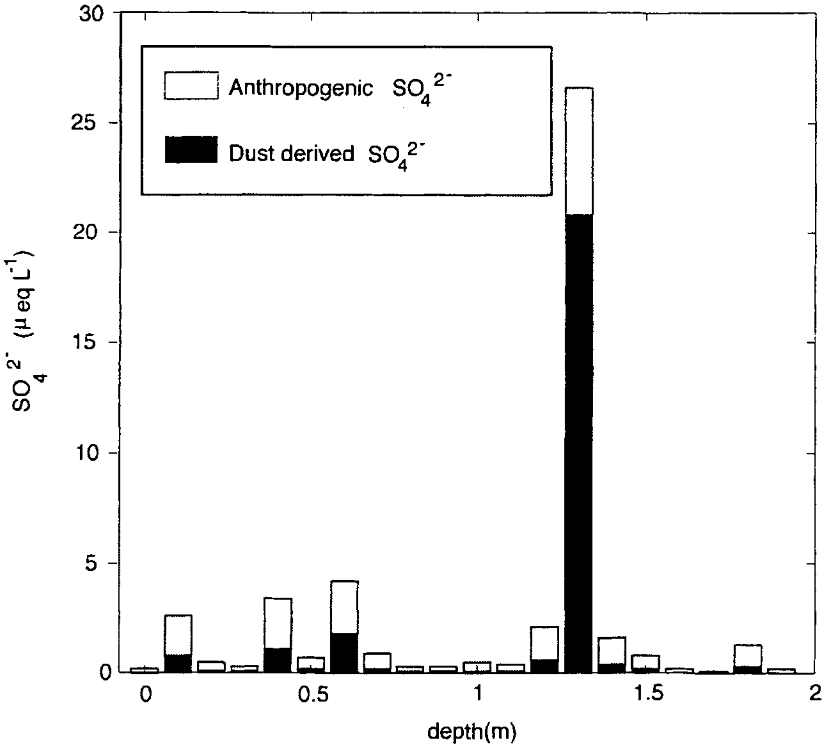


Figure 11. SO$_4^{2-}$ concentration divided into its two constituents (anthropogenic and dust).

There are two (out of 18) anomalous δ^{34}S data points at 1.6 m and 1.7 m. These samples contain the lowest SO$_4^{2-}$ concentration and also the lowest δ^{34}S (Table 4). Anthropogenic depositions are variable and the low δ^{34}S relative to the other samples could represent a change in pollutant source and/or composition. Russian coal has δ^{34}S values between 3‰ and 5‰, while coal from Bohemia has been measured at –1.4‰ to 0.1‰. Differences in pollution source can lead to differences in δ^{34}S (Krouse and Grinenko, 1991).

Based on the partitioning described above, 57% of the SO$_4^{2-}$ that accumulated in the snow pack during the summer came from a dust source, while 43% is anthropogenic in origin. A similar study of δ^{34}S was carried out in Japan to assess the contribution of anthropogenic sulfur to the atmosphere (Nakai *et al.*, 1991). Samples were taken in 1960 and again throughout the 1970's in order to assess changes in anthropogenic input to rural and urban areas. A comparison of rural and urban air samples taken between 1975 to 1978 showed the ratio of SO_2/H_2S to be roughly from 2 to 25 times greater in urban areas, indicating much higher urban SO_2 emissions (Tanaka and Hashimoto, 1977). The dominant source of SO_4^{2-} in rural areas is marine aerosols, whereas anthropogenic emissions dominate urban areas. The rural $\delta^{34}S$ values range from 12.3 to 14.7‰, while urban values range from 4.5 to 6.8‰. Using a mixing equation, the SO_4^{2-} components of urban precipitation were quantified. In 1960 anthropogenic emissions constituted 40-50% of the total atmospheric sulfur at rural and industrial locations. Anthropogenic emissions were 75% in 1973, and decreased to between 60-65% after this year.

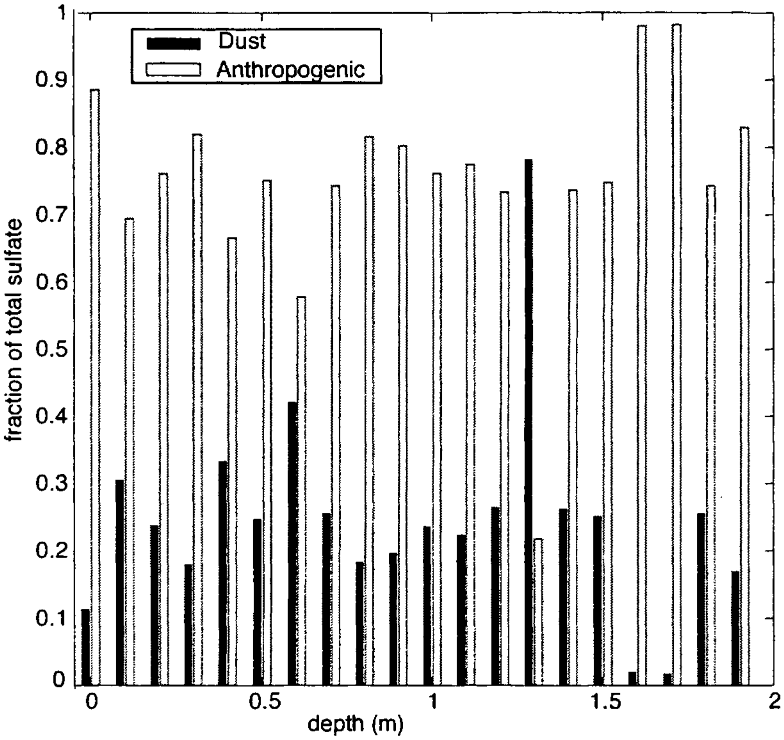


Figure 12. The two components of SO_4^{2-} represented as fractions of the total concentration.

Top Depth(m)	δ_{tot} (‰ CDT)	[SO_4^{2-}] (μeq/L)	*Contributions to total SO_4^{2-} (μeq/L)*	
			dust	**anthropogenic**
0.00	2.8	0.2	0.0	0.2
0.10	7.6	2.6	0.8	1.8
0.20	5.9	0.5	0.1	0.4
0.30	4.5	0.3	0.1	0.2
0.40	8.3	3.4	1.1	2.3
0.50	6.1	0.7	0.2	0.5
0.60	10.4	4.2	1.8	2.4
0.70	6.3	0.9	0.2	0.7
0.80	4.6	0.3	0.1	0.2
0.90	4.9	0.3	0.1	0.2
1.00	5.9	0.5	0.1	0.4
1.10	5.6	0.4	0.1	0.3
1.20	6.6	2.1	0.6	1.5
1.30	19.4	26.6	20.8	5.8
1.40	6.5	1.6	0.4	1.2
1.50	6.2	0.8	0.2	0.6
1.60	0.5	0.2	0.0	0.2
1.70	0.4	0.1	0.0	0.1

Table 4. $\delta^{34}S$ and SO_4^{2-} data from the 2m snow pit.

3.5 Conclusions

Snow pit samples collected in the Tien Shan Mountains during the summer of 1999 were analyzed for $\delta^{34}S$. Previous studies suggest that anthropogenic SO_4^{2-} and evaporite dust SO_4^{2-} are the two sources of atmospheric SO_4^{2-} in the Inilchek Glacier region. This study used $\delta^{34}S$ to confirm the presence of these two components and to assess the relative contribution of each. The samples yielded high-resolution isotope data that was then used to partition the SO_4^{2-} signal into its anthropogenic and dust components. Ion data reflect a series of dust events that cause short-term changes in the regional SO_4^{2-} sources, and therefore albedo. $\delta^{34}S$ varied directly with respect to changes in SO_4^{2-} concentration. The dust component has a well-constrained $\delta^{34}S$ value of 20‰. The anthropogenic component is generally constrained to 0 to 5‰ for coal emissions. A linear regression was used to estimate the regional $\delta^{34}S$ value of anthropogenic SO_4^{2-} at 4.77‰. These two values (20‰ and 4.77‰) were then used in a mixing equation to determine the concentration of anthropogenic and dust SO_4^{2-} in each sample.

Sulfur isotopes were successfully applied to snow pit data in order to analyze SO_4^{2-} deposition during the summer of 1999. Because only one season was captured by these data, it is necessary to look at a full annual record in order to assess the seasonality of the dust and anthropogenic inputs. This technique will be useful for further ice core studies to assess changes in SO_4^{2-} production over time for longer term trends, particularly changes since the industrial revolution.

4. CONCLUSIONS

Stable sulfur isotope ratios ($\delta^{34}S$) were analyzed in two environmentally distinct regions (West Antarctica and central Asia) in order to assess regional SO_4^{2-} deposition. West Antarctica is considered an ideal location for assessing the natural sulfur cycle, free from anthropogenic contamination (Legrand and Mayewski, 1997; Shaw, 1982). The Tien Shan mountain region in Central Asia has only two sources of SO_4^{2-}, anthropogenic and dust, and is therefore useful for assessing changes in the SO_4^{2-} production due to anthropogenic input. These records are useful for assessing the applicability of sulfur isotopes to ice core studies.

A low-resolution sulfur isotope ($\delta^{34}S$) record spanning the years 1935-1976 was obtained from the RIDSA ice core from West Antarctica. $\delta^{34}S$ values range from –0.7 to 6.8‰. Each measurement covers 2 to 4 years, depending on the accumulation rate. These data reflect both background and volcanic periods and were lower than the only other sulfur isotope measurements from Antarctica. To interpret the SO_4^{2-} sources, it is necessary to look at other chemistry measured for each sample. Based on Na^+ concentration, there is a strong marine biogenic influence at the RIDSA site, which has a corresponding $\delta^{34}S$ value (18 to 21‰).

In order to account for $\delta^{34}S$ values that are much lower than this, SO_4^{2-} sources therefore must be some combination of high and low $\delta^{34}S$ precipitation. Volcanic plume studies have shown that SO_4^{2-} aerosols form with increasingly negative $\delta^{34}S$ as time after an eruption progresses due to the influence of the ash on aerosol formation and the predominance of heterogeneous SO_4^{2-} aerosol formation. Other factors such as temperature, transport and height within the atmosphere can also affect the isotopic signature. Highly fractionated stratospheric air therefore provides a mechanism for the $\delta^{34}S$ values measured in the RIDSA core.

In Antarctica, the combination of three potential sources along with the lack of sub-annual and spatial data made a quantification scheme through the use of sulfur isotopes inconclusive. With sub-annual and spatial data will come a better understanding of the nuances and seasonal variations of the natural sulfur cycle. Once this is understood it may be possible to use low-resolution samples to infer changes in the sulfur cycle. Snow pit samples were collected along the US ITASE traverses in 2000-2001 and 2001-2002 in order to examine the seasonal changes in $\delta^{34}S$ in West Antarctica. Fresh snow samples were also collected along the traverses to provide a spatial study of $\delta^{34}S$ over West Antarctica. These samples have been sent to the Memorial University of Newfoundland for $\delta^{34}S$ analysis and will provide a more detailed look at the SO_4^{2-} sources in this region. Preliminary data, ion concentrations and $\delta^{18}O$, are presented in the appendix.

A 1999 snow pit sulfur isotope record from the Tien Shan Mountains in Kyrgyzstan illuminates an entirely different sulfur cycle. Dating based on $\delta^{18}O$ measurements indicates that the $\delta^{34}S$ data represent only the summer, possibly the spring/summer, making this a high-resolution sulfur isotope record. Based on ion ratios within the dataset compared to seawater ratios, there is no marine source of SO_4^{2-}. Episodic dust events increase the SO_4^{2-} in precipitation by two orders of magnitude. The background SO_4^{2-} comes from anthropogenic emissions. Because these two sources of SO_4^{2-} are distinct and have different $\delta^{34}S$, sulfur isotopes were successfully applied to the snow pit data in order to further quantify SO_4^{2-} sources.

$\delta^{34}S$ values ranged from 0.4 to 19.4‰, indicating two distinct end members that can be quantified through a mixing equation. During background periods, SO_4^{2-} production is dominated by anthropogenic emissions, which account for between 57 to 98% of the total SO_4^{2-}, with dust emissions contributing 2 to 43% of the SO_4^{2-}. This record captured one large dust event. This event was dominated by dust-derived SO_4^{2-}, which accounted for 78% of the SO_4^{2-}. Dust events bring in more anthropogenic SO_4^{2-} along with the dust-derived SO_4^{2-}. This is because these events indicate an increase in vertical convective atmospheric transport, and as such they also facilitate an increase in the amount of anthropogenic SO_4^{2-} transported to the sample site.

When applied to the ice core record, sulfur isotopes can be useful for elucidating further information about SO_4^{2-} deposition and therefore the sulfur cycle. In order to better assess the effects of atmospheric SO_4^{2-} on paleo-climate, it is necessary to understand the background SO_4^{2-} conditions and to what extent these conditions change with time and anthropogenic influence. The use of sulfur isotopes for this goal is most effective when applied to high-resolution samples. It is difficult to achieve high-resolution sampling from an ice core because a relatively large amount of SO_4^{2-} (100 μg) is necessary to perform sulfur isotopic analysis using the current method (isotope ratio mass spectrometry (IRMS) technique). This method has high precision, but is time consuming. In clean areas such as Antarctica, a large volume of sample is needed to get the mass necessary for analysis.

Recently, the inductively coupled plasma mass spectrometry (ICP-MS) technique was used to make $\delta^{34}S$ measurements and offers several advantages over the traditional method (IRMS). Sulfur isotopes were analyzed with high precision on an ICP-MS with a sample concentration of as low as 1 ppb with a precision of 0.09 RSD (Prohaska *et al.*, 1999). This high precision was achieved also with high sample throughput, making this technique less time consuming than IRMS. Measurements performed on an ICP-MS will make it possible to obtain high resolution data from low sample volume, thereby making sulfur isotopic analysis a more efficient and tenable tool for ice core paleo-climate studies.

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Appendix: Snow Pit and Fresh Snow Ion and $\delta^{18}O$ Data From the 2000-2001 and 2001-2002 US ITASE Traverses

Ion concentrations and the $\delta^{18}O$ profile for snow pit samples collected along the ITASE traverses in 2000-2001 and 2001-2002 are presented in this appendix, along with the ion concentrations for fresh snow samples. $\delta^{18}O$ dating of the snow pit collected from Site 1 along the 2000-2001 traverse shows it to cover approximately 2.5 years. A $\delta^{18}O$ peak (~ -32‰) occurs at the top of the snow pit and reflects summer conditions. Winter lows (~ -36‰) occur twice, and provide a basis for dating. The ion concentrations (Na^+, Ca^{2+}, SO_4^{2-} and NO_3^-) show no discernable pattern, with several peaks through the record.

Site 3 from the 2001-2002 ITASE traverse is dated based on the $\delta^{18}O$ values (peaks ~ -32‰ and lows ~ -38‰) and covers approximately one year. The ion concentrations (Na^+, Ca^{2+}, SO_4^{2-} and NO_3^-) show several peaks through the record, but no discernable seasonality.

Samples were sent to the Memorial University of Newfoundland in the summer of 2002 for $\delta^{34}S$ analysis. Snow pit samples are at 10 cm resolution. There are 15 samples from site 1 (2000-2001 traverse) and 9 samples from site 3 (2001-2002 traverse). There are 7 fresh snow samples from the 2000-2001 traverse that range from 80°S to 77.4°S and 111.13°W to 124.28°W. There are 5 fresh snow samples from the 2001-2002 traverse that range from 77.06°S to 79.16°S and 89.14°W to 104.97°W.

Based on the results of this thesis, $\delta^{34}S$ measured from snow pits might be expected to show a maximum in the summer and a minimum in the winter. The summer maximum might be due to an increase influx of marine biogenic emissions (with a high

$\delta^{34}S$). The winter minimum might occur because of the influence of stratospheric precipitation (with a negative $\delta^{34}S$) and the decrease of marine biogenic emissions.

$\delta^{34}S$ might be expected to vary spatially, with higher values at sites closer to an ocean source, where the precipitation is heavily dominated by marine precipitation. Lower values can be expected at sites further inland because there is likely less marine influence.

Depth	Na$^+$	K$^+$	Mg^{2+}	Ca^{2+}	Cl$^-$	NO$_3^-$	SO$_4^{2-}$	MSA	Excess SO$_4^{2-}$	Terr. SO$_4^{2-}$	R value	δ^{18}O
(ITASE 00-01), Site 1 *79.22° S, 111.13° W*												
0-10 cm	9.25	2.67	1.39	5.41	16.48	21.10	21.01	11.27	18.68	0.91	0.60	-29.24
10-20 cm	13.26	0.57	1.77	1.47	19.87	36.50	18.40	4.52	15.06	0.17	0.30	-30.43
20-30 cm	17.91	1.10	2.20	1.22	35.80	82.98	17.10	4.94	12.59	0.10	0.39	-34.2
30-40 cm	54.99	2.35	6.23	2.99	98.55	72.35	23.53	4.09	9.67	0.16	0.42	-34.56
40-50 cm	6.55	0.32	1.14	0.72	14.64	32.70	9.77	7.39	8.12	0.08	0.91	-35.7
50-60 cm	7.90	0.75	0.98	0.77	18.72	41.14	13.06	9.87	11.07	0.08	0.89	-32.79
60-70 cm	20.50	0.98	2.51	1.07	36.67	40.91	21.52	17.7	16.35	0.05	1.08	-31.05
70-80 cm	7.62	0.68	1.14	0.67	20.63	49.84	53.64	22.55	51.72	0.07	0.44	-31.56
80-90 cm	16.80	0.94	2.11	1.17	30.92	42.86	45.85	11.64	41.62	0.10	0.28	-32.01
90-100 cm	32.56	1.54	4.19	2.16	52.24	72.23	30.90	4.54	22.69	0.17	0.20	-34.51
100-110 cm	32.38	1.18	4.13	1.66	57.46	36.11	14.09	3.63	5.93	0.08	0.61	-35.2
110-120 cm	12.98	0.63	1.74	0.95	25.02	23.68	9.41	5.69	6.14	0.08	0.93	-35.66
120-130 cm	7.33	0.14	1.10	0.61	18.42	49.69	18.19	16.8	16.34	0.06	1.03	-34.6
130-140 cm	36.36	1.24	4.43	1.71	61.97	36.50	54.08	17.34	44.92	0.06	0.39	-32.03
140-150 cm	63.32	2.05	8.01	2.60	108.64	17.09	34.94	11.42	18.98	0.03	0.60	-31.96
(ITASE 01-02) Site 3 *78.12° S, 95.65° W*												
0-10 cm	51.32	3.63	6.15	3.03	82.08	32.69	28.71	8.25	15.78	0.19	0.52	-34.81
10-20 cm	43.49	2.54	5.18	1.65	69.92	37.01	23.66	8.64	12.70	0.00	0.68	-35.35
20-30 cm	19.83	2.86	2.79	1.19	35.85	36.07	17.04	4.32	12.04	0.08	0.36	-31.01
30-40 cm	14.87	1.21	2.24	0.85	28.88	32.30	12.01	4.39	8.26	0.05	0.53	-37.61
40-50 cm	25.92	1.79	3.31	1.23	45.88	52.59	16.28	4.02	9.75	0.04	0.41	-32.41
50-60 cm	16.39	1.11	2.23	1.00	28.24	37.72	17.79	9.34	13.66	0.07	0.68	-32.31
60-70 cm	4.68	1.37	0.75	0.69	15.13	45.02	33.42	19.57	32.24	0.09	0.61	-32.19
70-80 cm	3.90	0.53	0.88	0.97	22.38	98.26	64.79	12.37	63.81	0.15	0.19	-30.41
80-90 cm	2.82	0.24	0.68	0.40	18.15	80.68	33.80	8.2	33.09	0.05	0.25	-30.73

Table A1. Snowpit data for Site 1 from the 2000-2001 ITASE traverse and Site 3 from the 2001-2002 ITASE traverse.

Location (lat., lon.)	Site	Sample	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}	MSA	Excess SO_4^{2-}	Terr. SO_4^{2-}	R value	$\delta^{18}O$
(ITASE '00-'01)														
79.22° S, 111.13° W	2	1	9.2	1.0	1.6	1.0	19.6	34.5	9.2	1.0	1.6	1.0	19.6	34.5
		2	8.8	0.7	1.2	0.9	18.1	32.5	8.8	0.7	1.2	0.9	18.1	32.5
78.25° S, 115.55° W	3	1	16.6	1.7	1.9	1.7	52.9	132.0	16.6	1.7	1.9	1.7	52.9	132.0
		2	15.5	2.5	2.0	0.9	46.0	118.0	15.5	2.5	2.0	0.9	46.0	118.0
78.4° S, 120.4° W	4	1	19.7	1.7	2.3	1.6	52.6	94.3	19.7	1.7	2.3	1.6	52.6	94.3
77.40° S, 123.59° W	5	1	27.4	1.4	3.6	1.6	66.3	95.2	27.4	1.4	3.6	1.6	66.3	95.2
		2	26.9	1.5	3.5	1.3	69.1	97.9	26.9	1.5	3.5	1.3	69.1	97.9
78.19° S, 124.28° W	6	1	4.0	0.8	0.9	1.2	34.4	87.0	4.0	0.8	0.9	1.2	34.4	87.0
		2	4.9	0.4	0.8	1.1	36.8	87.1	4.9	0.4	0.8	1.1	36.8	87.1
79.8° S, 122.16° W	7	1	19.7	0.5	2.6	1.1	32.1	42.6	19.7	0.5	2.6	1.1	32.1	42.6
		2	15.3	0.8	1.9	0.8	37.0	73.3	15.3	0.8	1.9	0.8	37.0	73.3
80.00° S, 119.42° W	Byrd	1	8.2	0.6	1.3	0.7	41.5	115.4	8.2	0.6	1.3	0.7	41.5	115.4
		2	13.6	0.8	1.6	0.7	52.2	122.8	13.6	0.8	1.6	0.7	52.2	122.8
(ITASE '01-'02)														
79.16° S, 104.97° W	1	1	21.1	0.7	2.5	0.7	40.1	45.1	21.1	0.7	2.5	0.7	40.1	45.1
		2	23.3	1.6	2.7	1.3	44.3	44.7	23.3	1.6	2.7	1.3	44.3	44.7
77.84° S, 102.91° W	2	1	12.0	0.3	1.8	1.2	23.9	58.1	12.0	0.3	1.8	1.2	23.9	58.1
		2	12.7	0.6	1.8	1.3	24.3	56.0	12.7	0.6	1.8	1.3	24.3	56.0
78.12° S, 95.64° W	3	1	13.5	0.5	2.0	2.8	38.5	83.1	13.5	0.5	2.0	2.8	38.5	83.1
		2	11.5	0.7	1.6	1.3	38.0	73.4	11.5	0.7	1.6	1.3	38.0	73.4
77.61° S, 92.25° W	4	1	12.4	0.4	1.9	1.3	36.1	63.6	12.4	0.4	1.9	1.3	36.1	63.6
		2	11.8	0.4	1.8	1.2	33.8	62.3	11.8	0.4	1.8	1.2	33.8	62.3
77.06° S, 89.14° W	5	1	68.6	2.3	8.1	3.6	108.7	45.9	68.6	2.3	8.1	3.6	108.7	45.9
		2	65.1	2.4	7.4	3.0	110.1	31.3	65.1	2.4	7.4	3.0	110.1	31.3

Table A2. Ion and $\delta^{18}O$ data from fresh snow samples collected along the US ITASE traverses.

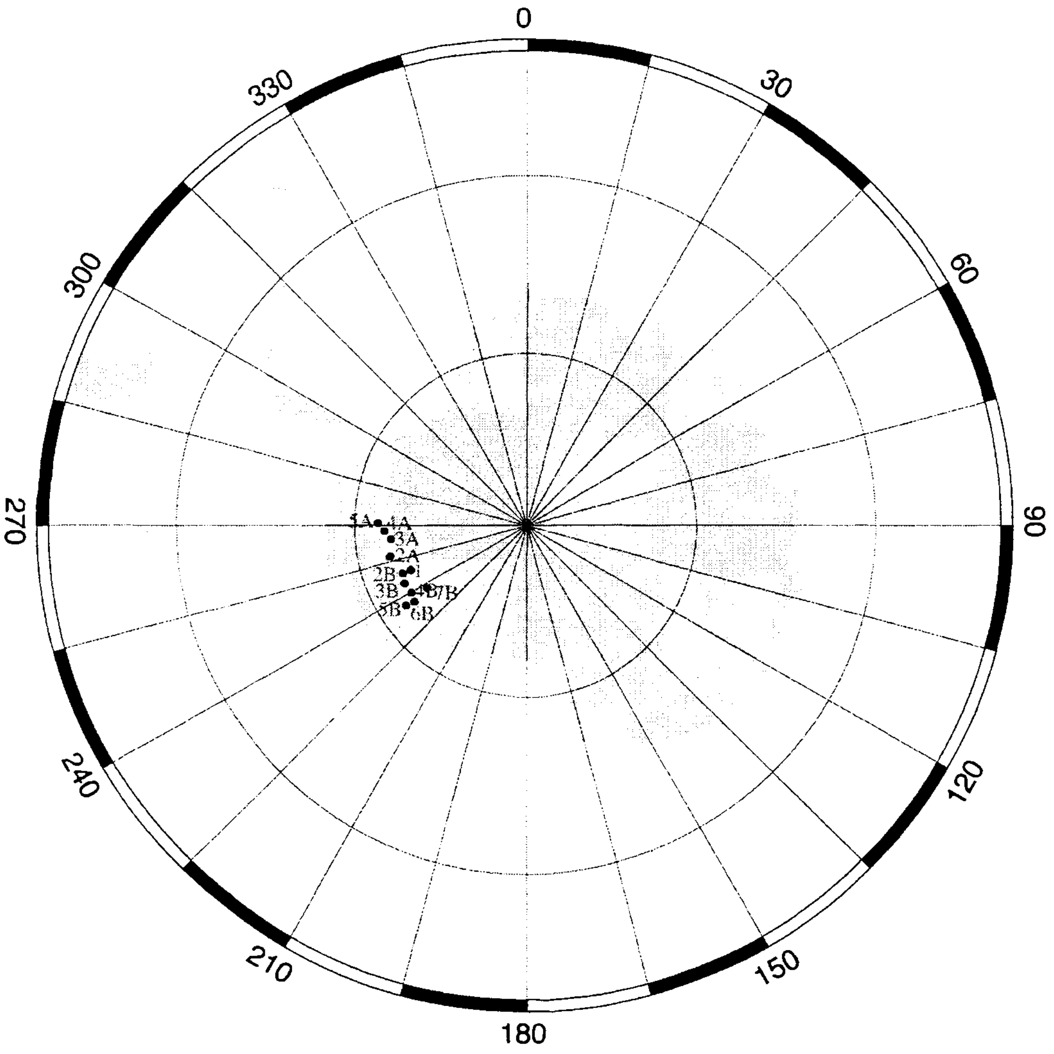

Figure A1. Location of samples collected along US ITASE traverses for $\delta^{34}S$ analysis. Numbers accompanied by B indicate sites along the 2000-2001 traverse, while A indicates the 2001-2002 traverse.

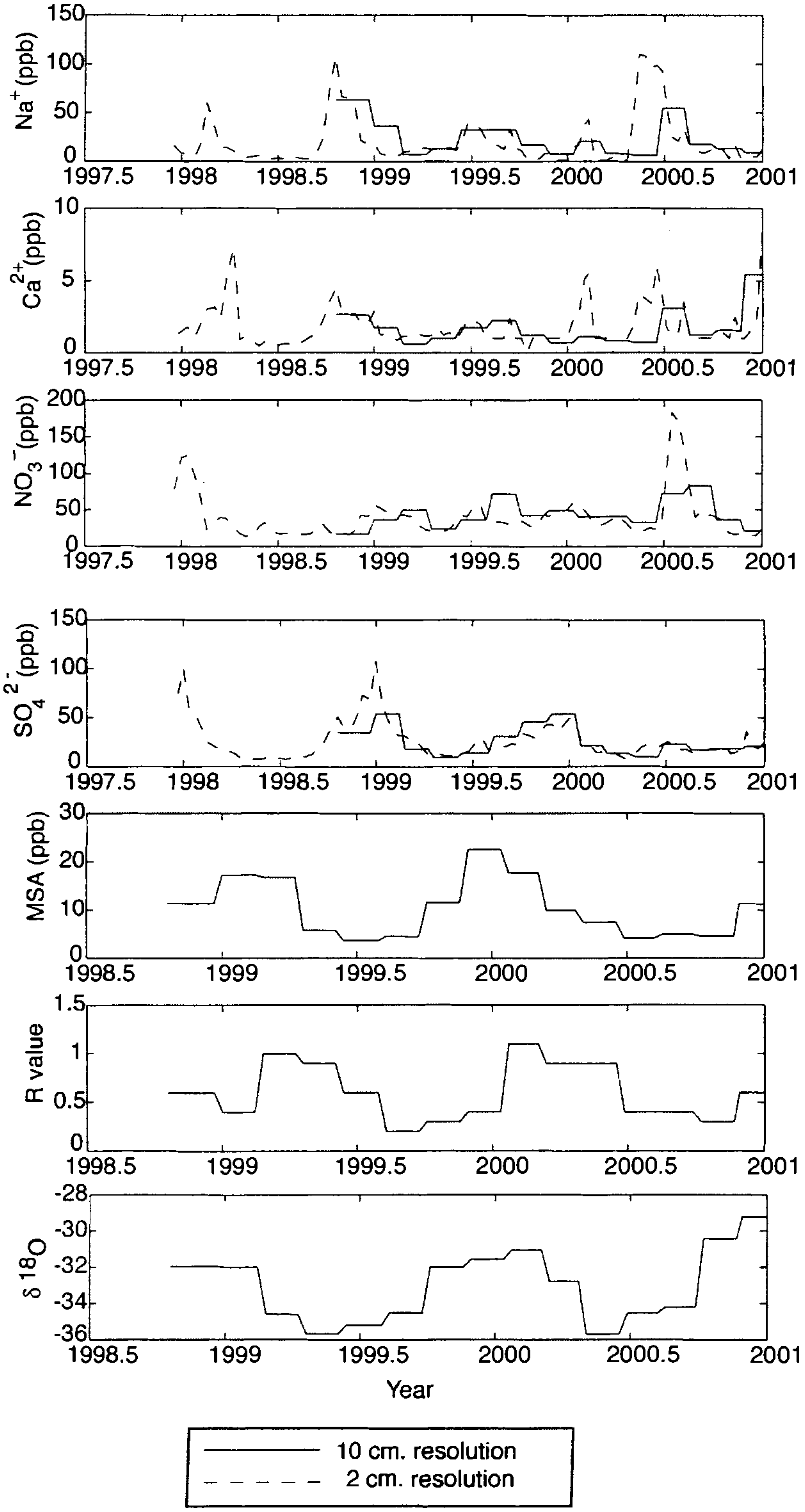

Figure A2. Snow pit data from Site 1 along the 2000-2001 US ITASE traverse. 2 cm resolution is not available for MSA, R value and δ^{18}O.

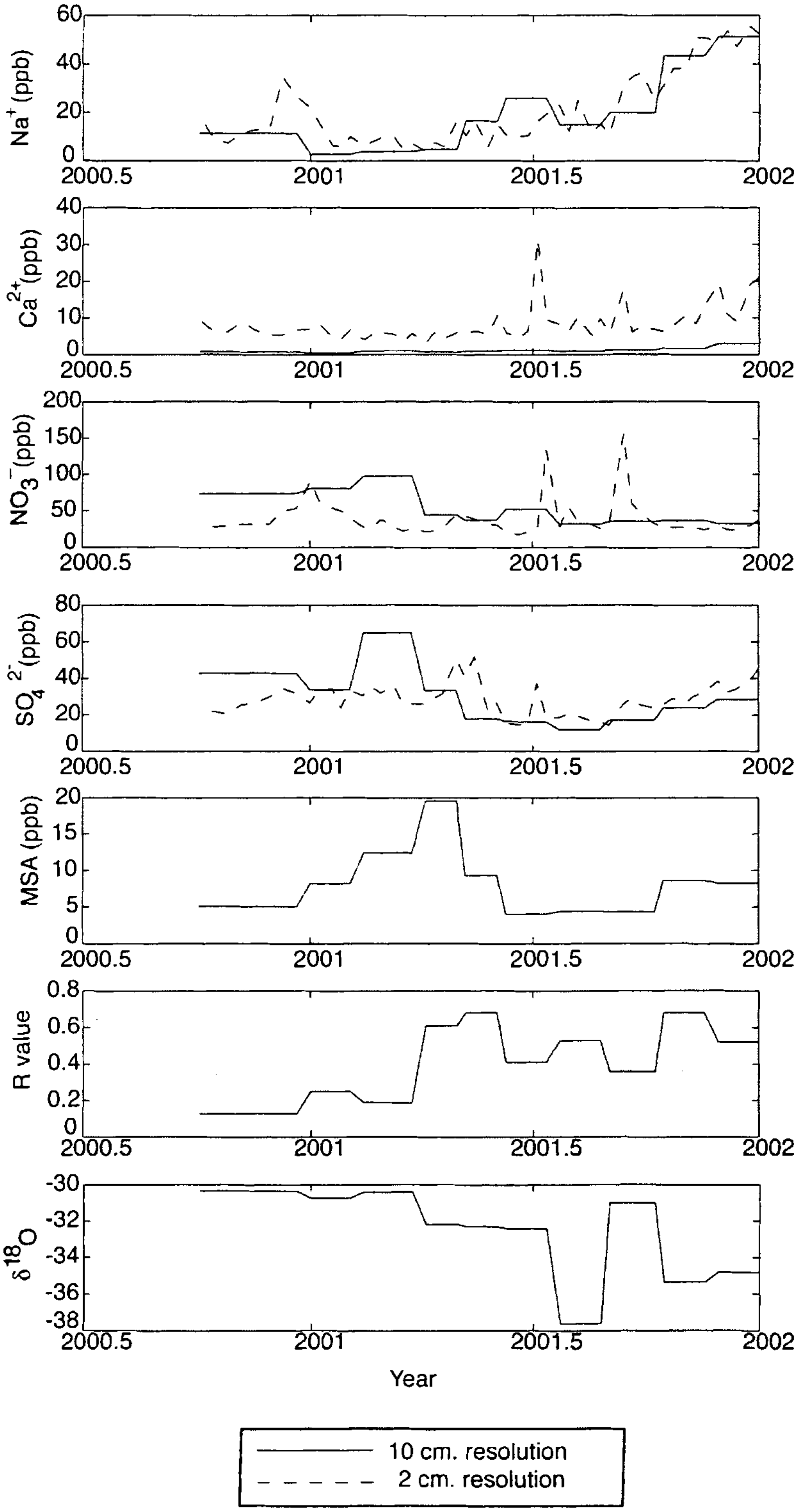

Figure A3. Snow pit data from Site 3 along the 2001-2002 US ITASE traverse. 2 cm resolution is not available for MSA, R value and δ^{18}O.

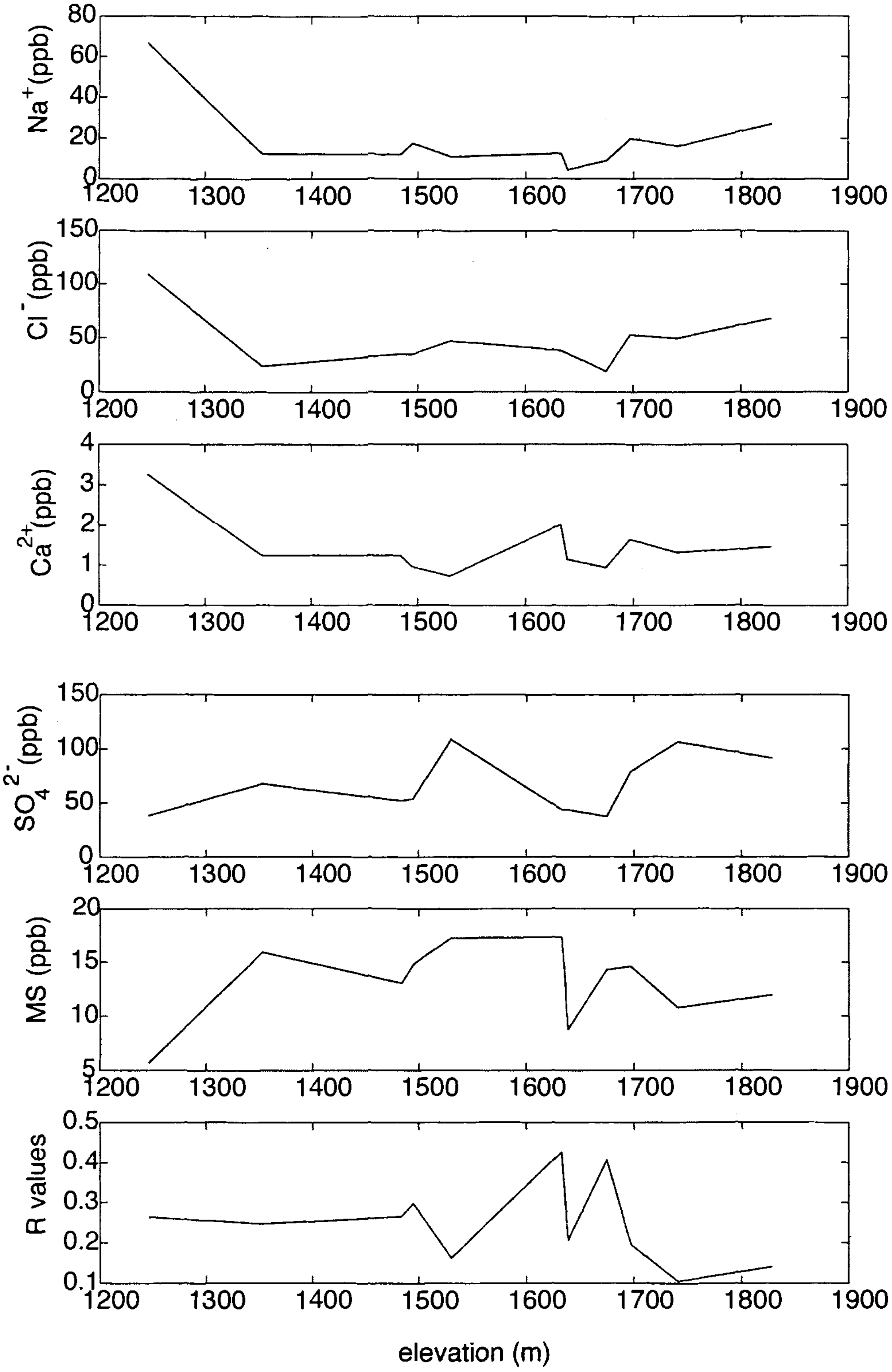

Figure A4. Chemical species vs. elevation.

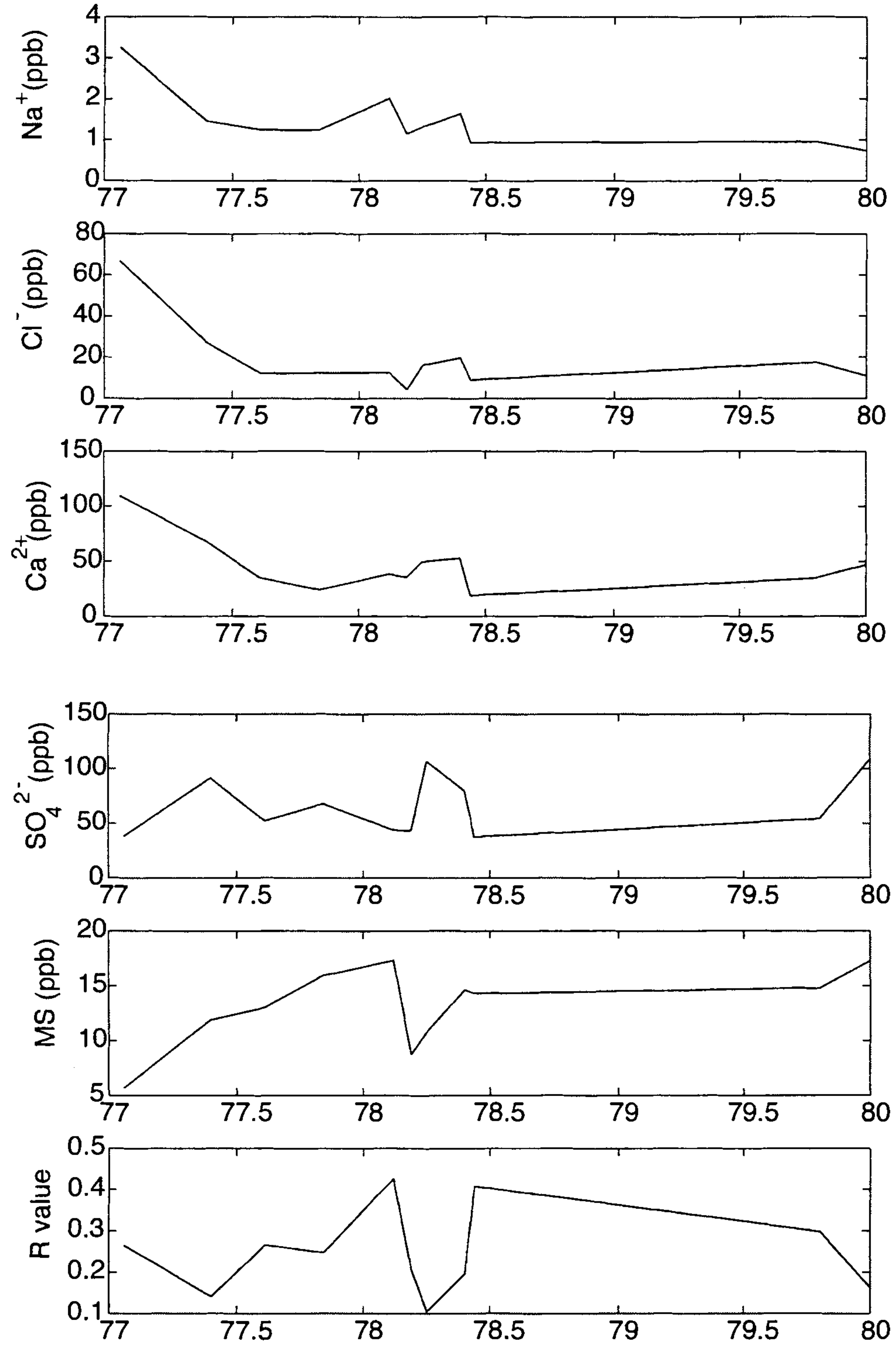

Figure A5. Chemical species vs. latitude.

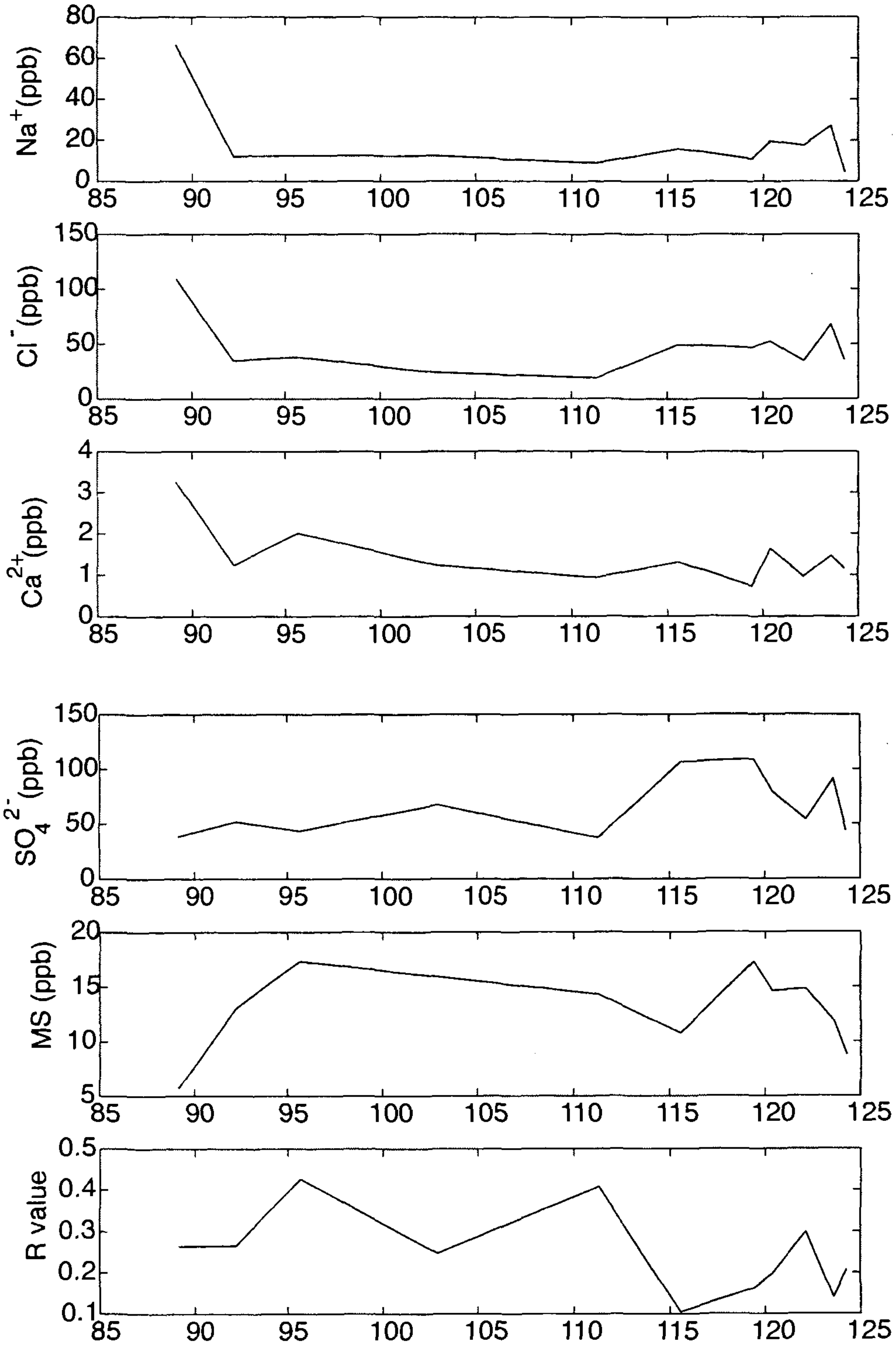

Figure A6. Chemical species vs. longitude.

BIOGRAPHY OF THE AUTHOR

Lee Pruett was born in Sikeston, MO on June 16, 1977. She graduated from Cactus Shadows High School in Cave Creek, AZ in 1995. Lee received a Bachelor of Arts degree from the Department of Geophysical Sciences and completed the requirements for a double major in Philosophy from The University of Chicago in 1999. She participated in a year of community service through Americorps and was a personal assistant/bookkeeper/transcriber prior to enrolling at The University of Maine. Lee served as a Research Assistant in the Climate Change Institute. Lee is a candidate for the Master of Science degree in Quaternary and Climate Studies from The University of Maine in August, 2003.