

East Antarctic ice core sulfur isotope measurements over a complete glacial-interglacial cycle

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[1] Both sulfur and oxygen isotopes of sulfate preserved in ice cores from Greenland and Antarctica have provided information on the relative sources of sulfate in the ice and their chemical transformation pathways in the atmosphere over various time periods. The mass-independent fractionation in the oxygen isotopes of sulfate from the Vostok ice core from east Antarctica suggests that gas-phase oxidation by the hydroxyl radical (OH) was relatively greater than aqueous-phase oxidation by O₃ and H₂O₂ during the last glacial period than during the Eemian and preindustrial Holocene. The complete sulfur isotopic composition ($\delta^{33}\text{S}$, $\delta^{34}\text{S}$, $\delta^{36}\text{S}$) from the same Vostok ice core samples along with $\delta^{34}\text{S}$ measurements from the Dome C, east Antarctic ice core from this study lend support to these conclusions and reveal significant isotopic fractionation of $\delta^{34}\text{S}$ during chemical transformation and transport to east Antarctica. These findings reveal that conservation of sulfur isotopic signatures upon transport cannot be assumed for the East Antarctic plateau over the time periods considered. *INDEX TERMS*: 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 1040 Geochemistry: Isotopic composition/chemistry; 1610 Global Change: Atmosphere (0315, 0325); *KEYWORDS*: isotopes, sulfur cycle, atmosphere

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1. Introduction

[2] Sulfur isotope measurements ($\delta^{34}\text{S}$) of atmospheric sulfate and its precursors have been shown useful both for source apportionment [Mcardle and Liss, 1995; Wadleigh *et al.*, 1996; Mast *et al.*, 2001; Norman *et al.*, 1999] and for the study of relative oxidation pathways of sulfur species (SO₂ → SO₄²⁻) in the atmosphere [Tanaka *et al.*, 1994; Salzman *et al.*, 1983]. Source contributions can be determined from $\delta^{34}\text{S}$ measurements provided the isotopic signature of the source is known, and the isotope distribution is preserved during transport and chemical transformation in the atmosphere. Transformation and sink processes can be followed by measured isotopic fractionations when the physical and chemical processes that contribute to the fractionations are understood.

[3] Ice core sulfate is a conservative tracer of past atmospheric conditions. It preserves its isotopic composition during the thousands of years that it is trapped in the ice, and these sulfur and oxygen isotopic compositions trace past sources, sinks, and chemical transformations. $\delta^{34}\text{S}$ of sulfate preserved in shallow ice cores from Antarctica [Patris *et al.*, 2000] and Greenland [Patris *et al.*, 2002] have been used to quantify source contributions to the deposited sulfate and their evolution over the past ~700 years. Measurements of $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ of sulfate in Antarctica [Alexander *et al.*, 2002] and Greenland (B. Alexander *et al.*, manuscript in preparation, 2003) ice cores have provided information on changes in the oxidative pathways of sulfur species in the atmosphere due to major climate change (glacial/interglacial cycle) and anthropogenic influences (pre and post-Industrial Revolution). The mass-independent fractionation (MIF) in the oxygen isotopes defined by $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.512*\delta^{18}\text{O}$, has been shown to reflect the relative contribution of gas-phase OH oxidation and aqueous-phase oxidation by O₃ and H₂O₂ [Savarino *et al.*, 2000]. The value of 0.512 was determined from multiple analysis of three mass-dependently fractionated sulfate standards [see Savarino *et*

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al., 2001]. These three oxidants, OH, O₃, and H₂O₂, are the main oxidizing species in the atmospheric sulfur cycle and largely regulate the oxidation efficiency of the atmosphere [Thompson, 1992].

[4] Sulfur isotope ratios are expressed in delta notation defined according to the equation given below with respect to the Canyon Diablo Triolite (CDT) standard where x represents the heavy isotope.

$$\delta^X\text{S}(\text{‰}) = \left[\left(\frac{X\text{S}/^{32}\text{S}}{\text{sample}} / \left(\frac{X\text{S}/^{32}\text{S}}{\text{standard}} - 1 \right) \right) * 1000 \right]$$

Sulfur has a total of four stable isotopes (³²S, ³³S, ³⁴S and ³⁶S) whose abundances are 95.0%, 0.75%, 4.20% and 0.017% respectively. Equilibrium and kinetic fractionation is highly sensitive to isotopic mass, producing the following relationships on a three-isotope plot of $\delta^{33}\text{S}$ versus $\delta^{34}\text{S}$, and $\delta^{36}\text{S}$ versus $\delta^{34}\text{S}$:

$$\delta^{33}\text{S} = 0.515 * \delta^{34}\text{S}$$

$$\delta^{36}\text{S} = 1.91 * \delta^{34}\text{S}$$

However, mass-independent fractionation (MIF), where the above relationships do not apply, have been observed in the photopolymerization of CS₂ [Zmolek et al., 1999], the photolysis of SO₂ and H₂S [Farquhar et al., 2000a], and SF₅ + SF₅ → S₂F₁₀ [Bains-Sahota and Thiemens, 1989]. Deviation from normal mass-dependent fractionation patterns is measured by:

$$\Delta^{33}\text{S} = \delta^{33}\text{S} - 1000 * \left(\left(1 + \delta^{34}\text{S}/1000 \right)^{0.515} - 1 \right)$$

$$\Delta^{36}\text{S} = \delta^{36}\text{S} - 1000 * \left(\left(1 + \delta^{34}\text{S}/1000 \right)^{1.91} - 1 \right)$$

[5] Although the physical-chemical origin of the mass independent fractionation in sulfur isotopes is not known, $\delta^{33}\text{S}$, $\delta^{34}\text{S}$ and $\delta^{36}\text{S}$ measurements have been used to track atmospheric-derived sulfur species in Martian meteorites [Farquhar et al., 2000a] and Precambrian rocks [Farquhar et al., 2000b]. The authors attributed the large mass-independent fractionation ($-1.29\text{‰} \leq \Delta^{33}\text{S} \leq 2.04\text{‰}$, $-2.5\text{‰} \leq \Delta^{36}\text{S} \leq 3.1\text{‰}$) observed prior to 2090 to 2450 Ma in their Precambrian rock samples to the photolysis of SO₂ at wavelengths less than 220 nm because of a reduced column depth of ozone and oxygen during this time period. The photolysis of SO₂ has been shown [Farquhar et al., 2001; Pavlov and Kasting, 2002] to result in mass-independently fractionated ($\Delta^{33}\text{S} \neq 0$, $\Delta^{36}\text{S} \neq 0$) product sulfate and residual SO₂, the relationship between $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ being highly wavelength dependent.

[6] Mass-independent fractionation has also been observed in atmospheric sulfate aerosols [Romero and Thiemens, 2000] near industrial areas; however, the source of the effect in the present atmosphere is not known. Savarino et al. [2002] measured the MIF of sulfate in Antarctic ice cores from the Pinatubo and 1259 A.D. volcanic eruptions and compared this to the background

sulfate. The 1991 Pinatubo and 1259 A.D. eruptions were large enough for their SO₂ emissions to enter the stratosphere where they are oxidized to sulfate. The sulfate eventually travels to the poles where it subsidizes within the polar vortex, and is deposited on the ice. Measurement of such ice core samples is thus a means to measure stratospheric sulfate. Both the Pinatubo and 1259 A.D. eruptions showed MIF in the sulfur isotopes of sulfate while the background (tropospheric) sulfate did not, representing a potential means to distinguish between stratospheric and tropospheric derived sulfate in ice cores.

[7] Here we present the $\delta^{34}\text{S}$ profile from the Vostok and Dome C ice core in east Antarctica, in addition to $\delta^{33}\text{S}$ and $\delta^{36}\text{S}$ measurements from the Vostok ice core. The isotope measurements were undertaken as a source apportionment indicator to complement oxygen isotopic measurements from the same samples, and to assess potential stratospheric input to east Antarctica from the $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ measurements. We were unable to attribute the observed variation in the $\Delta^{17}\text{O}$ of the oxygen isotopes from the Vostok ice core to changes in the concentrations of the atmospheric oxidants themselves, due to the unknown effect of cloud processing efficiency on the degree of the aqueous versus gas-phase oxidation pathways. In addition, we were unable to determine the effect of stratospheric intrusions on the $\Delta^{17}\text{O}$ of Vostok sulfate. Source apportionment using $\delta^{34}\text{S}$ measurements, in addition to comparing our $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ with the since measured stratospheric-derived sulfate (J. Savarino et al., manuscript in preparation, 2003) provide further insight into the oxygen isotopic measurements and the variations in sulfate sources to east Antarctica during a major climate cycle.

2. Methods

[8] Sulfate was extracted from the Vostok (78°30'S, 106°54'E, 3420 m a.s.l.) and Dome C (74°39'S, 124°10'E, 3240 m a.s.l.), east Antarctica ice core samples after ice decontamination via ion chromatographic concentration and separation. The H₂SO₄ was then converted to the silver salt (Ag₂SO₄) form, and pyrolyzed to yield Ag(s), O₂ and SO₂ as described in Alexander et al. [2002]. This method is quantitative in regard to sulfur. The SO₂ gas was frozen at liquid nitrogen temperature (−96°C) immediately after pyrolysis, and subsequently cryotransferred to a sample tube containing 30% H₂O₂ solution as described in Savarino et al. [2001]. After the samples were thawed and sulfur species are oxidized to sulfate, 1M BaCl₂ was added to each sample to form a solid barium sulfate (BaSO₄) precipitate. Each sample represents a resolution of 50–100 years (~2 kg of ice each) depending on the depth of the samples. Details on the depth, age and time period of each sample are detailed in Table 1.

[9] For the Vostok samples, in which all four (³²S, ³³S, ³⁴S, ³⁶S) stable isotopes were measured, the barium sulfate was converted to SF₆ using well-established procedures [Farquhar et al., 2000c] and measured for its sulfur isotopic composition on a Finnigan MAT 252 mass spectrometer. Using SF₆ as the working gas allows for the measurement of all four stable isotopes. Uncertainties for the mass spectrometric analysis are less than ±0.05‰ for $\delta^{34}\text{S}$, ±0.03‰ for $\delta^{33}\text{S}$ and ±0.3‰ for $\delta^{36}\text{S}$. For the Dome C samples, in

Table 1. Details on the Vostok and Dome C Ice Core Samples Including Sulfur and Oxygen Isotopic Measurements^a

| Sample | Top Depth, m | Age, kya | Time Period | % sea-salt sulfate | % mineral sulfate | Na ⁺ ppb | Ca ²⁺ ppb | Mg ²⁺ ppb | NO ₃ ⁻ ppb | δ ³⁴ S ‰ (CDT) | δ ³⁴ S _{nss} ‰ (CDT) | Δ ¹⁷ O ‰ (SMOW) |
|---------|--------------|----------|-------------|--------------------|-------------------|---------------------|----------------------|----------------------|----------------------------------|---------------------------|--|----------------------------|
| Vostok1 | 167 | 5.7 | Holocene | 5.2 | 0 | 23.4 | 3.2 | 4.9 | 14.8 | 11.2 | 10.7 | 3.1 |
| Vostok2 | 237 | 8.7 | Holocene | 1.9 | 2.1 | 16.3 | 9.7 | 4.4 | 18.4 | 14.3 | 14.0 | 3.4 |
| Vostok3 | 289 | 11.2 | Holocene | 6.9 | 0.1 | 43.2 | 7.6 | 8.7 | 13.4 | 9.5 | 8.5 | 2.3 |
| Vostok4 | 345 | 14.3 | Glacial | 10.8 | 6.7 | 94.3 | 24.8 | 28.5 | 26.5 | 12.6 | 11.4 | 1.9 |
| Vostok5 | 933 | 60.2 | Glacial | 9.1 | 7.0 | 106.7 | 36.0 | 32.4 | 46.5 | 12.0 | 10.8 | 1.3 |
| Vostok6 | 1532.9 | 109.9 | Glacial | 9.0 | 1.8 | 47.8 | 7.1 | 12.1 | 12.2 | 12.4 | 11.4 | 2.8 |
| Vostok7 | 1674.2 | 121.9 | Eemian | 4.8 | 0.1 | 20.4 | 4.5 | 4.2 | 16.8 | 15.4 | 15.1 | 4.7 |
| Vostok8 | 1791 | 130.2 | Eemian | 2.4 | 0.8 | 12.2 | 4.3 | 2.9 | 13.9 | 13.6 | 13.3 | 4.8 |
| DomeC1 | 115.8 | 2.5 | Holocene | 7.2 | 0 | 20.2 | 2.6 | 4.0 | 13.0 | 12.5 | 10.9 | 2.9 |
| DomeC3 | 240.8 | 5.5 | Holocene | 6.7 | 1.8 | 19.3 | 3.4 | 5.4 | 12.0 | 12.0 | 10.5 | 4.1 |
| DomeC4 | 277.0 | 6.5 | Holocene | 7.3 | 0 | 21.0 | 3.8 | 2.6 | 13.5 | 12.4 | 10.8 | 2.9 |
| DomeC5 | 366.7 | 9.4 | Holocene | 5.8 | 0 | 16.3 | 3.0 | 2.2 | 17.1 | 13.4 | 12.1 | 3.1 |
| DomeC6 | 481.2 | 13.9 | Transition | 9.2 | 0 | 41.0 | 5.2 | 6.9 | 4.5 | 12.1 | 9.9 | 2.8 |
| DomeC8 | 788.6 | 30.7 | Glacial | 10.9 | 3.8 | 53.2 | 8.2 | 15.5 | 10.1 | 12.7 | 10.2 | 3.8 |
| DomeC9 | 882.5 | 36.4 | Glacial | 11.0 | 0 | 69.2 | 5.3 | 8.8 | 16.9 | 10.1 | 7.5 | 2.2 |

^aSee text for details on the δ³⁴S measurements and Alexander *et al.* [2002] for information on the oxygen isotopic measurements. Percent sea-salt and terrestrial sulfate were calculated based upon ion chromatographic concentration measurements of Na⁺, Ca²⁺, Mg²⁺ and NO₃⁻ as described in Legrand *et al.* [1988].

which only ³²S and ³⁴S were measured, prepared barium sulfate samples were analyzed as SO₂ according to the procedure described in Grassineau *et al.* [2001]. The reproducibility for the δ³⁴S is ±0.1‰ (1σ).

3. Results and Discussion

[10] The δ³⁴S measurements, along with the nonsea-salt sulfate component (δ³⁴S_{nss}), from both the Vostok and Dome C cores are shown in Table 1, and are plotted in Figure 1 relative to the age of the sample. Figure 1 shows a climate signal in the δ³⁴S_{nss} measurements, with lower values during the glacial period. Table 2 shows the δ³³S and δ³⁶S for the Vostok ice core. Unfortunately, due to the small sample sizes and low isotopic abundance of ³⁶S, the

uncertainty in the δ³⁶S measurements is large (±4‰). However, both the Δ³³S and Δ³⁶S data show results consistent with fractionation by purely mass-dependent processes (Δ³⁶S = Δ³³S = 0).

3.1. Source Apportionment

[11] Sulfate in preindustrial Antarctic snow and ice has three major sources, marine biogenic (DMS), sea-salt, and continental (including mineral dust, continental biogenic, and volcanic), with DMS being the dominant source. Patris *et al.* [2000] used δ³⁴S measurements of sulfate and methane sulfonic acid (MSA) from shallow ice cores near the South Pole to determine the relative partitioning of these sources at the central Antarctic ice cap. They assumed conservation of isotopic signatures during long-range trans-

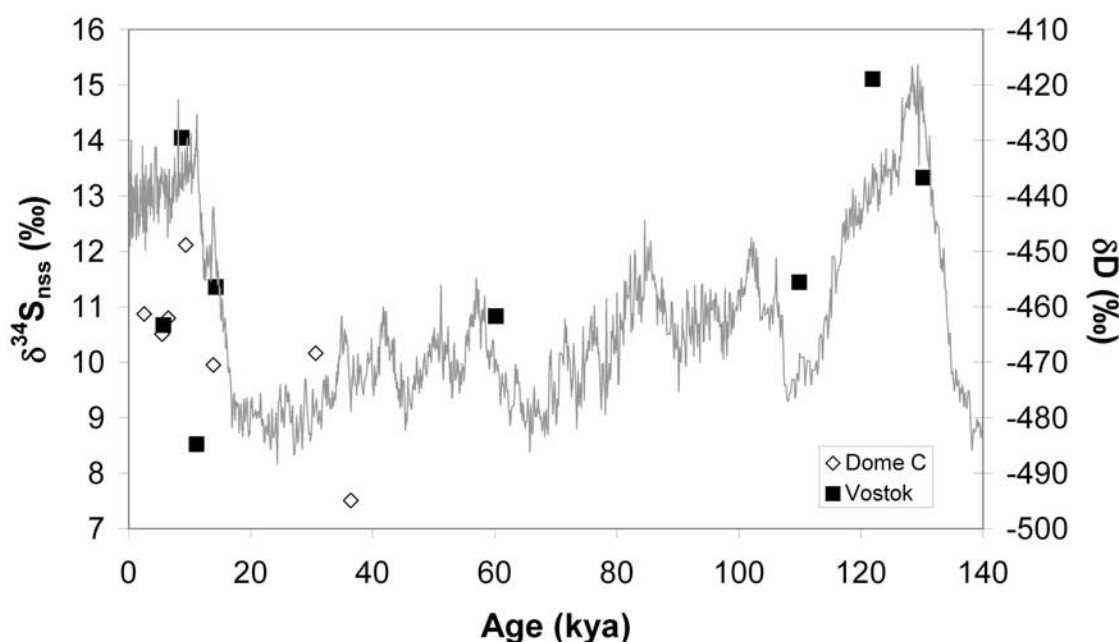


Figure 1. δ³⁴S_{nss} measurements from the Vostok (solid squares) and Dome C (open diamonds) ice cores as a function of age plotted with δD [Jouzel *et al.*, 1987] measurements from the Vostok ice core relative to age of ice [Lorius *et al.*, 1985]. Reproducibilities for the δ³⁴S measurements are ±0.1‰.

Table 2. $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ Measurements From the Vostok Ice Core Reveal Fractionation of Sulfur Isotopes by Purely Mass-Dependent Fractionation Processes^a

| Sample | $\Delta^{33}\text{S}$ | $\Delta^{36}\text{S}$ |
|----------|-----------------------|-----------------------|
| Vostok 1 | -0.1 | -1.7 |
| Vostok 2 | 0 | -2.5 |
| Vostok 3 | -0.1 | 0.6 |
| Vostok 4 | 0 | -1.0 |
| Vostok 5 | -0.1 | -0.2 |
| Vostok 6 | 0.1 | -0.7 |
| Vostok 7 | 0 | -4.0 |
| Vostok 8 | 0 | |

^aThe uncertainty for $\Delta^{33}\text{S}$ is 0.1‰ while $\Delta^{36}\text{S}$ is large (~4‰) due to low isotopic abundance and small sample sizes.

port and deposition processes, and their results confirmed the dominance of marine biogenic origin (DMS) of background sulfate in this region (~90%), with the remainder coming from sea-salt (3%) and volcanic emissions (0–4%).

[12] Upon first glance, our measured $\delta^{34}\text{S}$ values (Table 1) are lower (^{32}S enriched) than those from *Patris et al.* [2000] by around 6‰, compared to their background samples with little or no volcanic influence. The measured isotopic ratio of *Patris et al.* [2000] reflects total sulfur (sulfate and MSA), while results reported in this study include the sulfate component only. MSA represents no more than 11% of total sulfur (sulfate plus MSA) in our samples. Assuming a sulfur isotopic composition of MSA similar to marine biogenic sulfate (see Figure 2) [*Patris et al.*, 2000; *Calhoun et al.*, 1991], the addition of MSA to our sample analysis would have raised our $\delta^{34}\text{S}$ values by less than 1‰, not enough to account for the ~6‰ difference between our measurements and those of *Patris et al.* [2000]. Our lower $\delta^{34}\text{S}$ values can be attributed to either a relatively large continental sulfate (^{34}S depleted) source, or nonconservative behavior of isotopic signatures during long-range transport.

[13] To test this, we first assume no fractionation during transport of sulfate and its precursors to east Antarctica as in *Patris et al.* [2000], and use our $\delta^{34}\text{S}$ values to calculate varying source contributions during the complete glacial/interglacial cycle. The $\delta^{34}\text{S}$ signature of sea-salt sulfate has been well established at 21‰ [*Rees et al.*, 1978]. *Patris et al.* [2000] assigned $\delta^{34}\text{S}$ values to the other two main sources of sulfate to Antarctica, marine biogenic (DMS) and continental (volcanic, mineral, continental biogenic, and in the case of their shallow Antarctic cores, anthropogenic). The $\delta^{34}\text{S}$ signatures assigned to each of these three major sources is shown in Figure 2. *Patris et al.* [2000] calculated individual source contributions from the following equations:

$$\delta^{34}\text{S}_{\text{measured}} = f_{\text{ss}}\delta_{\text{ss}} + f_{\text{mb}}\delta_{\text{mb}} + f_{\text{c}}\delta_{\text{c}} = f_{\text{ss}}\delta_{\text{ss}} + f_{\text{nss}}\delta_{\text{nss}}$$

f_{ss} , f_{mb} , f_{c} , f_{nss} are the fractions of sea-salt, marine biogenic, continental, and nonsea-salt respectively with their corresponding $\delta^{34}\text{S}$ values. f_{ss} was calculated for each sample based upon Na^+ concentration measurements as described in *Legrand et al.* [1988] and are shown in Table 1. Using our calculated value of f_{ss} for each sample, the $\delta^{34}\text{S}$ signatures from Figure 2, and the above equations, we can

determine f_{mb} and f_{c} for each sample. Results of these calculations yield f_{mb} and f_{c} each accounting for approximately half of f_{nss} (where $f_{\text{nss}} = f_{\text{mb}} + f_{\text{c}}$).

[14] The amount of continental derived sulfate calculated in our samples is rather high compared to the background sulfate from *Patris et al.* [2000], and the general assumption that DMS emissions are the dominant source of sulfate in Antarctica. There are two possible explanations for these low $\delta^{34}\text{S}$ values, in the Vostok and Dome C ice cores, assuming that the isotopic source signatures are correct. The first is that the continental source represents ~50% of the nonsea-salt sulfate in our samples during one full climate cycle, and the general assumption that DMS emissions are the dominant source of east Antarctic ice core sulfate is incorrect. Alternatively, the assumption of no fractionation of $\delta^{34}\text{S}$ during transport to east Antarctica could be incorrect, and a Rayleigh-type fractionation during transport to east Antarctica could be altering the original isotopic signatures of our source sulfate. Both of these possibilities are discussed in more detail below.

3.2. Continental Contribution

[15] By definition, continental sulfate comprises volcanic, mineral/dust, continental biogenic and anthropogenic sources. The age of our samples rules out an anthropogenic source. The remoteness of the Antarctic continent from other landmasses also limits the mineral and continental biogenic sources. The mineral dust contribution to East Antarctic ice core sulfate can be roughly calculated based upon our ion chromatographic measurements of Ca^{2+} , Na^+ , Mg^{2+} and NO_3^- as in *Legrand et al.* [1988]. Dust accounts for no more than 7% of total sulfate in our samples (see Table 1) and cannot account for the ~50% continental sulfate calculated directly from our $\delta^{34}\text{S}$ measurements. After ruling out anthropogenic, continental biogenic, and mineral dust as being significant sources of sulfate in our samples, this leaves volcanic sulfur emissions as being the only potential significant source of continental sulfate in our samples.

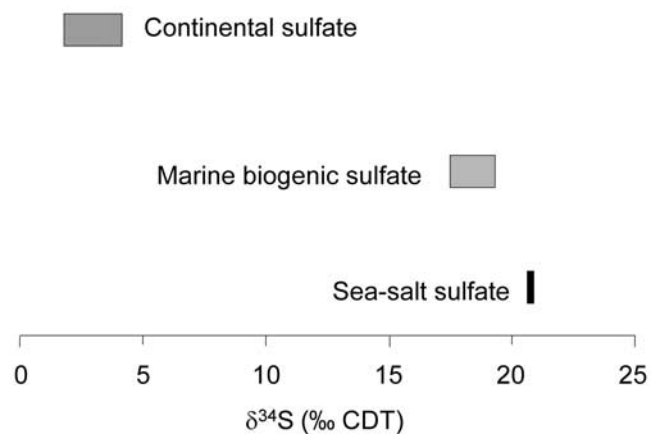


Figure 2. Sulfur isotopic signatures of the three main components of sulfate in Antarctic ice cores. The values for volcanic and marine biogenic sulfate are from *Patris et al.* [2000] and the sea-salt sulfate value is from *Rees et al.* [1978].

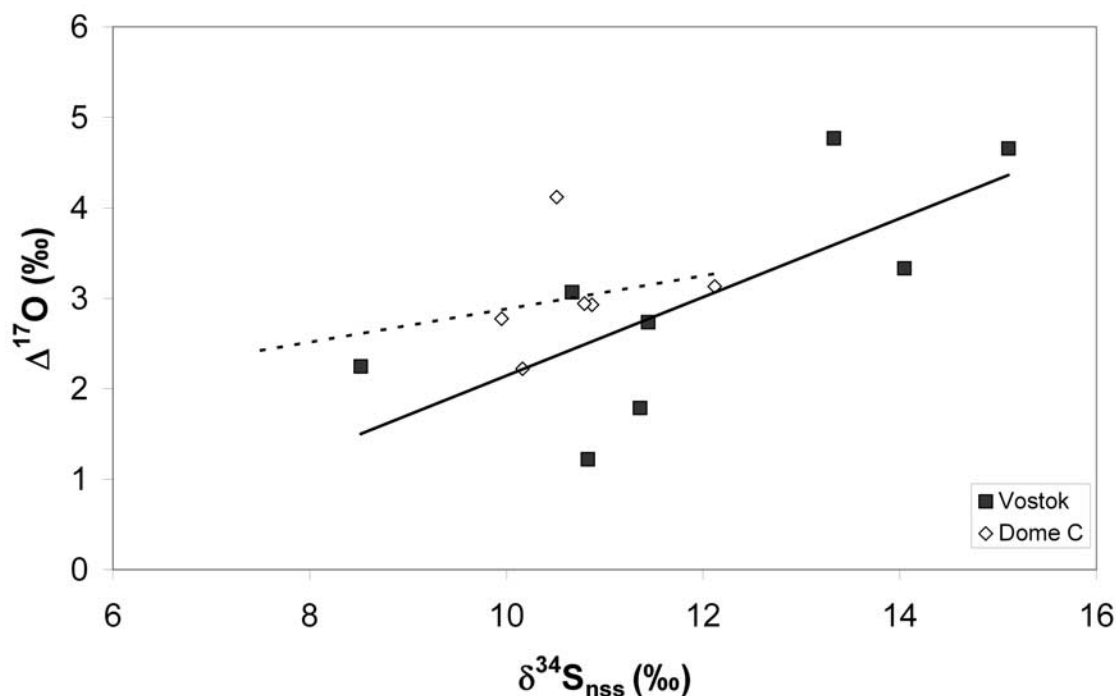


Figure 3. $\delta^{34}\text{S}_{\text{nss}}$ versus $\Delta^{17}\text{O}$ measurements for the Vostok (solid squares) and Dome C (open diamonds) ice core samples.

[16] Volcanic sulfate can be transported either through the troposphere from volcanic emissions in the southern hemisphere, or through the stratosphere from volcanic eruptions large enough so that the SO_2 emissions penetrate the tropopause. As discussed in *Alexander et al.* [2002], internal radio echo layering at Vostok station reveals 5 potential volcanic peaks at depths between 800 and 2200 meters [*Siegert et al.*, 1998]. Sulfate concentration measurements also do not indicate major volcanic influences. Volcanic disturbances span only short time periods (2 years) [*Legrand et al.*, 1988], and unlike *Patris et al.* [2000] whose firn samples had much higher resolution (2–7 years compared to 50–100 years), are unlikely to be a major source of sulfate in our samples.

[17] There is also a possibility that the polar vortex could form over east Antarctica, and subsidence within the vortex could be a significant source of sulfate. The main sources of sulfate in the stratosphere are OCS emissions originating from the troposphere, and direct injection of SO_2 from large volcanic eruptions. OCS will be photodissociated in the stratosphere and subsequently oxidized to SO_2 and sulfate within the stratosphere predominantly through the gas-phase reaction with OH. Using a photochemical equilibrium model for short-lived radical species, *Lyons* [2001] calculated a $\Delta^{17}\text{O}$ value of stratospheric OH of 2 to 45‰ from isotopic exchange between OH and O_2 . This is in contrast to tropospheric OH that has a similar mass-dependent composition as water due to isotopic exchange with water. Sulfate formed in the stratosphere is therefore expected to have large $\Delta^{17}\text{O}$ values through oxidation by anomalous OH. Stratospheric sulfate has been measured for its sulfur isotopic composition ($\delta^{34}\text{S}$) to have a background value of $2.6 \pm 0.3\text{‰}$ [*Castleman et al.*, 1973, 1974], which is isotopically light compared to the marine component. On

the basis of this, if ~50% of the nonsea-salt sulfate in east Antarctica originated from the stratosphere, we would expect to see an anti-correlation between the $\delta^{34}\text{S}$ and $\Delta^{17}\text{O}$ values. Figure 3 shows just the opposite, with $\delta^{34}\text{S}$ values increasing with larger MIF in the oxygen isotopes. This suggests that the anomaly of background sulfate in the oxygen isotopes is not originating from the stratosphere. In addition, our $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ measurements from the Vostok ice core (Table 2) reveal that our sulfate samples are purely mass-dependently fractionated in the sulfur isotopes, unlike the stratospheric-derived sulfate in Antarctic ice as discussed above. This reinforces the conclusion that the stratosphere does not represent a significant source of sulfate in our Vostok and Dome C samples.

3.3. Transport Effects

[18] On the basis of the above discussion, it seems highly unlikely that we are observing such a large continental source of sulfate in east Antarctica throughout a full glacial/interglacial cycle, and we will explore the possibility of a Rayleigh-type fractionation during transport to Vostok and Dome C. *Patris et al.* [2002] observed sulfur isotopic fractionation of volcanic sulfate during tropospheric transport to central Greenland, hypothesizing that the oxidized species is enriched in ^{34}S during heterogeneous processing. This results in the ^{34}S depletion of the gaseous burden being more pronounced as it travels farther away from the source, resulting in lower $\delta^{34}\text{S}$ values in their Greenland ice cores by about 10‰ with respect to the bulk volcanic source. *Castleman et al.* [1974] observed a similar trend in $\delta^{34}\text{S}$ measurements of volcanic-derived sulfate in the lower stratosphere. Their results showed an increasing degree of ^{34}S depletion at progressively later times, indicating that oxidation of ^{34}S is favored over ^{32}S . Since the dominant

oxidation mechanism of SO₂ in the stratosphere is gas-phase oxidation by OH, this suggests that the gas-phase mechanism also results in a Rayleigh type distillation.

[19] *Tanaka et al.* [1994] used ab initio quantum mechanical calculations to investigate the fractionation resulting from the gas-phase oxidation (OH) of SO₂ to sulfate in the atmosphere. Their results indicate a fractionation factor (α) of 0.991, with ³²SO₂ reacting faster than ³⁴SO₂. Since fractionation by heterogeneous oxidation in the troposphere is expected to result in the enrichment ($\alpha = 1.0165$) of ³⁴SO₄²⁻ [*Eriksen*, 1972a, 1972b], the authors suggest that $\delta^{34}\text{S}$ measurements can be used to quantify the relative importance of homogenous and heterogeneous oxidation pathways. However, *Loung et al.* [2001] used RRKM transition state theory to calculate the fractionation resulting from the gas-phase oxidation (OH) of SO₂ to sulfate. Their results indicate an inverse kinetic isotope effect, with ³⁴SO₂ reacting faster than ³²SO₂ ($\alpha > 1.07$ under atmospheric conditions), the opposite of that calculated by *Tanaka et al.* [1994], but consistent with the measurements by *Castleman et al.* [1974]. These results indicate that a Rayleigh fractionation during oxidation of SO₂ to sulfate in the atmosphere occurs, with ³⁴S being enriched in the sulfate product. This will leave the remaining gaseous SO₂ depleted in ³⁴S, with ³⁴SO₄²⁻ being washed out progressively as it is transported across the Antarctic continent.

[20] From Figure 1, we observe that $\delta^{34}\text{S}$ values are lower during the glacial than the surrounding interglacial periods. This is the opposite of what we would expect from source fluctuations alone. The ³⁴S-enriched contribution (DMS) is believed to be significantly higher during the glacial periods based on MSA/SO₄²⁻ measurements [*Legrand et al.*, 1991]. This suggests that Rayleigh fractionation during the glacial period is greater than during the Eemian and preindustrial Holocene. This could be explained by changes in transport, or changes in the oxidation pathways (the gas-phase oxidation pathway possesses a higher fractionation factor) as indicated from $\Delta^{17}\text{O}$ measurements [*Alexander et al.*, 2002].

[21] Meteorological conditions in Antarctica are complicated, as transport from the source is not direct. Because tropospheric air masses circulate in a spiral-like fashion around the continent, it is difficult to predict air mass trajectories and determine the degree of Rayleigh fractionation. It is believed that glacial periods in Antarctica were characterized by more vigorous large-scale atmospheric circulation [*Petit et al.*, 1999]. The isotopic composition of dust from the Vostok and Dome C ice cores indicates that the relatively high atmospheric dust fluxes during glacial periods were due to intensified transport from the dust origin (Patagonian plateau) [*Basile et al.*, 1997]. However, other factors such as lower atmospheric moisture content and the expansion of continental deserts and margins can also partially explain the increased dust flux during the glacial period. If transport was intensified during the last glacial period, Rayleigh distillation due to meteorological conditions would be reduced. However, the extension of sea-ice during this time may have increased the transport pathway of sulfate resulting in a larger degree of Rayleigh fractionation. The effect of this is difficult to assess due to the complicated meteorology in the region. In contrast, back trajectories initialized from Dome C, Antarctica suggest that transport efficiency from dust source regions (mainly Patagonia) was

lower during the glacial period than the present-day [*Lunt and Valdes*, 2001]. At present, the direction and magnitude of changes in atmospheric transport due to meteorological conditions is not well understood. Concentration measurements of sulfate throughout the full climate cycle indicate however that more sulfate is reaching east Antarctica during the glacial period primarily due to increases in DMS emissions. This increased contribution during the glacial period is from a heavy source of sulfate, relative to the continental source (see Figure 2). It is not clear whether changes in transport efficiency were large enough to account for the glacial/interglacial differences in $\delta^{34}\text{S}$ ($\sim 4\%$) while accounting for the observed increases in the ³⁴S-enriched DMS source.

[22] Oxygen isotope measurements from the same samples in the Vostok core [*Alexander et al.*, 2002] indicate that the ratio of gas-phase oxidation over aqueous-phase oxidation was greater during the last glacial than the surrounding interglacials. Assuming the fractionation factor for the homogenous oxidation [*Loung et al.*, 2001] is greater than the heterogenous oxidation [*Eriksen*, 1972a, 1972b] ($\alpha_{\text{hom}} > 1.07$; $\alpha_{\text{het}} = 1.0165$), our $\delta^{34}\text{S}$ measurements support the conclusion that OH oxidation of S(IV) species is more important during the glacial period than during the surrounding interglacial periods, resulting in more depleted $\delta^{34}\text{S}$ values during this period. There is a small temperature dependence in the homogenous oxidation [*Loung et al.*, 2001]; however, assuming $\sim 10^\circ\text{C}$ difference between glacial and interglacial periods in Antarctica, this effect would only increase α by 0.003, and should not be large enough to account for the differences in $\delta^{34}\text{S}$ that we observe.

4. Conclusions

[23] Sulfur isotope measurements ($\delta^{34}\text{S}$) from two east Antarctica ice cores (Vostok and Dome C), from a complete glacial/interglacial cycle, are significantly lower ($\sim 6\%$) than previous measurements in shallow ice cores from the South Pole [*Patris et al.*, 2000]. Although we cannot completely rule out the possibility of an isotopic composition change for one source with time, our analysis suggests that these light values can be explained by a Rayleigh-type fractionation as S(IV) species are oxidized and transported toward the East Antarctic plateau. Aerosol observations indicate that transport of particulate matter to the South Pole occurs in the lower troposphere [*Hogan et al.*, 1982] while transport to central east Antarctica is believed to be representative of the upper part of the troposphere [*DeAngelis et al.*, 1984]. The complicated meteorology in Antarctica makes it difficult to quantify the effect of such transport differences on the measured $\delta^{34}\text{S}$ values; however, our results show that conservation of isotopic signatures upon transport cannot be assumed for sulfate in this region over such time periods.

[24] Our sulfur isotope measurements show lower $\delta^{34}\text{S}$ values (by $\sim 4\%$) during the last glacial period relative to the surrounding interglacial periods, even though the ³⁴S enriched, marine biogenic component is significantly larger during this time [*Legrand et al.*, 1991]. This can be explained either by changes in transport efficiency, and/or by variations in the homogenous versus heterogeneous oxidation pathways of S(IV) species during different climate regimes. Oxygen isotope measurements [*Alexander et*

al., 2002] from the same Vostok samples presented here, reveal that the ratio of homogenous over heterogenous S(IV) oxidation was larger during the last glacial period than the surrounding interglacials. The complete sulfur isotopic measurements (^{32}S , ^{33}S , ^{34}S , ^{36}S) presented here combined with the oxygen isotope measurements (^{16}O , ^{17}O , ^{18}O) from Alexander et al. [2002] reveal that a stratospheric origin of $\Delta^{17}\text{O}$ variations can be ruled out, and confirms that the $\Delta^{17}\text{O}$ variation is due only to changes in gas and aqueous-phase oxidation pathways. The low $\delta^{34}\text{S}$ values during the glacial period gives further evidence to this conclusion, assuming the fractionation factor for OH oxidation is larger than the heterogeneous pathway.

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