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Soluble salts in deserts as a source of sulfate aerosols in an Antarctic ice core during the last glacial period



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ABSTRACT

Chemical proxy data from ice cores provide information for understanding environmental changes. Despite large climate shifts, the flux of sulfate onto the ice in Antarctica has remained relatively stable over glacial-interglacial cycles. However, the mechanism behind the stable flux is controversial because of a lack of evidence for changes in multiple source emissions. Here, we present the sulfur isotopic record in the Antarctic Dome Fuji ice core, which provides a new constraint on the interpretation of sulfate aerosols. During the Last Glacial Maximum (LGM), the sulfur isotope ratio was depleted compared to that during the Holocene and was negatively correlated with terrestrial contributions. The isotope data suggest that the contributions from terrestrial gypsum were enhanced during the LGM. A potential source area for gypsum in the Antarctic ice core is the high-altitude region around the Atacama Desert, although other regions cannot be excluded. These results suggest that the salts in deserts should be considered a terrestrial source of Antarctic sulfate during the LGM.

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1. Introduction

Atmospheric aerosols affect the global climate by modulating Earth's radiative energy balance through aerosol-radiation and aerosol-cloud interactions (Boucher et al., 2013). Ice core data show a generally "dusty" environment in Antarctica during glacial periods compared to interglacial periods. For example, insoluble dust records show 10-25-fold higher values during glacial periods than at present (Lambert et al., 2008). The ion chemistry in ice cores is routinely measured in ice core studies and is mainly representative of aerosols. Among the fluxes of many water-soluble components (e.g., Ca^{2+} , Na^+ , SO_4^{2-}), the non-sea salt calcium $(nss-Ca^{2+})$ flux is a dust flux proxy that shows large variations, and its values during glacial maxima are approximately ten times higher than those during interglacial periods (Fischer et al., 2007). The flux of sea salt Na (ssNa⁺) also undergoes large variations: the maximum during glacial periods is approximately triple that during the interglacial values (Wolff et al., 2006). These fluctuations are interpreted as changes in enhanced emissions from

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Interestingly, the flux of non-sea-salt sulfate $(nss-SO_4^{2-})$, a proxy for sulfate aerosols, from Antarctic ice cores appears to have changed little over glacial cycles (Kaufmann et al., 2010; Wolff et al., 2006). What led to such stable behavior is unclear. One difference between $nss-SO_4^{2-}$ and dust is that sulfate aerosols have multiple sources, including marine phytoplankton, sea salt, volcanic gas, and terrestrial dust. In the present-day climate, the dominant source of Antarctic $nss-SO_4^{2-}$ aerosols is dimethylsulfide (DMS), a degradation product of metabolites from marine phytoplankton (Cosme et al., 2005; Uemura et al., 2016). Thus, the relatively stable Antarctic $nss-SO_4^{2-}$ records over glacial-interglacial cycles are interpreted as small changes in DMS emissions south of a polar front (Kaufmann et al., 2010; Wolff et al., 2006). This result also suggests that sulfate aerosol-climate feedback via marine biogenic activity is not evident over glacial cycles (Wolff et al., 2006).

These previous studies assumed that the sulfate contribution from terrestrial sources is negligible. Some data, however, suggest a possible significant terrestrial contribution during the Last Glacial Maximum (LGM). Analysis of particles in the Antarctic Dome-F (DF) ice core suggests that most SO_4^{2-} is present as CaSO₄ and Na₂SO₄ during glacial periods (lizuka et al., 2012). The presence

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of CaSO₄ in glacial periods implies a contribution from terrestrial calcium sulfate (gypsum (CaSO₄·2H₂O) and/or anhydrite (CaSO₄)). Recently, aerosol records from the DF core showed that the sulfate and calcium fluxes during glacial periods appear to have an upper limit with a Ca²⁺/SO₄²⁻ molar ratio of 1 (i.e., the molar ratio of gypsum) (Goto-Azuma et al., 2019). This suggests a large terrestrial contribution and decreased marine biogenic sulfate emissions during glacial periods (Goto-Azuma et al., 2019). The result is puzzling in view of the limited distribution of gypsum compared to that of CaCO₃ in the Southern Hemisphere (Nickovic et al., 2012; Scanza et al., 2015). Thus, the source areas for such gypsum-rich aerosols during glacial periods are unknown. In addition, CaSO₄ can also be formed via a reaction between terrestrial CaCO₃ and marine biogenic sulfate in the atmosphere.

The stable isotopic composition of sulfur (δ^{34} S) in sulfate offers an important constraint for these problems because the δ^{34} S value shows distinct variations depending on its origin (e.g., Patris et al., 2002; Uemura et al., 2016). To date, the sparse number of δ^{34} S data points from ice cores has prevented detailed analysis. There are limited data on glacial δ^{34} S, which are interpreted as fractionation during transport on the assumption of negligible terrestrial influence (Alexander et al., 2003). Thus, it is necessary to re-evaluate the impact of terrestrial sulfur with high-temporal-resolution data and updated geochemical data from potential source areas (PSAs). This study tests the terrestrial origin hypothesis with a new δ^{34} S record from an Antarctic ice core. The $\delta^{34}S$ data will provide key information to distinguish whether the sulfur in CaSO₄ during the LGM was derived from land (i.e., gypsum) or oceans (i.e., the reaction between SO_4^{2-} and CaCO₃). Furthermore, if the terrestrial hypothesis is true, the provenance of sulfate aerosols is a central issue for paleoclimate studies because identifying the transport pathway from the origin to polar regions clarifies the changes in atmospheric circulation patterns over glacial cycles. Thus, we will explore the PSAs based on the geographical distribution of the δ^{34} S and mineral composition values.

2. Materials and methods

2.1. Ice core sample and age scale

The Dome Fuji first (DF1) ice core was used to investigate sulfur isotope composition. The 2503-m ice core was drilled at Dome Fuji station in East Antarctica (77°19'S, 39°42'E, 3,810 m above sea level) (Kawamura et al., 2007). We cut 35 ice samples from depths of 197 m to 576 m. Each sample was 50 cm in length and 300 g in weight. To remove surface contaminants, we cut away the surface of the ice (10% of the weight) using a ceramic knife on a clean bench. The ice sample was sealed in dust-free plastic bags and melted at room temperature. Aliquots of 25 mL were used for ion concentration determination. The rest of each sample was used for sulfur isotope analyses.

We used the DFO2006 age scale based on O_2/N_2 data (Kawamura et al., 2007). The accumulation rates at DF were also calculated based on this age scale. The ice samples that we used for this study cover the last termination from 24.6 kyr BP to 6.0 kyr BP. A 50-cm-length sample represents 15 to 30 years (average of 20 years) of accumulated snow from every 200- to 1,200-year interval (i.e., the sampling interval of the 50-cm ice ranged from 5.0 to 30.4 m in depth, which corresponds to a temporal resolution of 200 to 1,200 years (500 years on average)). The accumulation rate was used to calculate the flux of SO_4^{2-} .

2.2. Isotopic and ion analyses

The sulfur isotope composition was measured as described in Uemura et al. (2016). Briefly, 86-255 mL melted ice samples were

evaporated on a 70 °C hot plate and concentrated to a volume of 2 mL. Then, each sample was dripped slowly into a tin cup (5×9 mm) containing 100 μ L of 0.01 mol/L BaCl₂ solution. To enhance evaporation, the cup was purged with dry N₂ gas and heated at 60 °C on a hot plate. Subsequently, we obtained 0.21–0.30 μ mol of dried BaSO₄ in a tin cup. The tin cup folded with 0.5 mg of V₂O₅ was flash combusted to yield SO₂ in a 1040 °C furnace (Flash 2000, Thermo Fisher Scientific Inc.). The furnace was filled with copper oxide and reduced copper. The SO₂ gas was measured using continuous-flow isotope ratio mass spectrometry (CF-IRMS; Delta V advantage, Thermo Fisher Scientific Inc.) at the University of the Ryukyus.

Sulfur isotope compositions were calibrated using three reference materials: NBS-127, IAEA SO-5, and IAEA SO-6. The isotopic compositions are reported using δ notation, expressed in %⁰ relative to the Vienna Canyon Diablo Troilite (V-CDT) scale. The 1σ for the repeated δ^{34} S measurements of NBS-127 during the measurement period of this study was $\pm 0.17\%$ (n = 45). Four ice core samples were measured twice in different measurement batches, and the 1σ of the difference between the duplicate δ^{34} S measurements was $\pm 0.2\%$. We adopted a δ^{34} S value of $21.17 \pm 0.09\%$ for NBS127, which is recommended by the National Institute of Standards and Technology (NIST). We used the updated δ^{34} S values of IAEA SO-5 (0.15 \pm 0.05‰) and SO-6 ($-34.04 \pm 0.11\%$) (Halas and Szaran, 2001).

We should note that the surface snow observation data (Uemura et al., 2016) were calibrated against the IAEA recommended value. Thus, we updated these published data based on NIST recommended values (Table A1) to maintain consistency with this study. Such calibration resulted in a small (0.4‰ higher than the previous values) shift on average, and thus, the choice of a reference value did not affect the conclusions of previous studies or this study.

The concentrations of anions $(SO_4^{2-}, Cl^-, NO_3^-, CH_3SO_3^-)$ and cations $(Na^+, Ca^{2+}, Mg^{2+}, K^+, and NH_4^+)$ were measured using an ion chromatograph (DX-500, Dionex Corporation) at the National Institute of Polar Research.

Three exceptionally high SO_4^{2-} flux data points (> 2σ + mean for the Holocene, T1 and the LGM) are considered episodic volcanic events based on a detection method (Castellano et al., 2004) and were removed for the subsequent analysis (Fig. 1).

2.3. Isotope mixing model

A sulfur isotope mixing model for sulfate aerosols can be written as follows:

$$\delta^{34}S = \delta^{34}S_{ss}f_{ss} + \delta^{34}S_{nss}f_{nss}$$
(1)

where the subscripts ss and nss indicate sea salt and non-sea salt, respectively. f_{ss} (or f_{nss}) indicates the fraction of $ss-SO_4^{2-}$ (or nss- SO_4^{2-}) relative to total SO_4^{2-} (i.e., $f_{ss} = [ss-SO_4^{2-}]/[SO_4^{2-}])$). The sum of the fractions is unity ($f_{ss} + f_{nss} = 1$). The $\delta^{34}S$ value of sea salt, $\delta^{34}S_{ss}$, is 21% (Rees et al., 1978). The sulfate contributed by sea salt, $[ss-SO_4^{2-}]$, was calculated as follows:

$$[ss-SO_4^{2-}] = k[ss-Na^+]$$
⁽²⁾

where *k* is the sulfate-to-sodium ratio $([SO_4^{2-}]/[Na^+]))$. We adopted the bulk ocean water value (k = 0.060 (0.25 for the mass ratio)) used for high-altitude Antarctic sites (e.g., Kunasek et al., 2010; Patris et al., 2000). A set of equations was used to calculate the sea salt correction for the Na⁺ and non-sea salt Ca²⁺ concentrations (Bigler et al., 2006) as follows:



Fig. 1. Sulfur isotope composition and fluxes of soluble ions in the DF ice core. (a) Reconstructed air temperature at the DF site (ΔT_{site} , black line) (Uemura et al., 2018). The temperature is shown as a deviation from the average of the past 2000 years. (b) δ^{34} S in the DF core (red circles). The red triangle indicates the present-day observation in Antarctic snow (Uemura et al., 2016). Red open circles show the volcanic peak data. (c) Total SO₄²⁻ (green circles and dotted line) and nss-SO₄²⁻ (or-ange dotted line) fluxes in the DF core (brown circles). (e) Fractions of the total flux of sulfate originating from terrestrial (brown) and marine biogenic (blue) sulfates based on *m* values of 0.67 (solid line) and 1.0 (dotted line).

$$[ss-Na^+] = c\{[Na^+] - [Ca^{2+}] \cdot (Na^+/Ca^{2+})_{nss}\}$$
(3)

$$[nss-Ca2+] = c\{[Ca2+] - [Na+] \cdot (Na+/Ca2+)-1_{ss}\}$$
(4)

with
$$c = [(1 - (Na^+/Ca^{2+})_{nss} \cdot (Na^+/Ca^{2+})_{ss}^{-1})]^{-1}$$
 (5)

where $(Na^+/Ca^{2+})_{nss}$ (or $(Na^+/Ca^{2+})_{ss}$) is the ion molar ratio of Na^+ and Ca^{2+} in water-soluble continental (or sea salt) aerosols. We used a $(Na^+/Ca^{2+})_{nss}$ value of 1.6 (0.94 for the mass ratio) and a $(Na^+/Ca^{2+})_{ss}$ value of 40 (from 23 for the mass ratio) based on exceptionally high Ca^{2+} and Na^+ peaks in ice core data (Bigler et al., 2006). Note that f_{ss} is very small for DF data ($6 \pm 2\%$); thus, the uncertainty in these sea salt corrections does not affect the main conclusions.

By neglecting the volcanic influence, a sulfur isotope mixing model for the non-sea salt component of sulfate aerosols can be written as:

$$\delta^{34}S_{nss} = \delta^{34}S_{mb}f_{mb} + \delta^{34}S_{ter}f_{ter}$$
(6)

where the subscripts mb and ter indicate marine biogenic and terrestrial sources, respectively. f_{mb} (or f_{ter}) indicates the fraction of $mb\text{-}SO_4^{2-}$ (or $ter\text{-}SO_4^{2-}$) relative to $nss\text{-}SO_4^{2-}$ (i.e., f_{mb} = [mb- SO_4^{2-}]/[nss- SO_4^{2-}])). The sum of the fractions is unity (f_{mb} + f_{ter} = 1).

2.4. Generation of the mineral map

We made the maps showing geographical distribution of minerals based on the silt data in the mineral database (Nickovic et al., 2012). The SO_4^{2-}/Ca^{2+} ratio (*m* value; see Section 4.1) was calculated using the following equation:

$$m = (R_{gyp}/172)/((R_{cal}/100) + (R_{gyp}/172)))$$
(7)

where R_{gyp} and R_{cal} are the relative abundance of gypsum and calcite, respectively. The numbers are the molecular weights of gypsum and calcite. We assumed that the contributions of soluble Ca²⁺ from other calcium-containing minerals were negligible.

2.5. Global model simulation

We used the Community Atmosphere Model version 5 with the Aerosol Two-dimensional bin module for foRmation and Aging Simulation version 2 (CAM5/ATRAS) (Matsui, 2017; Matsui and Mahowald, 2017) for global simulations of airborne mineral dust on 24 July 2009. Mineral dust emissions were calculated online in the Community Land Model version 4 (Zender, 2003). The model simulations were performed with a horizontal resolution of $1.9^{\circ} \times$ 2.5° and 30 vertical levels from the surface to ~40 km and were nudged by the Modern-Era Retrospective analysis for Research and Applications version 2 (MERRA2) reanalysis data. The emissions and transport processes of mineral dust simulated by CAM5/ATRAS have been evaluated (Matsui and Mahowald, 2017).

3. Results

3.1. Sulfur isotope record from the DF ice core

We analyzed the δ^{34} S of sulfate in the DF ice core, from East Antarctica, to investigate the variations in sulfate sources (Fig. 1b and Table A2). The new record, covering between 6 and 25 thousand years before present (kyr BP), involves three climate periods: the Holocene (0-11.7 kyr BP), Termination I (TI; 11.7-18.0 kyr BP), and the Last Glacial Maximum (LGM; 18.0-24.6 kyr BP). The δ^{34} S record is shown along with reconstructed air temperature at the DF site (ΔT_{site}), which was corrected for changes in the moisture source temperature and ocean isotope ratio (Uemura et al., 2018) (Fig. 1a). During the Holocene, the average δ^{34} S value in the DF core was $15.8\pm0.8\%$, which agrees well with the average from present-day snow data $(16.2\pm0.8\%)$ in East Antarctica (Uemura et al., 2016) (the snow value was revised slightly; see Table A1 and the Materials and Methods). This result suggests that the source of sulfur in sulfate during the Holocene did not differ significantly from that for the present day (i.e., originated from DMS). During the LGM, the average $\delta^{34}S$ was 12.2 $\pm0.8\%$, which was depleted by 3.6% compared to that during the Holocene. For TI, the δ^{34} S values were intermediate. As previous δ^{34} S data from Antarctic cores (Alexander et al., 2003) are sparse over this time interval, our δ^{34} S record represents the first data showing clear changes in δ^{34} S from the LGM to the Holocene.



Fig. 2. Sulfur isotope values in the DF ice core and potential sources versus terrestrial contributions. (a) δ^{34} S values of sulfur compounds without Ca²⁺: DMS and DMSP in ocean water (Amrani et al., 2013; Oduro et al., 2012) (purple) and DMSP from Antarctic sea ice (Carnat et al., 2018) (light blue); nss-SO₄²⁻ in southern Pacific aerosols (Calhoun et al., 1991) (light blue bar); volcanic sulfur (Nielsen et al., 1991) (brown bar). (b) $\delta^{34}S_{nss}$ data from the DF ice core for the Holocene (open blue circles), TI (light blue circles) and LGM (dark blue circles). The blue dotted line indicates a linear regression line with a 95% prediction interval (light blue shading). The f_{ter} is calculated based on m = 1.0. (c) The δ^{34} S values of surficial gypsum in the Atacama Desert (Rech et al., 2003) (red dots), Australia (Chivas et al., 1991) (brown dots), and the Dry Valleys, Antarctica (Bao and Marchant, 2006; Lyon, 1978; Nakai et al., 1975; Tomiyama and Kitano, 1985) (blue dots). The box plot shows the 9th and 91st percentiles. Atmospheric depositions in the Atacama Desert (Li et al., 2019) (red triangles).

The average SO_4^{2-} fluxes for the Holocene and LGM were 31.1±6.2 and 36.0±5.5 (µmol m⁻² year⁻¹), respectively (Fig. 1c). In contrast, the average flux of nss-Ca²⁺ increased significantly from 2.3±0.9 in the Holocene to 21.9±4.8 in the LGM (µmol m⁻² year⁻¹) (Fig. 1d). The nss-Ca²⁺ was calculated using the sea-water ratio of Ca²⁺/Na⁺ (Eqs. (4) and (5)). Since the main component (77-96%) of total Ca²⁺ is nss-Ca, the uncertainty in the sea salt correction does not affect the following discussion.

4. Discussion

4.1. Testing the large terrestrial contribution hypothesis

We evaluated the sulfur source contributions by using an isotope mixing model from Section 2.3. Sulfate with lower values of δ^{34} S may originate from volcanic gas or from terrestrial sulfate. Volcanic sulfur is typically characterized by low $\delta^{34}S$ values of 0-5‰ (Nielsen et al., 1991). However, the present-day mean contribution of volcanic sulfur in inland Antarctica is only 2% based on a modeling study (Cosme et al., 2005). Moreover, Antarctic ice cores show no glacial-interglacial changes in eruption frequency (Castellano et al., 2004), and the greatest volcanic activity occurred approximately 10 kyr BP (Bay et al., 2004). Thus, there is no evidence for increased volcanic activity during the last glacial period. For this reason, we assumed that there are two endmembers, marine biogenic (mb) and terrestrial (ter) sources, for the non-sea salt $\delta^{34}S$ ($\delta^{34}S_{nss}$) value. The sea salt contribution to total sulfate is very low (6 \pm 2%), resulting in small differences between the total SO_4^{2-} and nss- SO_4^{2-} fluxes (Fig. 1c) and between $\delta^{34}S$ and $\delta^{34}S_{nss}$ $(0.5 \pm 0.2\%)$.

By rearranging Eq. (6), the $\delta^{34}S_{nss}$ value can be written as:

$$\delta^{34} S_{nss} = (\delta^{34} S_{ter} - \delta^{34} S_{mb}) f_{ter} + \delta^{34} S_{mb}$$
(8)

where the subscripts ter and mb refer to terrestrial and marine biogenic sources, respectively. f_{ter} indicates the fraction of sulfate from terrestrial sources relative to nss-SO₄²⁻ ($f_{ter} = [ter-SO_4^{2-}]/[nss-SO_4^{2-}]$). [ter-SO₄²⁻] can be estimated using the following equation (Kaufmann et al., 2010; Patris et al., 2002; Uemura et al., 2016):

$$[ter-SO_4^{2-}] = m[nss-Ca^{2+}]$$
(9)

where $[nss-Ca^{2+}]$ indicates the concentration of $nss-Ca^{2+}$ and mdenotes the SO_4^{2-}/Ca^{2+} ratio of terrestrial dust. An *m* value of 0.06-0.08 (in molar ratio), which is a mean soil value (Bowen, 1979), was commonly adopted in previous polar studies (e.g., Alexander et al., 2003; Kunasek et al., 2010; Legrand et al., 1997; Patris et al., 2002). A higher value of 0.21, based on aerosols in the Sahara, was used for other Antarctica ice core analyses (Kaufmann et al., 2010). A low m value results in a small terrestrial fraction of sulfate, f_{ter} (ca. 0-21%), even in the glacial period. The largest value of *m* proposed is 1.0 (i.e., all $[nss-Ca^{2+}]$ originated from CaSO₄), which is empirically derived from the upper limit of the DF core data (Goto-Azuma et al., 2019). It is difficult to estimate ideal *m* for DF accurately because it is ultimately a contribution-weighted average of *m* from multiple aerosol origins for the DF core. Here, to test the large terrestrial contribution hypothesis, we first assume that m is 1.

If $\delta^{34}S_{ter}$ and $\delta^{34}S_{mb}$ in Eq. (8) are constants, $\delta^{34}S_{nss}$ plotted against f_{ter} should follow a regression line with a slope of $(\delta^{34}S_{ter} - \delta^{34}S_{mb})$ and an intercept of $\delta^{34}S_{mb}$. There is a significant correlation between $\delta^{34}S_{nss}$ and f_{ter} ($\delta^{34}S_{nss} = -5.7$ f_{ter} + 15.2; R² = 0.47; p <0.01; Fig. 2), suggesting the validity of the two-component mixing model. Most of the lower f_{ter} data (<0.1) correspond to the Holocene. The intercept of the regression line, 15.2‰±3.2‰ (95% prediction interval), agrees with the observed $\delta^{34}S_{mb}$ values, such as 15.6±3.1‰ for nss-SO₄²⁻ aerosols over the ocean (Calhoun et al., 1991) and 14–22‰ for DMS and dimethyl-sulfoniopropionate (DMSP) in ocean water and Antarctic sea ice (Amrani et al., 2013; Carnat et al., 2018; Oduro et al., 2012) (Fig. 2). The $\delta^{34}S_{nss}$ value decreases as the terrestrial contribution increases

(i.e., with an increase in nss-Ca²⁺). This observation is difficult to explain with previous hypotheses ascribing the low δ^{34} S value during the glacial period to an increase in transition metal-catalyzed oxidation (Harris et al., 2012) or Rayleigh distillation of SO₂ during transport (Alexander et al., 2003). Thus, our data implicate the source signature (Delmonte et al., 2008; Patris et al., 2000; Uemura et al., 2016; Ishino et al., 2019) as the major factor controlling the changes in the δ^{34} S value in inland Antarctica.

This result does not support the hypothesis that CaSO₄ during the LGM was formed via a reaction between CaCO₃ and marine biogenic sulfate in the atmosphere (Legrand et al., 1988) because the oceanic δ^{34} S value is high, which contradicts the result that δ^{34} S_{nss} decreases during the LGM. Instead, this result suggests that the large flux of CaSO₄ during the LGM originated from terrestrial sulfate.

Our results revealed the mechanism behind the lack of significant changes in the total SO_4^{2-} flux over glacial cycles. During the LGM, f_{mb} decreased to $38\pm13\%$, which was significantly lower than the value ($93\pm3\%$) during the Holocene based on an *m* value of 1.0. In contrast, the f_{ter} increased to $62\pm13\%$ during the LGM, which was significantly higher than the value ($7\pm3\%$) during the Holocene (Fig. 1e). Thus, our data favor the hypothesis that the small changes in total SO_4^{2-} flux resulted from weakened marine biogenic activity during the LGM counterbalanced by the enhanced contribution of terrestrial sulfate (Goto-Azuma et al., 2019). This does not support the hypothesis of relatively stable variations in DMS emissions over a glacial cycle (Kaufmann et al., 2010; Wolff et al., 2006). Since the implications of weakened DMS emissions were discussed in Goto-Azuma et al. (2019), we focus on the origin of the terrestrial source.

The LGM data show a large f_{ter} (0.4-0.8), and the terrestrial endmember ($f_{ter} = 1$) indicates a low $\delta^{34}S_{ter}$ value of $9.5\pm3.5\%$. The linear correlation between $\delta^{34}S_{nss}$ and f_{ter} implies that terrestrial sulfate originates from isotopically uniform sources and/or a single source region. Considering that the $\delta^{34}S$ value of continental calcium sulfate, including gypsum, shows large variability (approximately 7-28‰) (Nielsen et al., 1991), such PSAs are likely limited in number. First, we explore the $\delta^{34}S$ values of PSAs for sulfate aerosols during the LGM. The surface of PSAs should be covered with highly gypsiferous soil or gypsum itself. Then, we discuss the validity of the large *m* assumption and the PSA based on the surface mineral distribution.

4.2. Potential source areas for low- δ^{34} S sulfate

Based on the δ^{34} S values, Australia and Antarctica can be excluded as PSAs for DF glacial sulfate. Surficial gypsum in southern Australia ranges from ca. 14‰ in inland areas to ca. 21‰ in coastal areas (Chivas et al., 1991) (Fig. 2). In the Dry Valleys of Antarctica, the δ^{34} S values of gypsum (Lyon, 1978; Nakai et al., 1975; Tomiyama and Kitano, 1985) and surface soil (Bao and Marchant, 2006) were higher (15-20‰) (Fig. 2). These values are inconsistent with the low δ^{34} S values expected for DF glacial sulfate. While the data are very limited, low δ^{34} S values of gypsum (1.6±3.6‰) were reported around the Schirmacher Oasis and Lake Untersee, central Queen Maud Land, East Antarctica (Wand et al., 1991). It is, however, unlikely that such a small area is a major sulfate source.

Interestingly, the δ^{34} S data for the Atacama Desert are consistent with the δ^{34} S_{ter} value estimated from the DF ice core. Extensive observation of surficial gypsum salt conducted in the Atacama Desert showed that the δ^{34} S values were $6.6 \pm 1.9\%$ ($\pm 1\sigma$) at altitudes higher than 1200 m a.s.l. (Rech et al., 2003). Furthermore, the δ^{34} S values of aeolian dust deposition observed in the Atacama Desert (Li et al., 2019) are similar to those of surface gypsum (Fig. 2). The low δ^{34} S is believed to be derived from evaporated groundwater, in which the dissolved solutes originate from water-



Fig. 3. Sensitivity test for the SO₄²⁻/**Ca**²⁺ **ratio of terrestrial dust.** Estimated δ^{34} S_{ter} (grey shading: 95% prediction interval) versus *m* values (the SO₄²⁻/Ca²⁺ ratio of terrestrial dust). The red line indicates the δ^{34} S values observed in the Atacama Desert (above 1200 m a.s.l.) (Rech et al., 2003). (For interpretation of the colors in the figure, the reader is referred to the web version of this article.)

bedrock interactions (Rech et al., 2003). Note that the δ^{34} S values are high (>14‰) in low-altitude (below 800 m) areas of the Atacama due to the strong influence of marine aerosols (Rech et al., 2003); thus, the low-altitude zone is excluded as a source area. Therefore, the δ^{34} S data suggest that the gypsum from the high-altitude regions of the Atacama Desert is an important PSA for the sulfate in the DF ice core during the LGM.

The m value in Eq. (9) is an important parameter because it directly affects the estimated $\delta^{34}S_{ter}$ value. Our first assumption (m = 1.0) is consistent with the aerosol deposition observation $(m = 1.1 \pm 0.1)$ in the Atacama Desert (Li et al., 2019; Wang et al., 2014), excluding coastal and Andes Mountain sites. Basically, a lower *m* value results in a smaller f_{ter} value (Eqs. (8) and (9)). However, the correlation between $\delta^{34}S_{nss}$ and f_{ter} does not change, resulting in a smaller value of endmember ($\delta^{34}S_{nss}$ value at $f_{ter}=1$), $\delta^{34}S_{ter}$. Fig. 3 shows that $\delta^{34}S_{ter}$ values estimated for different m values. For example, if the previously used smaller m values (0.07-0.21) were adopted, the estimated $\delta^{34}S_{ter}$ value was very low (-66.8 to -12.1%). Such a low value is unreasonable compared to the general range of δ^{34} S values for calcium sulfate (approximately 7-28‰) (Nielsen et al., 1991) or all oxidized sulfur (approximately -5-30%) (Nielsen et al., 1991). Conversely, we can estimate the lower limit of the *m* value based on the endmember δ^{34} S values. From the value of Atacama Desert salt, the PSA with the lowest δ^{34} S value, the lower limit of *m* for the DF core is found to be 0.67 (Fig. 3). If the *m* value is lower than this, PSAs with such low δ^{34} S values cannot be found. Note that this *m* value, 0.67, does not fundamentally change our results regarding the correlation between δ^{34} S and f_{ter} (Figs. 1e and A1).

4.3. Potential source areas based on mineral distributions

We investigate the origin of terrestrial sulfate on the basis of surface mineral distributions. Based on the surface mineral database (Nickovic et al., 2012), gypsum is very widespread throughout South America, including Patagonia and the Andes (Fig. 4a). However, in most areas, the gypsum abundance is low (1% or less). Considering only the areas where the abundance of gypsum is 1% or more, the major gypsum-rich area is around the Atacama Desert (19-30°S) and scattered around the central Andes and Argentina (Fig. 4b). Notably, in the Patagonia region (35-50°S), where many previous studies have suggested a major source of dust to Antarctica, gypsum is not abundant.



Fig. 4. Mineral distributions in South America. a) Distribution of gypsum. **b)** The same as **a)**, but only areas where the abundance is 1% or more are shown. **c)** The SO_4^{2-}/Ca^{2+} ratio (=*m*). **d)** The same as **c)**, but only areas where the gypsum abundance is 1% or more are shown. **e)** The regions mentioned in the text; the Atacama Desert (Tapia et al., 2018) (yellow area) and Patagonia (green area). **f)** An enlarged view around the Atacama Desert. Locations of surficial gypsum salt at altitudes higher than 1200 m a.s.l. (Rech et al., 2003) (yellow circles) and atmospheric deposition (Li et al., 2019) (purple diamonds). The blue dotted line indicates the Puna-Altiplano region (Tapia et al., 2019).

We further investigated the spatial distribution of the *m* values by using the ratio of gypsum to calcite in the surface mineral database (Nickovic et al., 2012). On average, the *m* value is generally low, which is roughly consistent with a soil mean *m* of 0.06-0.08 (Fig. 4c). However, the spatial distribution of *m* varies significantly (range of 0.00-0.37), suggesting that it is inappropriate to adopt the average soil value without specifying the PSA. Focusing on only areas with high gypsum abundance (>1%), the Atacama and surrounding areas have relatively high *m* values (Fig. 4d).

We should note, however, that there is considerable uncertainty in the estimation of atmospheric aerosol components based on this mineralogical map. In fact, the *m* value for the Atacama region in this surface mineral map is approximately 0.2. This value is clearly lower than that from the present-day observations of aerosol deposition ($m = 1.1 \pm 0.1$) (Li et al., 2019; Wang et al., 2014) and surface soil observations (Voigt et al., 2020) in the Atacama Desert. Furthermore, an atmospheric model based on this mineralogical map considerably underestimates gypsum mass abundance in the atmosphere compared to observations at the other sites (Scanza et al., 2015). The cause of this discrepancy is not clear, but it could result from uncertainty in the spatial distribution of gypsum, acidic processes converting calcite to calcium sulfate in the atmosphere, and/or chemical fractionation during emission. Therefore, although this map is useful for a first screening, it does not provide conclusive evidence.

4.4. Atacama Desert as a potential source area for glacial sulfate

In summary, the compilation of geochemical data suggests that the area around the Atacama Desert is a PSA for sulfate aerosols during the LGM. First, the δ^{34} S and *m* values of the DF ice core during the glacial period are consistent with the aerosol (Li et al., 2019; Wang et al., 2014) and surface soil (Rech et al., 2003) observation data in the Atacama Desert. Second, based on the mineral distribution, this area is the only region in South America that meets the following conditions: (i) the abundance of gypsum on the surface is > 1%, (ii) the value of *m* is relatively large, and (iii) there is significant dust emission (i.e., the Atacama Desert is the largest natural source of dust in South America, based on satellite observations (Ginoux et al., 2012)).

As additional geochemical evidence, the oxygen isotope anomaly, Δ^{17} O, of sulfate in another Antarctic ice core supports our hypothesis. The Δ^{17} O of sulfate in the Antarctic Vostok core shows a low value for the glacial period (1.2‰) compared to that for the Holocene (ca. 3‰), which was attributed to changes in oxidation pathways (Alexander et al., 2002). However, considering that the Δ^{17} O value of total sulfate in the Atacama Desert is low, at 0-1 ‰ (Bao et al., 2004), the low glacial Δ^{17} O value can be alternatively explained by increased terrestrial contributions during the glacial period. Furthermore, another unique analysis of dust in the Antarctic core revealed lithium-enriched spikes during the Holocene, suggesting subtropical sources such as the Bolivian salt planes (Siggaard-Andersen et al., 2007).

4.5. Other potential source areas

Complementary information on the PSAs for sulfate can be obtained from analyses of insoluble dust. Isotopic analyses of Sr, Nd and Pb in ice cores from the East Antarctic Plateau suggest that the dust mainly originated from South America, particularly Patagonia (Basile et al., 1997; Delmonte et al., 2004; Sugden et al., 2009). The Puna-Altiplano Plateau was suggested as the second most important source during glacial periods (Delmonte et al., 2008; Gaiero, 2007). Similarly, climate modeling of dust suggests that the South American continent serves as a major source area for Antarctica, especially for the Dronning Maud Land (Albani et al., 2011), including the DF site, both at present and during the LGM. Regional contributions from within South America, however, depend on the model: north of the 32°S region (Albani et al., 2011) or Patagonia (35-50°S) (Albani et al., 2014; Li et al., 2008). Other areas are expected to be minor dust sources for East Antarctic Plateau during the LGM. During interglacials, Australian dust, in addition to South American dust, may contribute to dust in East Antarctica (Revel-Rolland et al., 2006). The Antarctic Dry Valleys can be a PSA of East Antarctic dust, but is not a dominant source (Delmonte et al., 2004).

These PSAs for dust, Patagonia and the Puna-Altiplano, may also be PSAs for the sulfate aerosols. However, the PSAs for insoluble dust and soluble sulfate (CaSO₄) are not necessarily the same because (i) soluble Ca^{2+} is only a small part (weight ratio of ca. 0.03-0.2) of insoluble dust and (ii) the nss-Ca²⁺ to insoluble dust mass ratio fluctuate between over glacial-interglacial cycles (low ratio corresponds to glacial maxima) in Antarctic Dome C ice core (Lambert et al., 2012). Considering that the Ca²⁺/dust ratio was the lowest during the LGM (0.03-0.04), the origin of soluble sulfate aerosols would be a limited part of the source regions for insoluble dust. Unfortunately, observations of δ^{34} S and *m* values of aerosols in Patagonia and the Puna-Altiplano are very limited. Thus, more data in PSAs are needed for further investigations. Even in the Atacama Desert, where a relatively large amount of data is available, most of the δ^{34} S observations were conducted mainly in the central arid core area (Fig. 4e and 4f).

Although the possibility of Patagonia as a PSA for sulfate aerosols cannot be excluded, limited data do not positively support that Patagonia is the major PSA during the LGM. First, based on the mineralogical distributions, gypsum abundance and m value are not high in Patagonia (Fig. 4). Second, major dust sources could be outwash plains during glacial periods, where large amounts of dust particles were deposited from glacial abrasion. A link between Antarctic dust deposition during the last glacial period and the variable sediment supply from Patagonian glaciers was suggested (Sugden et al., 2009). Gypsum-laden dust may originate from glacial abrasion resulting from solute transport to outwash areas. In the case of such glaciogenic dust, both insoluble dust and water-soluble sulfate originate from the same source. However, particle analysis of DF ice core shows that sulfate-adhered dust (i.e., sulfate particles containing Si) did not increase during glacial periods, in contrast to the significant increase in total dust (lizuka et al., 2012). This implies that the Patagonia region, the major source area for insoluble dust in Antarctica during the LGM, was not the major source area for sulfate aerosols.

The Puna-Altiplano Plateau, the second most important source for insoluble dust during the LGM, is another PSA for sulfate aerosols in the DF core. The Puna-Altiplano plateau is in the Central Andes next to the Atacama Desert (Fig. 4f). First, although δ^{34} S data are scarce (three sampling points), the δ^{34} S value from surface gypsum at elevations higher than 4000 m a.s.l. was $5.3\pm2.4\%$ (Rech et al., 2003). An observation of δ^{34} S of aerosols in the Andean region was similar, at 5.8% (Li et al., 2019). These values are consistent with the end member δ^{34} S value of the DF ice core. Generally, such unique low δ^{34} S values result from the fact that this area is a large volcanic area. Second, based on the mineral distribution map, the area shows relatively high gypsum abundance with a high *m* value (Fig. 4d). This is consistent with the fact that there are large volumes of evaporites, whose dominant minerals are halite and gypsum (Alonso et al., 1991).

The exact source region for glacial sulfate aerosols cannot be determined based on currently available data. More data on watersoluble aerosols (including δ^{34} S data) in PSAs are needed for further analyses. In general, soluble components tend to leach from the surface in regions with a certain amount of precipitation; thus, moderately soluble substances, such as gypsum, are present in extremely arid areas, such as deserts, and are easily scattered as aerosols. Our data (high *m* and low δ^{34} S values) indicate that water-soluble salts in arid areas were an important source of Antarctic sulfate aerosols during the LGM. Since the influence of soluble ion data from Antarctic ice cores, the impact of such terrestrial sources should be considered.

4.6. Atmospheric pathways

Atmospheric pathways between the Atacama Desert and Antarctica are limited. To illustrate a possible pathway, we analyzed dust storm events that occurred in present-day winter in the Puna-Altiplano region (Gaiero et al., 2013) using an atmospheric general circulation model (Matsui, 2017; Matsui and Mahowald, 2017) (see the Methods). High dust concentrations were present in the Atacama Desert and the South Atlantic Ocean (Fig. 5), which is consistent with satellite observations (Gaiero et al., 2013). Accord-



Fig. 5. Simulated dust transport pathway during a dust storm event in the Atacama region. a) Map of the dust deposition rate (mg m⁻² d⁻¹) on 24 July 2009, which is three days after a major dust storm occurred on 21 July 2009 (Gaiero et al., 2013). Stars connected with a black line indicate a transport pathway from the Atacama Desert to the DF site. b) Vertical section (longitude vs. altitude) of the dust concentration (μ g m⁻³) along the transport pathway shown in **a**). The left end of the figure is the Atacama Desert, and the right end is the DF site. **c)** An enclosed view of polar region (corresponds to orange box in **b**), in which the concentration was multiplied by a factor of 100.

ing to the vertical section, aerosols from the Atacama Desert were transported to the high-altitude zone of Antarctica, likely via the subtropical jet stream. This result is consistent with a modeling study showing that dust transport from South America and Antarctica preferentially takes place in the mid-high troposphere (Albani et al., 2011). However, the concentrations in inland areas were significantly reduced, as expected from the deposition rate of the ice core (Fig. 5b and 5c). In fact, the present-day SO_4^{2-} deposition rate in the Atacama Desert (Li et al., 2019; Wang et al., 2014) is ca. 3000 times and ca. 300 times larger than the terrestrial SO_4^{2-} flux at the DF site in the Holocene and during the LGM, respectively. Thus, only a small fraction of the aerosols in the source region may reach Antarctica.

The physical mechanism of the increase in gypsum during the LGM is not yet clear. Regional climate changes in the source region would not have been the primary controlling factors. In fact, wet periods in the central Atacama Desert, such as the Central Andean Pluvial Event (15.9-13.8 kyr BP and 12.7-9.7 kyr BP) (Quade et al., 2008), do not appear to have corresponding events in the DF ice core record. Rather, considering the present-day winter dust storm events, wind gustiness in the deserts (McGee et al., 2010) and the increased lifetime of aerosols in the upper troposphere caused by a reduced hydrological cycle (Yung et al., 1996) would be important factors driving the increase in glacial terrestrial sulfate.

5. Conclusions

Our new δ^{34} S record from the Antarctic DF ice core shows a negative correlation between $\delta^{34}S_{nss}$ and terrestrial contributions. This result supports the hypothesis of increased terrestrial sulfate during the LGM but does not favor the constant marine biogenic sulfate hypothesis. Thus, the balance between reduced marine biogenic sulfate and increased terrestrial sulfate flux can explain the relatively stable variations in the total sulfate flux over the glacial cycle. The δ^{34} S value of the terrestrial endmember suggests that the PSA for the DF sulfate during the LGM is characterized by low δ^{34} S and a high SO₄²⁺/Ca²⁺ ratio of terrestrial dust (*m* value). Compilation of the δ^{34} S data revealed that the terrestrial gypsum in the high-altitude region of the Atacama Desert is consistent with such unique δ^{34} S and *m* values. The mineral distribution in South America also supports the importance of this area.

Contributions from other regions cannot be ruled out because of the limited geochemical data in source regions. For example, geochemical data suggest that the Puna-Altiplano Plateau is another important PSA for dust. Although Patagonia was the major source region for East Antarctic insoluble dust during the LGM, soluble Ca^{2+} is only a small part of insoluble dust. The characteristics of the chemical data (e.g., gypsum abundance) also do not match those of the Patagonia region. Thus, the origin of the soluble sulfate aerosols may be biased to specific areas. These results demonstrate that the estimation of changes in sources of sulfate significantly affects the interpretation of the relationship between climate and sulfate flux records in ice cores. The identification of source areas, combined with an atmospheric model considering mineral composition, will provide constraints on past atmospheric circulation patterns, such as the position and intensity of the subtropical jet stream. Therefore, the contribution of soluble salts in deserts, which has been neglected, should be considered when interpreting ion data in Antarctic cores.

CRediT authorship contribution statement

Ryu Uemura: Conceptualization, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing. **Kosuke Masaka:** Investigation, Methodology. **Yoshinori lizuka:** Investigation, Writing – review & editing. **Motohiro Hirabayashi:** Investigation, Writing – review & editing. **Hitoshi Matsui:** Funding acquisition, Investigation, Visualization, Writing – review & editing. **Risei Matsumoto:** Methodology. **Miki Uemura:** Investigation, Methodology. **Koji Fujita:** Writing – review & editing. **Hideaki Motoyama:** Funding acquisition, Resources.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

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Supplementary Material

Earth and Planetary Science Letters

Soluble salts in deserts as a source of sulfate aerosols in an Antarctic ice core during the last glacial period

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- Table A1* and references for Table A1
- Table A2*
- Figure A1

*Tables are also provided as Excel files.

		Altitude	Latitude	Longitude	$\delta^{34}S$
Location	Sampling date	(m, a.s.l.)	(°S)	(°S)	(‰, VCDT)
Z2	25 Nov. 2012	1924	70.033	42.433	17.2
Mizuho (IM0)	27 Nov. 2012	2215	70.709	44.273	17.4
NMD196	3 Dec. 2012	2845	72.233	44.283	15.3
NMD304	5 Dec. 2012	3192	73.083	42.883	16.3
NMD370	8 Dec. 2012	3338	74.067	42.983	15.9
MD590	12 Dec. 2012	3684	76.033	41.133	15.4
DF	20 Dec. 2012	3803	77.317	39.703	15.4
NDF	25 Dec. 2012	3763	77.789	39.053	17.1
Plateau S	28 Dec. 2012	3678	79.362	40.514	15.6
S80	2 Jan. 2013	3625	80.000	40.500	16.2
Fuji pass	8 Jan. 2013	3787	77.427	41.478	16.7
DF	13 Jan. 2013	3803	77.317	39.703	16.4

Table A1 Isotope compositions and ion concentrations in Antarctic snow samples recalculated with new sulfur isotope reference values.

These are the same data used in Uemura et al. (2016), but the δ^{34} S values were recalculated with reference values recommended by NIST. Traditionally, the International Atomic Energy Agency (IAEA) recommended a δ^{34} S value of 20.3 ± 0.4‰ for NBS127, but the National Institute of Standards and Technology (NIST) currently recommends a δ^{34} S value of 21.17 ± 0.09‰ [NIST, 2013] based on recent measurements of the reference materials [Brand et al., 2014; Halas and Szaran, 2001]. Here, we adopted the latter updated value to normalize our measurement data. We also used the updated δ^{34} S values of IAEA SO-5 (0.15 ± 0.05‰) and SO-6 (-34.04 ± 0.11‰) [Halas and Szaran, 2001]. These values are slightly different from the IAEA interlaboratory comparison values of SO-5 (0.5 ± 0.2‰) and SO-6 (-34.1 ± 0.2‰).

References for Table A1

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Table A2 Sulfur isotope ratio for sulfate and ion concentrations and their flux from the Dome Fuji ice core

depth (Top) de pth (Bottom)	Age (DFO2006)	Accumulation	del_34S	SO_4^2	Ъ	NO3-	MSA	Na ⁺	Ca^{2+}	Mg ²⁺	K⁺	⁺ ⁺ HN	SO_4^2	b	NO3	MSA	Na ⁺	Ca ²⁺	Mg ²⁺	¥	°H4,⁺
Ē	1	0.0		permil vs	1.00	1.000	1.011	1.000	1.000	I/orr	1/200	1.000	1.000	micro-mol	micro-mol .	micro-mol 1	nicro-mol 1	nicro-mol n	uicro-mol mi	icro-mol mi	icro-mol m	icro-mol
	=	10.16	cm-ice yr	VCDT	- Jak	n An	- And	n /Sm	n/ån	- And	n And	n An	n An	m ⁻² yr ⁻¹ n	n ⁻² yr ⁻¹ n	n ⁻² yr ⁻¹	n ⁻² yr ⁻¹					
01-168 197.0	08 197.58	6004	3.07	16.00	94.06	41.33	21.38	6.80	19.95	2.88	3.17	2.08	2.32	27.57	32.83	9.71	1.99	24.43	2.02	3.68	1.50	3.62
02-045 222.0	01 222.51	6899	2.75	15.05	109.58	46.29	24.39	8.24	24.47	5.32	3.44	2.88	6.11	28.78	32.94	9.92	2.16	26.85	3.35	3.57	1.86	8.56
02-101 250.0	02 250.52	7935	3.24	16.04	90.99	43.74	24.82	7.81	22.17	5.14	3.76	2.30	3.60	28.18	36.71	11.91	2.42	28.70	3.82	4.61	1.75	5.94
02-155 276.5	96 277.46	8926	3.05	15.82	98.25	40.44	22.32	8.80	21.10	3.44	2.80	2.61	3.15	28.65	31.96	10.09	2.57	25.71	2.40	3.23	1.87	4.90
*03-015 307.4	40 307.90	10012	3.20	14.14	146.61	37.97	30.06	8.24	18.50	4.29	3.44	2.53	2.62	44.82	31.45	14.24	2.52	23.63	3.14	4.15	1.90	4.27
03-041 320.4	40 320.90	10467	3.38	16.34	109.71	34.67	26.17	8.25	16.33	1.96	2.35	1.57	1.70	35.36	30.27	13.07	2.66	21.99	1.51	3.00	1.24	2.91
03-070 334.5	90 335.40	10976	3.08	16.44	102.57	35.95	24.12	7.20	18.49	3.69	2.58	2.07	2.27	30.13	28.61	10.98	2.11	22.69	2.59	2.99	1.49	3.55
03-094 346.5	92 347.42	11396	3.19	16.69	84.23	29.26	24.24	3.92	13.58	1.96	2.11	1.89	1.36	25.69	24.18	11.45	1.20	17.31	1.43	2.54	1.41	2.22
03-125 362.4	44 362.94	11959	2.85	14.39	95.70	48.64	12.82	7.92	19.42	3.73	3.05	3.60	2.35	26.02	35.83	5.40	2.15	22.06	2.43	3.27	2.40	3.41
03-153 376.4	46 376.96	12536	2.73	13.58	117.22	60.63	12.84	12.07	28.72	4.85	3.93	2.80	1.88	30.60	42.88	5.19	3.15	31.33	3.03	4.05	1.79	2.62
03-175 387.:	31 387.81	13017	2.45	14.13	115.99	40.87	15.10	8.04	44.97	5.26	5.49	3.38	1.50	27.15	25.92	5.48	1.88	43.97	2.95	5.08	1.94	1.88
03-186 392.5	81 393.31	13273	2.37	14.71	114.45	58.72	15.55	7.70	43.09	6.63	5.45	4.21	1.92	25.90	36.00	5.45	1.74	40.74	3.60	4.87	2.34	2.32
*04-004 401.8	84 402.34	13682	2.59	11.23	234.59	49.66	12.79	6.44	39.53	4.72	5.14	3.25	1.37	58.01	33.27	4.90	1.59	40.84	2.80	5.02	1.97	1.81
04-015 407.5	34 407.84	13929	2.50	13.05	111.10	31.11	15.70	11.59	33.51	6.32	4.72	2.82	2.71	26.49	20.10	5.80	2.76	33.39	3.61	4.45	1.65	3.44
04-033 416.5	35 416.85	14336	2.50	15.44	93.44	44.25	15.67	11.62	39.08	5.78	4.93	3.23	1.04	22.31	28.62	5.80	2.77	38.98	3.31	4.65	1.89	1.33
04-043 421.5	35 421.85	14558	2.60	16.63	95.77	41.82	14.56	11.50	43.67	6.89	5.26	3.91	1.55	23.79	28.15	5.60	2.86	45.32	4.10	5.16	2.39	2.05
04-055 427.5	35 427.85	14835	2.24	16.08	175.64	82.36	14.96	16.94	50.06	7.09	7.17	3.76	1.50	37.64	47.82	4.97	3.63	44.82	3.64	6.07	1.98	1.72
04-070 434.	85 435.35	15194	2.33	10.72	156.70	65.36	10.95	14.80	51.27	8.65	7.46	4.50	1.06	34.90	39.45	3.78	3.30	47.71	4.62	6.57	2.46	1.26
04-082 440.	85 441.35	15486	2.34	13.56	118.65	47.97	12.49	12.36	46.94	10.81	6.16	5.23	1.52	26.54	29.08	4.33	2.76	43.88	5.79	5.45	2.88	1.81
04-095 447.:	35 447.83	15807	2.20	13.84	116.44	57.46	18.11	15.33	42.76	9.86	7.00	4.06	2.74	24.40	32.63	5.88	3.21	37.44	4.95	5.80	2.09	3.07
04-109 454.	35 454.85	16163	2.11	14.56	119.98	76.31	34.36	6.06	53.78	16.19	8.72	4.80	1.62	24.18	41.67	10.73	1.22	45.29	7.82	6.94	2.38	1.74
04-122 460.8	85 461.35	16526	2.08	13.17	130.95	66.92	49.48	14.57	58.68	25.20	9.97	5.65	1.31	25.98	35.98	15.21	2.89	48.65	11.98	7.82	2.76	1.39
04-134 466.8	85 467.35	16871	1.83	17.78	271.97	89.46	45.47	17.49	69.03	21.40	13.47	5.42	3.08	47.58	42.41	12.32	3.06	50.45	8.97	9.31	2.33	2.87
04-144 471.	85 472.35	17189	1.82	12.63	180.62	139.46	53.34	19.39	84.58	32.85	14.65	11.04	1.78	31.32	65.53	14.33	3.36	61.28	13.65	10.04	4.70	1.65
04-155 477.:	35 477.85	17525	1.78	13.15	170.67	149.44	47.76	17.90	90.23	38.02	15.03	8.26	1.78	29.00	68.81	12.57	3.04	64.06	15.48	10.10	3.45	1.61
04-165 482.	35 482.85	17859	1.74	12.90	258.93	161.08	98.02	19.99	91.10	55.50	19.46	9.35	3.19	43.00	72.48	25.22	3.32	63.21	22.09	12.78	3.82	2.82
04-184 491.	85 492.35	18513	1.69	11.47	237.27	185.11	75.64	15.22	117.53	52.11	22.56	9.83	1.33	38.27	80.90	18.90	2.45	79.20	20.14	14.38	3.89	1.15
04-195 497	35 497.85	18894	1.69	11.15	213.77	141.10	101.59	18.61	95.80	51.12	19.14	12.07	3.74	34.49	61.68	25.39	3.00	64.58	19.77	12.21	4.79	3.21
05-009 504.	35 504.85	19389	1.67	11.65	248.21	170.80	86.37	15.69	112.53	58.14	22.32	10.00	1.42	39.48	73.60	21.28	2.49	74.78	22.16	14.03	3.91	1.20
05-025 512.:	33 512.83	19953	1.67	13.16	176.05	145.31	84.69	22.35	88.95	46.85	17.44	11.00	2.95	28.02	62.67	20.88	3.56	59.16	17.87	10.97	4.30	2.50
05-051 525.2	25 5.75	20889	1.65	11.53	216.27	176.17	122.11	17.98	100.43	62.99	21.10	11.28	3.53	34.01	75.08	29.75	2.83	66.00	23.74	13.12	4.36	2.96
05-080 539.2	25 539.75	21909	1.60	11.56	215.03	178.23	106.19	18.67	105.21	61.60	20.88	11.39	3.33	32.84	73.76	25.13	2.85	67.14	22.55	12.60	4.28	2.72
05-115 555.1	95 556.45	23146	1.79	12.66	206.56	135.07	66.44	20.02	87.06	35.71	16.43	21.96	3.14	35.28	62.51	17.58	3.42	62.12	14.62	11.09	9.21	2.86
*05-135 565.	76 566.26	23832	1.65	13.03	303.29	167.56	104.36	19.43	95.38	79.06	20.63	14.50	4.07	47.91	71.73	25.54	3.07	62.95	29.93	12.88	5.63	3.43
05-155 576.0	00 576.50	24613	1.65	12.82	214.83	170.63	101.87	22.35	101.02	72.22	19.26	12.17	3.82	33.84	72.83	24.86	3.52	66.48	27.26	11.99	4.71	3.21

* Volcanic peaks

Figure A1



Figure A1 Sulfur isotope values for the DF ice core and potential sources versus the terrestrial contributions

The same as Figure 2 but for m = 0.67.