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Sulfur isotopic measurements from a West Antarctic ice core: implications for sulfate source and transport

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ABSTRACT. Measurements of δ^{34}S covering the years 1935–76 and including the 1963 Agung (Indonesia) eruption were made on a West Antarctic firn core, RIDSA (78.73 S, 116.33 W; 1740 m a.s.l.), and results are used to unravel potential source functions in the sulfur cycle over West Antarctica. The δ^{34}S values of SO_4^{2-} range from 3.1‰ to 9.9‰. These values are lower than those reported for central Antarctica, from near South Pole station, of 9.3–18.1‰ (Patris and others, 2000). While the Agung period is isotopically distinct at 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 δ^{34}S values indicate, however, that this marine biogenic SO_4^{2-}, with a well-established δ^{34}S of 18‰, is mixing with SO_4^{2-} that has extremely negative δ^{34}S values to produce the measured isotope values in the RIDSA core. We suggest that the transport and deposition of stratospheric SO_4^{2-} in West Antarctica, combined with local volcanic input, accounts for the observed variance in δ^{34}S values.

INTRODUCTION

Deconvoluting the biogeochemical cycling of atmospheric sulfur is important for understanding climate change. Sulfate (SO_4^{2-}) aerosols play a key role in moderating the Earth's climate. They function as cloud condensation nuclei 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 and others, 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 (Bates and others, 1987; Charlson and others, 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 particles derived from sea-salt particles are generally >1 µm in diameter and play an important role in the marine boundary layer (Murphy and others, 1998). 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 (Shaw, 1982; Legrand and Mayewski, 1997). Unlike ice-core records from Greenland, which clearly show an increase in background SO_4^{2-} concentration since the industrial revolution (Mayewski and others, 1993), Antarctica shows no increase

in total SO_4^{2-} concentration with time (Legrand, 1997; Legrand and Mayewski, 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 $xsSO_4^{2-}$ in the Antarctic comes primarily from marine biogenic sources (Pszenny and others, 1989; Minikin and others, 1998). Mount 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 and others, 1991; Legrand, 1997) and have been used to assess the sulfur cycle in Antarctica (Delmas and Boutron, 1980; Legrand and Feniet-Saigne, 1991; Meyerson and others, 2002). 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 and others, 1998). Excess SO_4^{2-} concentrations are independent of accumulation rate and elevation on a continent-wide scale (Mulvaney and Wolff, 1994; Kreutz and Mayewski, 1999). Distance inland correlates to a decrease in the concentration of $xsSO_4^{2-}$, which may be due to the portion of SO_4^{2-} that is derived from marine productivity. The 1998 Italian ITASE (International Trans-Antarctic Scientific Expedition) traverse in East Antarctica demonstrated that the decrease inland of $xsSO_4^{2-}$ extended only 250 km and then SO_4^{2-} increased in concentration from 250 to 770 km (Proposito and others, 2002). In surface snow measurements, there is a negative correlation between both distance inland and elevation and methanesulfonic acid

(MSA) concentration. As with $xsSO_4^{2-}$, accumulation rate does not affect MSA concentration, except perhaps at low-accumulation-rate sites (Legrand and others, 1992; Wagnon and others, 1999). A seasonal variation of MSA occurs in several cores. The presence of the seasonal signal depends on location, with only an interannual signal at South Pole and a stronger signal in coastal areas (Legrand and others, 1992; Meyerson and others, 2002). In other Antarctic studies, there is no seasonal variation, unlike both sea-salt SO_4^{2-} and $xsSO_4^{2-}$ (Ivey and others, 1986). Recent aerosol studies and data from snow pits and firn cores indicate that MSA and $xsSO_4^{2-}$ correlate on a seasonal basis, with summer peaks and winter lows (Legrand and others, 1992; Stenni and others, 2000; Arimoto and others, 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. Stable sulfur isotopes provide a potentially useful 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 (Calhoun and others, 1991; Nriagu and others, 1991; Wadleigh and others, 1996). Sulfur isotopes are useful in studying atmospheric transport mechanisms and chemistry during volcanic eruptions (Castleman and others, 1973) and during anthropogenic emissions (Newman and others, 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 central Antarctica (Patris and others, 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 and others (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 and others, 2002). Applying sulfur isotope studies to ice-core records can greatly improve 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. These measurements are used to infer differences between the sources of SO_4^{2-} in West Antarctica and central Antarctica. These data indicate the potential of sulfur isotopes as a tool for partitioning the SO_4^{2-} sources (marine biogenic, sea-salt and volcanic) to West Antarctica.

METHODS

Core processing

The 147 m RIDSA ice core (78.73 S, 116.33 W; 1740 m a.s.l.) (Fig. 1) was retrieved in West Antarctica in 1995 (Kreutz and Mayewski, 1999). Core processing was performed in clean
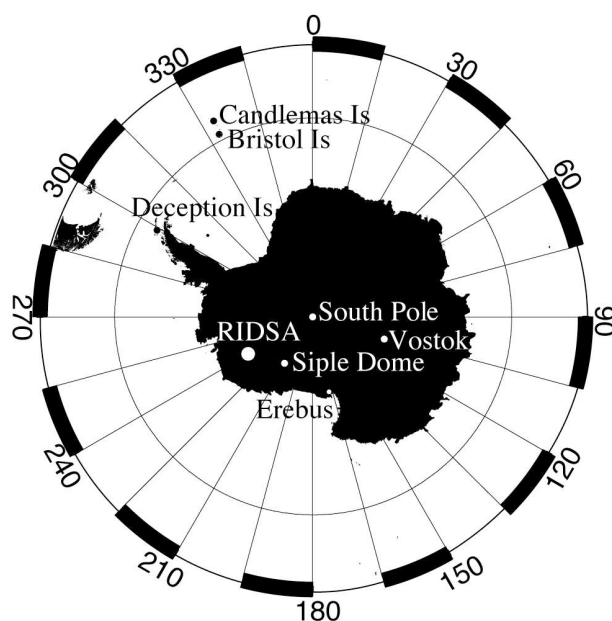

Fig. 1. RIDSA location map. Several other cores are denoted in white text. Volcanoes that are known to have been active during the time period covered by isotopic measurements presented in this paper are represented with black text.

conditions, with samples collected into pre-cleaned containers and stored below –15ôC 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. From meter 60 to 147, processing was done at 60 cm intervals. One-meter sections of core from 10 to 26 m were used for sulfur isotopic analysis, covering the period 1935–76. The time covered by individual samples in this dataset (RIDSA 2001) was 2–3 years, depending on accumulation rate.

Sections of the RIDSA core from 67.2 to 69.6 m, covering the years 1796–1805, and from 13.8 to 15.9 m, covering the years 1961–67, were used for isotopic method development. These samples are designated as RIDSA 2000.

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 and others, 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). It is possible to count back to the global horizon using summer peaks in $nssSO_4^{2-}$. Dating is therefore based on seasonal $nssSO_4^{2-}$ cycles (Kreutz and others, 2000). These dating techniques show that the entire core covers the time period 1506–1995.

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

Table 1. Ion concentrations for each RIDSA sample. Units are ngg^{-1} except for Cl/Na mass ratio and R value, which have no units. The R value is the ratio $MSA/xsSO_4^{2-}$ and is often used to assess the marine biogenic portion of total SO_4^{2-}

Depth	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	MSA	NSS SO_4^{2-}	Cl^-/Na^+ mass ratio	R value
m											
RIDSA 2001											
10–11	20.3	1.4	1.5	3.1	1.4	42.8	32.6	5.6	22.8	2.1	0.25
11–12	22.7	1.3	1.4	2.9	1.6	46.1	35.5	5.3	28.5	2.0	0.19
12–13	25.7	1.4	2.3	3.4	1.7	53.0	36.6	6.6	23.0	2.1	0.29
13–14	26.2	1.8	1.7	3.5	2.1	53.3	39.2	7.2	30.1	2.0	0.24
14–15	26.2	1.7	1.5	3.4	1.6	53.7	37.7	8.9	49.6	2.0	0.18
15–16	19.9	1.3	1.1	2.6	1.3	37.2	32.5	9.4	31.6	1.9	0.30
16–17	21.0	1.4	1.2	3.1	1.6	47.4	31.1	6.1	20.9	2.3	0.29
17–18	17.1	1.4	1.1	2.3	1.2	34.5	32.2	8.8	24.9	2.0	0.35
18–19	39.4	1.9	2.0	5.2	2.2	77.8	36.6	8.1	28.6	2.0	0.28
19–20	22.7	1.4	1.2	2.9	1.3	45.8	32.7	10.2	29.5	2.0	0.35
20–21	30.3	1.7	4.4	4.0	1.8	60.8	33.8	11.3	27.5	2.0	0.41
21–22	17.0	1.7	1.1	2.3	1.4	37.3	43.3	8.8	32.4	2.2	0.27
22–23	19.0	1.8	1.3	2.5	1.3	41.4	34.9	5.7	22.6	2.2	0.25
23–24	24.0	1.9	1.5	3.2	1.5	48.4	39.4	7.5	27.2	2.0	0.28
24–25	17.6	2.0	2.5	2.2	1.2	36.5	37.5	9.3	22.4	2.1	0.42
25–26	38.2	2.1	2.5	5.1	3.0	74.5	28.8	8.8	17.6	2.0	0.5
RIDSA 2000											
13.8–15.9	25.8	1.7	1.5	3.3	1.6	50.9	37.8	9.0	36.4	2.0	0.25
67.2–69.6	28.6	0.9	1.6	3.7	1.3	60.0	38.3	8.1	25.9	2.1	0.31

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

where k is equal to the sea-water (SO_4^{2-}/Na^+) mass ratio, 0.251 (Wilson, 1975).

Isotope 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 and others, 2000). The RIDSA 2000 samples are aggregated residual from samples taken from the RIDSA core that were previously aliquoted for chemical analysis. Sampling was initially performed at 3 cm intervals for analysis of major ions. Two time periods, one covering the Agung (Indonesia) period (1963 eruption) and one covering a pre-industrial period, were chosen, and sample remaining from the initial chemical analysis was combined until a volume of 1 L was attained. The years covered by these two measurements were dependent on the volume needed for isotopic analysis (1 L). Additional isotopic analysis was performed on 1 m sections of the RIDSA core, including the Agung period. All core sections were melted in sterile conditions and then transferred to 1 L bottles for analysis at the Memorial University of Newfoundland. 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, High Efficiency Particle Air (HEPA)-filtered air fume hood, and the solutions were slowly evaporated until the volume was reduced to approximately 20 mol from an initial 1 L. The concentrated sample was then used to fill 10 û 10 û 10 mM tin capsules and evaporated to dryness. The process was repeated between two and five 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 the standard, Vienna Canyon Diablo Troilite (VCDT), and is represented by:

$$\delta^{34}S(\%) = \left\{ \left[\left(^{34}S/^{32}S\right)_{sample} / \left(^{34}S/^{32}S\right)_{VCDT} \right] - 1 \right\} * 1000.$$

$$(2)$$

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

RESULTS

Ion data

Ion averages for each of the meters taken for isotopic analysis (10–26 m; RIDSA 2001) and the RIDSA 2000 samples are presented in Table 1, along with the years covered. The one sample of overlap between the two RIDSA datasets is consistent with the other.

Sodium and $xsSO_4^{2-}$ have strong seasonal cycles, consistent with other studies in the Antarctic (Fig. 2) (Murozumi and others, 1969; Herron and Langway, 1979; Hammer, 1980; Legrand and others, 1992; Whitlow and others, 1992; Minikin and others, 1998; Kreutz and Mayewski, 1999; Reusch and others, 1999).

Na^+ peaks in the winter due to increased storm activity, while $xsSO_4^{2-}$ has a summer peak due to its marine biogenic component (Whitlow and others, 1992). During the summer months, sea ice retreats as solar radiation increases, leaving more open ocean in which primary productivity can thrive. One sign of increased productivity might be the increase in SO_4^{2-} concentration during the summer months. The MSA
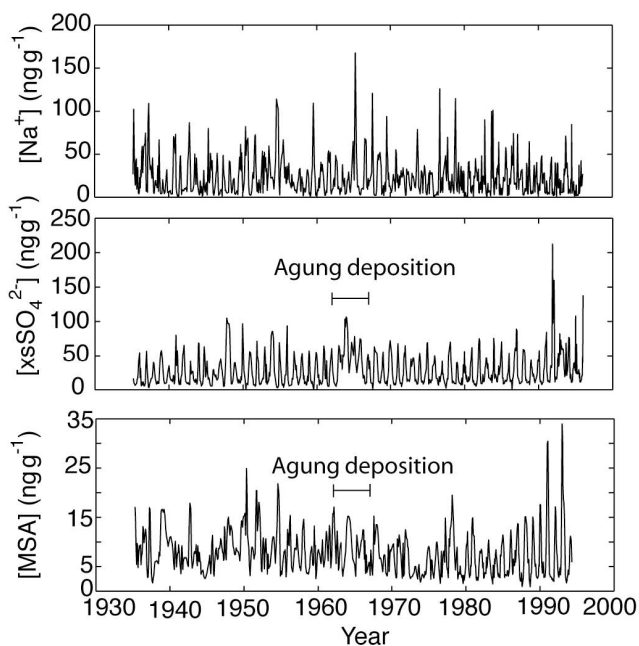
Fig. 2. High-resolution Na^+, $xsSO_4^{2-}$ and MSA data from the RIDSA core. These data show the portion of the core that was analyzed for sulfur isotopes and extend to the top of the core. A clear seasonal cycle can be seen for all species.

Fig. 3. Sulfur isotope measurements from the RIDSA core plotted with published data from central Antarctica (Patris and others, 2000). The linear regression is shown for each dataset. The $\delta^{34}S$ values are plotted against the inverse of the total sulfate concen-

profile shows a subdued seasonal signal relative to the $xsSO_4^{2-}$ signal (Fig. 2). In other glaciochemical studies performed in the Antarctic, MSA has also been found to correlate with $xsSO_4^{2-}$, with both showing a summer maximum (Kreutz and Mayewski, 1999). The $xsSO_4^{2-}$ is a combination of primarily, or perhaps exclusively, marine biogenic and volcanic SO_4^{2-}. Table 2 gives concentration data for the three possible contributors to total SO_4^{2-} for the RIDSA samples.

The Agung eruption (17 March 1963) is apparent in the $xsSO_4^{2-}$ profile (Fig. 2) and can be seen as an increase in the seasonal minima of SO_4^{2-} from late 1963 to 1966 (Devine and others, 1984). The eruption is recorded in the RIDSA core starting in late 1963, about 6 months after the eruption. This time difference of around 6 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 6 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-}, as is the case with the Agung eruption (Fig. 2). The other volcanic period shown in Figure 2, the 1991 Pinatubo–Hudson eruption, is an exception. This may be related to seasonal changes in atmospheric transport or accumulation rate.

Isotope data

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 central Antarctica, which range from 9.3‰ to 18.1‰ (Patris and others, 2000). The measured isotopic signature is plotted against the inverse of total SO_4^{2-}
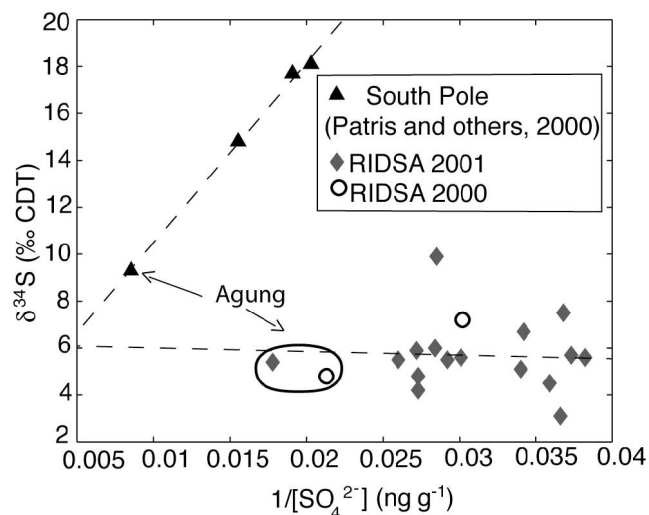
concentration to highlight isotope trends with concentration (Fig. 3).

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-}.

In West Antarctica, there is no discernible 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 1 m 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 and others, 2000):

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

where δ_{mes} is the measured isotopic signature as given in Table 2, δ_{ss}, δ_{vol} and 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 $xsSO_4^{2-}$, which was computed using the Na^+ concentration. The following equation represents the sea-salt fraction of a sample:

$$f_{ss} = \left([SO_4^{2-}] - [xsSO_4^{2-}]\right)/[SO_4^{2-}]. \quad (4)$$

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 and others, 1978). This reflects an enrichment in ^{34}S in ocean water compared to terrestrial sulfur. Rearranging Equation (3) yields:

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

Substituting the established value for δ_{ss} into the equation,

Table 2. Sulfur data from the RIDSA core. f_{ss} indicates the fraction of the total SO_4^{2-} concentration that comes from sea salt, δ_{tot} is the isotopic signature for total SO_4^{2-} and δ_{nss} is the isotopic signature for the non-sea-salt portion of total SO_4^{2-}

| Depth | Years | [SO_4^{2-}] | Contributions to total SO_4^{2-} | | f_{ss} | δ_{tot} | δ_{nss} |
| | | | Sea salt | Biogenic + volcanic | | | |
m		ng g^{-1}	ng g^{-1}	ng g^{-1}		‰	‰
RIDSA 2001							
10–11	1976–74	27.9	5.1	22.7	0.18	4.5	0.8
11–12	1974–71	34.2	5.7	28.4	0.17	5.5	2.4
12–13	1971–69	29.5	6.5	22.9	0.22	5.1	0.6
13–14	1969–66	36.6	6.6	29.8	0.18	4.8	1.3
14–15	1966–63	56.2	6.6	49.5	0.12	5.4	3.3
15–16	1963–60	36.6	5.0	31.5	0.14	4.2	1.5
16–17	1960–58	26.2	5.3	20.8	0.20	5.6	1.7
17–18	1958–55	29.2	4.3	24.8	0.15	6.7	4.2
18–19	1955–53	38.5	9.9	28.5	0.26	5.5	0.1
19–20	1953–50	35.2	5.7	29.4	0.16	6.0	3.1
20–21	1950–47	35.1	7.6	27.4	0.22	9.9	6.8
21–22	1947–45	36.7	4.3	32.3	0.12	5.9	3.9
22–23	1945–43	27.3	4.8	22.4	0.18	3.1	-0.7
23–24	1943–40	33.2	6.0	27.1	0.18	5.6	2.2
24–25	1940–37	26.8	4.4	22.3	0.16	5.7	2.7
25–26	1937–35	27.2	9.6	17.3	0.35	7.5	0.1
RIDSA 2000							
13.76–15.93	1961–67	42.9	6.5	36.3	0.15	4.8	1.9
67.2–69.6	1796–1805	33.1	7.2	25.9	0.22	7.2	3.4

The calculations are explained in the text.

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 xsSO$_4^{2-}$ concentration to yield a mixing diagram for the xs component in Figure 4. No significant correlation exists ($r = 0.38$).The highest $\delta^{34}S$ value (in the RIDSA time series) occurs in the sample covering the years 1947–50 (Fig. 5a). Mount Erebus eruptions are noted on the time series. The original xsSO$_4^{2-}$ data were smoothed using a high-tension robust spline to produce the data in Figure 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 underestimating sporadic processes (Meeker and others, 1995). The peaks in the smoothed data reflect changes in volcanic SO$_4^{2-}$. There appears to be a relationship between increases in background xsSO$_4^{2-}$ and $\delta^{34}S$.

DISCUSSION

The sulfur isotope ratios in the RIDSA ice core are lower than those in central Antarctica (Patris and others, 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 and others, 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‰ (De Hoog and others, 2001). Studies of volcanic gas emissions show a positive $\delta^{34}S$ value (Castleman and others, 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 Mount Erebus, Deception Island, Candlemas and Bristol Island as known eruptive volcanoes between 1935 and 1976. It is unlikely 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 11.7–35.3% 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 and others, 1991; Patris and others, 2000). This value is slightly lower than that of sea-salt SO$_4^{2-}$, which is close to 21‰ (Rees and others, 1978). The difference between these two marine constituents is the result of fractionation that occurs in the biological use of sea-water 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 central Antarctica determined that the background source of sulfur was almost exclusively of marine biogenic origin (Patris and others, 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 xsSO$_4^{2-}$ represent some combination of marine biogenic and volcanic SO$_4^{2-}$.The heavier isotope (^{34}S) is depleted faster than the lighter isotope (^{32}S) after volcanic eruptions, due to changes in
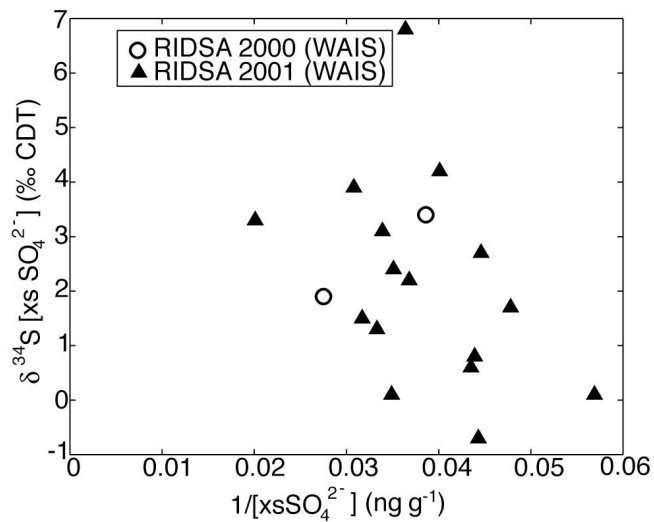
Fig. 4. The δ^{34}S measurements for the $xsSO_4^{2-}$ portion of the total sulfate from the RIDSA core plotted against the inverse of the $xsSO_4^{2-}$ concentration. The linear regression is represented by the dashed line.

Fig. 5. (a) Time-series δ^{34}S measurements for $xsSO_4^{2-}$ from the RIDSA core, along with Erebus eruptions (as noted by dashed lines with the year). The x-axis error bars depict the years that the data point represents. The variation on the y axis represents the analytical precision of the sample. (b) The smoothed $xsSO_4^{2-}$ time series from the RIDSA core. Smoothing was done with a robust spline. The peaks represent increases in the background sulfate concentration.

stratospheric chemistry and the pathway of SO_4^{2-} aerosol formation. Plume studies from anthropogenic emissions confirm this mechanism (Castleman and others, 1974; Newman and others, 1975). The lowest δ^{34}S values (–24.4‰) occur higher in the stratosphere (Castleman and others, 1974). One possibility in West Antarctica is that a large portion of the sulfur budget comes from a marine biogenic source with a δ^{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 δ^{34}S values could mix with local air masses with a relatively high δ^{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 δ^{34}S of the second contributor. Using the following mixing relationship between recalculated $xs\delta^{34}$S value and its two components

$$\delta_{mes} = f_{mb}\delta_{mb} + f_{vol}\delta_{vol} \qquad (6)$$

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

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 δ^{34}S values over time correspond to increases in the $xsSO_4^{2-}$ concentration over time. These $xsSO_4^{2-}$ peaks do not appear to reflect any global volcanism. Mount 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 1947–50. It coincides with a peak in the background $xsSO_4^{2-}$ and a known Erebus eruption. Local volcanism would cause an increase in the δ^{34}S value because newly erupted material
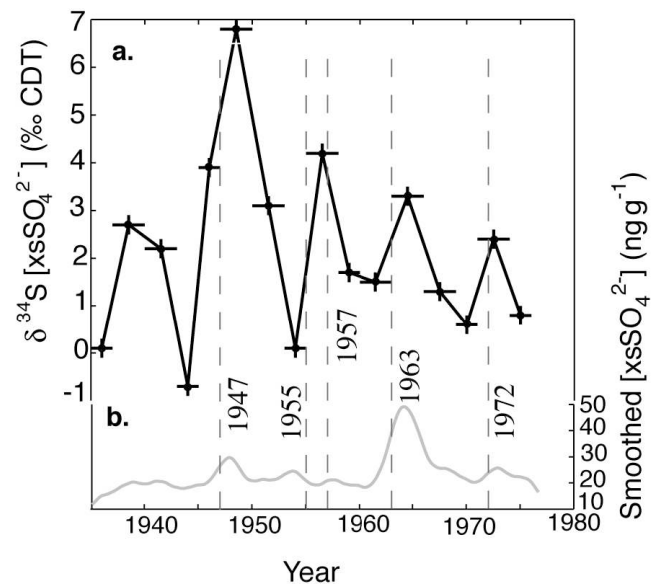
has a positive δ^{34}S value and is deposited relatively quickly, without the fractionation associated with transport (Castleman and others, 1974). The δ^{34}S peak during the 1947 Erebus event is much larger than the peak associated with the two other local events that occurred during 1957 and 1972. The peak in $xsSO_4^{2-}$ during the 1947 event is also much larger than the other peaks and is further evidence of the importance of local volcanism for the West Antarctic sulfur cycle (Delmas, 1982). There are not unusually high peaks in δ^{34}S associated with the 1957 and 1972 events and this may be because they were weak eruptions relative to the 1947 Erebus event and therefore did not deposit enough SO_4^{2-} to impact the isotopic signature in the same way.

The δ^{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 dataset 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 (Mount Erebus) also impacted deposition during this time and may provide an explanation for this discrepancy. If the 1963 Erebus eruption caused a higher δ^{34}S in local precipitation, then the subsequent mixing with precipitation from Agung (which carries a low δ^{34}S) might provide a mechanism by which the overall measured δ^{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 1947–50 sample.

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 to 1976. The measured δ^{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 $xsSO_4^{2-}$ δ^{34}S values range from –0.7‰ to 6.8‰, lower than those reported in central Antarctica (Patris and others, 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 δ^{34}S, and then become progressively lower over time due to a change in the chemical pathway of SO_4^{2-} aerosol formation. δ^{34}S values decrease with time and vertical distribution after an eruption (Castleman and others, 1973). Samples taken at the top of the stratosphere show more negative δ^{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 δ^{34}S air to produce the values seen in West Antarctica. Local volcanic emissions, specifically from Mount Erebus, also play a role in the sulfur cycle in West Antarctica, based on the correlation between increased δ^{34}S values, increased background $xsSO_4^{2-}$ and Mount Erebus eruptions.

Background peaks in $xsSO_4^{2-}$ 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 δ^{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.

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