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Reduced marine phytoplankton sulphur emissions in the Southern Ocean during the past seven glacials

K. Goto-Azuma ^{1,2}, M. Hirabayashi¹, H. Motoyama ^{1,2}, T. Miyake¹, T. Kuramoto ^{1,8}, R. Uemura ^{1,9}, M. Igarashi¹, Y. Iizuka³, T. Sakurai ^{1,10}, S. Horikawa^{3,11}, K. Suzuki ⁴, T. Suzuki ⁵, K. Fujita ⁶, Y. Kondo ¹, S. Hattori ⁷ & Y. Fujii¹

Marine biogenic sulphur affects Earth's radiation budget and may be an indicator of primary productivity in the Southern Ocean, which is closely related to atmospheric CO₂ variability through the biological pump. Previous ice-core studies in Antarctica show little climate dependence of marine biogenic sulphur emissions and hence primary productivity, contradictory to marine sediment records. Here we present new 720,000-year ice core records from Dome Fuji in East Antarctica and show that a large portion of non-sea-salt sulphate, which was traditionally used as a proxy for marine biogenic sulphate, likely originates from terrestrial dust during glacials. By correcting for this, we make a revised calculation of biogenic sulphate and find that its flux is reduced in glacial periods. Our results suggest reduced dimethylsulphide emissions in the Antarctic Zone of the Southern Ocean during glacials and provide new evidence for the coupling between climate and the Southern Ocean sulphur cycle.

¹ National Institute of Polar Research, Research Organization of Information and Systems, 10-3 Midori-cho, Tachikawa, Tokyo 190-8518, Japan. ² Department of Polar Science, Graduate University for Advanced Studies (SOKENDAI), 10-3 Midori-cho, Tachikawa, Tokyo 190-8518, Japan. ³ Institute of Low Temperature Science, Hokkaido University, Kita-19, Nishi-8, Kita-ku, Sapporo 060-0819, Japan. ⁴ Faculty of Science, Shinshu University, 3-1-1 Asahi, Matsumoto 390-8621, Japan. ⁵ Faculty of Science, Yamagata University, 1-4-12 Kojirakawa-cho, Yamagata 990-8560, Japan. ⁶ Graduate School of Environmental Studies, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8601, Japan. ⁷ Department of Chemical Science and Engineering, School of Materials and Chemical Technology, Tokyo Institute of Technology, Yokohama 226-8502, Japan. ⁸Present address: Department of Human Development, School of Humanities and Culture, Tokai University, 4-1-1 Kitakaname, Hiratsuka 259-1292, Japan. ⁹Present address: Graduate School of Environmental Studies, Nagoya University, Furo-cho, Chikusa-ku, Sapporo 062-8602, Japan. ¹⁰Present address: Earthquake and Volcano Research Center, Graduate School of Environmental Studies, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8601, Japan. ¹⁰Present address: Earthquake and Volcano Research Center, Graduate School of Environmental Studies, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8601, Japan. ¹⁰Present address: Earthquake and Volcano Research Center, Graduate School of Environmental Studies, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8601, Japan. ¹⁰Present address: Earthquake and Volcano Research Center, Graduate School of Environmental Studies, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8601, Japan. ¹⁰Present address: Earthquake and Volcano Research Center, Graduate School of Environmental Studies, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8601, Japan. Correspondence and requests for materials should be addressed to K.G.-A. (email: kumiko

imethylsulphide (DMS) emitted from oceanic phytoplankton plays an important role in controlling concentrations of sulphate (SO_4^{2-}) aerosols, which can act as cloud condensation nuclei (CCN)¹⁻³. Changes in CCN would influence cloud albedo, a key parameter of radiative forcing¹⁻³. Increased SO_4^{2-} can thus cool the Earth by indirect forcing, in addition to direct forcing owing to increased scattering of solar radiation³. To understand these effects, DMS emissions and their links to climate should be evaluated in a pristine environment². DMS and its oxidation products, SO_4^{2-} and methanesulphonate (CH₃SO₃⁻, hereafter MSA), are also indicators of primary productivity in the Southern Ocean (SO), which is important because they are closely related to atmospheric CO₂ variability through the biological pump⁴. SO_4^{2-} and MSA in Antarctic ice cores are therefore useful tools for investigating links between the sulphur cycle and climate.

High concentrations of non-sea-salt (nss) SO42- measured in glacial samples from Vostok ice core drilled in East Antarctica⁵ (Supplementary Fig. 1) have been interpreted as evidence of enhanced oceanic DMS emissions during glacials, assuming that $nssSO_4^{2-}$ is mainly of marine biogenic DMS origin. A subsequent study on the same ice core⁶ reports increased MSA concentrations in addition to $nssSO_4^{2-}$, further supporting the interpretation of [5] because MSA originates solely from DMS, whereas $nssSO_4^{2-}$ can come from other sources^{7,8}. Based on these results, DMS emissions and hence nssSO42- have been believed to exert positive feedback on climate. However, more recent studies refute the positive feedback hypothesis^{7,8}, showing that MSA is modified post-depositionally in the Antarctic interior where accumulation rates are low and does not represent DMS production around Antarctica. Furthermore, two deep ice cores drilled at Dome C (EDC) and Dronning Maud Land (EDML) in East Antarctica (Supplementary Fig. 1) show little change in nssSO₄²⁻ flux over glacial/interglacial cycles⁷⁻⁹, while concentrations increase during glacials. Wolff et al.7 point out that increased nssSO₄²⁻ concentrations in ice cores from sites with low accumulation rates (e.g., Vostok, EDC, EDML) are mainly caused by decreased accumulation rates in glacials, and can therefore not be interpreted as evidence of increased atmospheric $nssSO_4^{2-}$. The nearly constant $nssSO_4^{2-}$ fluxes at EDC and EDML, which face the Indian and Atlantic Ocean sectors of the SO, respectively, have been interpreted to reflect stable DMS emissions and hence stable marine biogenic productivity in the Antarctic Zone (AZ) of the SO over glacial cycles, assuming that the major source of $nssSO_4^{2-}$ is DMS^{7-9} . In contrast, marine sediment records show that export production decreases in the AZ during glacials but increases further north in the Sub-Antarctic Zone (SAZ) of the SO⁴. This implies reduced primary productivity in the AZ but increased primary productivity in the SAZ during glacials. The disparity between ice and marine core records has been attributed to differences in marine organisms that contribute to these records⁷.

The stable sulphur isotopic composition of SO_4^{2-} ($\delta^{34}S$) provides a useful signature of its origins^{10–12}. The $\delta^{34}S$ data measured from EDC and Vostok ice cores suggest 4–6‰ lower $\delta^{34}S$ for the last glacial than for the Holocene and last interglacials, although the data are scattered and sparse¹¹. This has been attributed to isotopic fractionation during transport, as terrestrial contribution of SO_4^{2-} has been assumed to be small¹¹. However, surface snow samples from a latitudinal transect between a coastal station (Syowa) and an interior site (Dome Fuji, hereafter DF, Supplementary Fig. 1) show remarkably uniform $\delta^{34}S$ in East Antarctica¹³. The results suggest that net isotopic fractionation during long-range transport is insignificant in East Antarctica and thus $\delta^{34}S$ in the ice cores from the East Antarctic interior can be used to infer source contributions. Lower $\delta^{34}S$ values in the

last glacial¹¹ might be due to an increased contribution of terrestrial SO_4^{2-} originating from increased terrestrial dust^{7,8}. Consequently, little change in the nssSO₄²⁻ flux over glacial/ interglacial cycles⁷⁻⁹ can be caused by increased terrestrial sulphate and decreased marine biogenic sulphate.

In this study, we propose this alternative interpretation of $nssSO_4^{2-}$ flux and make a revised calculation of DMS-derived sulphate, using new ice core records obtained at DF, spanning the last 720,000 years^{14,15}. On the basis of the revised calculation, we compare the DMS-derived sulphate record from DF with those from EDC and EDML. We find that DMS-derived sulphate fluxes decrease in glacials, which indicates reduced DMS emissions in the AZ of the SO. This suggests that primary production, as well as export production, decreases during glacials, which is consistent with marine sediment records⁴.

Results

Flux variability and potential sources of $nssSO_4^{2-}$. We calculated $nssCa^{2+}$ and $nssSO_4^{2-}$ from Ca^{2+} , Na^+ , and SO_4^{2-} concentrations^{7–9,16} (Supplementary Figs. 2a–c). Low accumulation rates (<30 kg m⁻² yr⁻¹ in the present day and <50 kg m⁻² yr⁻¹ throughout the last 720,000 years) (Supplementary Fig. 2d) at DF¹⁴ indicate that the dominant process for aerosol deposition is dry deposition and that the flux, rather than the concentration in ice, better represents the changes in atmospheric aerosol concentration^{7,16}. The flux of $nssCa^{2+}$ at DF covaries with that at EDC^{7,8} and EDML¹⁶, indicating high and low values during glacials and interglacials, respectively (Fig. 1, Supplementary Fig. 3); fluxes at DF are 2.0 and 0.6 times those at EDC and EDML, respectively.



Fig. 1 Temperature proxies and ion fluxes at Dome Fuji (DF) and Dome C (EDC). **a** The δ^{18} O (DF)¹⁴ and δ D (EDC)^{7,8} records averaged over 1000 years. Marine isotope stage numbers for interglacials are also shown. **b** Fluxes of nssCa²⁺ at DF and EDC averaged over 1000 years. **c** Fluxes of nssCa²⁺ at DF and EDC averaged over 1000 years. See Methods for DF chronology and flux calculations. The EDC fluxes are plotted on the AlCC12 timescale^{53,54} using previously published ion data^{7-9,16} and accumulation rates^{53,54}



Fig. 2 Variability of $nssSO_4^{2-}$ flux at Dome Fuji (DF). **a** DF $nssSO_4^{2-}$ flux plotted against DF $\delta^{18}O^{14,15}$. Data points represent 1000-year averages. Before averaging, the $\delta^{18}O$ depths that differ from the ion data depths have been interpolated to match. Gray bar indicates the lower threshold of $\delta^{18}O$ ($-58\%_0$), below which the $nssSO_4^{2-}$ flux decreases with $\delta^{18}O$, and the upper threshold ($-57\%_0$), above which the $nssSO_4^{2-}$ flux increases with $\delta^{18}O$. **b** DF $nssSO_4^{2-}$ flux plotted against DF $nssCa_2^{+}$ flux. Data points represent 1000-year averages. The slope of the solid red line (m = 2.4) represents the stoichiometric mass ratio of Ca/SO₄ as CaSO₄. The dashed red line shows the lower bound of the $nssSO_4^{2-}$ flux data with m = 2.4. Red and blue dots represent the data for warm and cold periods, respectively, corresponding to the $\delta^{18}O$ values above and below the thresholds

The dominant source of nssCa²⁺ is terrestrial dust^{7–9,16} and South America is a major source region for dust deposited in the Antarctic interior^{17–19}. Different nssCa²⁺ fluxes in three records can be explained by their different distances from the South American source region¹⁶. Contrary to previous studies on EDC and EDML cores, the nssSO₄^{2–} flux at DF is not constant (Figs. 1 and 2). The flux increases as δ^{18} O (a proxy for temperature at DF^{14,15}) decreases below approximately –58‰, and increases when δ^{18} O is above approximately –57‰.

Potential sources of $nssSO_4^{2-}$ are marine biogenic DMS, volcanic sulphate, and terrestrial dust^{7,8}. With the exception of a few years following large volcanic eruptions, the volcanic input is estimated to be less than 10% of the present-day and Holocene sulphate budgets⁷. Oceanic DMS was previously regarded as the dominant $nssSO_4^{2-}$ source over glacial/interglacial cycles, with only a small input from terrestrial sources^{7–9}. However, terrestrial sulphate can be a major source in glacials when the amount of dust increases. Fluxes of $nssCa^{2+}$ and $nssSO_4^{2-}$ at DF are

correlated during cold periods when δ^{18} O is below approximately -58%. The scatter plot of nssSO₄²⁻ against nssCa²⁺ (Fig. 2b) shows a lower bound whose slope is close to the stoichiometric ratio for CaSO₄, indicating that a large proportion of nssSO₄²⁻ during cold periods exists as CaSO₄. This same feature is reported for EDML and a similar but weaker correlation between nssCa²⁺ and $nssSO_4^{2-}$ fluxes is reported for EDC²⁰. These observations suggest that a large proportion of $nssSO_4^{2-}$ exists as CaSO₄ during cold periods at EDC and EDML²⁰, as well as DF. Micro-Raman spectroscopic analysis of DF samples from the Last Glacial Maximum (LGM) suggests that a large proportion of Ca^{2+} exists as gypsum $(CaSO_4 \cdot 2H_2O)^{21}$. Furthermore, analyses of DF samples from the LGM using scanning electron microscopy/energydispersive X-ray spectroscopy (SEM-EDS) show that the majority of Ca^{2+} originates from $CaSO_4^{22}$. Although the SEM-EDS analyses indicate that a large fraction of the particles consists of silicate minerals containing Ca, they do not dissolve in water. The majority of Ca²⁺ measured in this study using ion chromatography (see Methods) should therefore originate from CaSO₄.

CaSO₄ in DF core could originate from two potential sources. First is primary gypsum, i.e., terrestrial gypsum transported from arid source regions as dust^{8,9,20,23}. Second is secondary gypsum formed by the reaction of CaCO₃, one of the major components of terrestrial dust, with marine biogenic H_2SO_4 or $SO_2^{20,24,25}$ during dust transport. If primary gypsum is dominant, the major source of nssSO₄²⁻ during cold periods should be dust, not marine biogenic sulphate. But if secondary gypsum is dominant, the major source of nssSO₄ should be marine biogenic sulphate. So far, secondary gypsum has been considered dominant, assuming limited fractions of terrestrial sulphate^{7,9,11}. A mean sediment SO₄²⁻/Ca²⁺ ratio of 0.1⁹ or 0.18 observed for soils^{10,12} is often referred to as a basis of a small terrestrial contribution. To define an uppermost limit,⁹ uses a ratio of 0.5 observed in Sharan dust plumes and suggests a maximum terrestrial contribution of only 16%. However, ratios are highly variable and sourcedependent⁸.

Although the compositions of South American minerals are poorly documented, there is some evidence supporting the hypothesis that SO_4^{2-}/Ca^{2+} ratios could be much higher than previously assumed. Soil samples from northeastern and central Patagonia, one of the potential source regions, show SO_4^{2-}/Ca^{2+} ratios close to or larger than the stoichiometric ratio of $CaSO_4^{26,27}$. Because some of these soil samples have high Na^+/Ca^{2+} and Mg^{2+}/Ca^{2+} ratios (often much higher than 1), which is not the case for nssNa⁺/nssCa²⁺ and nssMg²⁺/nssCa²⁺ in the Antarctic ice samples (see [28] for nssNa⁺/nssCa²⁺ and Supplementary Discussion for nssMg²⁺/nssCa²⁺), such soils may not be the source for CaSO₄ in the Antarctic ice cores. However, high SO_4^{2-}/Ca^{2+} ratios reported in Patagonia cast doubt on the assumption that the SO_4^{2-}/Ca^{2+} ratio of 0.5 observed in Sharan dust plumes gives an uppermost limit⁹.

Gypsum is a major mineral in evaporites²⁹. A distribution of evaporites has been reported in wide regions of South America³⁰. Large areas of the Puna-Altiplano, one of the potential source regions of dust deposited in the Antarctic interior, are covered by salt-lake beds¹⁹, which could be sources of gypsum-rich evaporites, although the compositions of these lakes are poorly documented and could vary substantially²⁹. Giant evaporite belts dominated by halite and gypsum are also found in this region³¹. Puna evaporites are uniquely characterized by scarce carbonates, whereas sulphates and chlorides are abundant³¹. Furthermore, ion ratios nssCl⁻/nssNa⁺ and nssNa⁺/nssCa²⁺ estimated from EDC core suggest a significant contribution of halides mobilized from continental evaporite deposits²⁸. The reaction of CaCO₃ with H₂SO₄ and SO₂ is slow^{20,25,32,33}, and only a partial neutralization of clay or carbonate particles has been observed

even in areas where SO_2 and H_2SO_4 concentrations are greatly enhanced by volcanic contributions^{20,34}. If this can also be extended to the different conditions over the Southern Ocean, then terrestrial gypsum would be needed to explain the relationship between $nsSCa^{2+}$ and $nssSO_4^{2-}$ in Antarctic ice cores and may be a major $CaSO_4$ source. To validate our idea, it will be important to establish what source areas could provide such a gypsum-rich source of dust.

Revised calculations of DMS-derived sulphate. To calculate the flux of DMS-derived $nssSO_4^{2-}$, the contribution of terrestrial sulphate should be removed. We first subtract the terrestrial nssSO₄²⁻ fraction as a case for a maximum contribution of terrestrial gypsum to nssSO₄²⁻flux. Assuming that the majority of $nssCa^{2+}$ originates from terrestrial sulphate and that $nssCa^{2+}$ is a major terrestrial cation, we make a first-order estimate of the marine biogenic sulphate flux by subtracting the CaSO₄ contribution (nssCa²⁺ multiplied by 2.4, the stoichiometric mass ratio of SO₄/Ca for CaSO₄) from the total $nssSO_4^{2-}$ flux. The residual $nssSO_4^{2-}$ is thus dominated by sulphate in the form of H₂SO₄ and/or Na₂SO₄. Both H₂SO₄ and Na₂SO₄ originate from DMS; the former is directly produced from DMS, whereas the latter is produced by the reaction between DMS-derived H₂SO₄ and NaCl³⁵ (sea salt and/or terrestrial). The residual nssSO₄²⁻ flux, a revised marine biogenic sulphate flux, co-varies with the temperature proxy δ^{18} O at DF (Fig. 3) and displays high and low values during interglacials and cold periods in glacials, respectively. Similarly, residual nssSO42- fluxes calculated for EDC and EDML show variability consistent with DF (Fig. 3). Opposite behaviors of marine biogenic and terrestrial sulphate would have led to small variability of the nssSO42- flux over glacial/interglacial cycles. Larger dust input at DF and EDML owing to their proximity to the South American source regions relative to EDC (Fig. 1b, Supplementary Fig. 3a) would have resulted in greater variability in the nssSO₄²⁻ flux at DF and EDML compared with EDC (Fig. 1c, Supplementary Fig. 3b).

As stated above, we first subtract the terrestrial gypsum contribution to calculate the marine biogenic $nssSO_4^{2-}$ flux. However, because $nssSO_4^{2-}$ could have other sources, we perform a sensitivity test as follows. If a major fraction of $nssSO_4^{2-}$ originates from evaporites, then other minerals commonly contained in evaporites could also contribute to the $nssSO_4^{2-}$ flux. We take into account Mg²⁺ and K⁺, which could originate from evaporites and exist as sulphates²⁹, as well as the contribution of CaCO₃, a major mineral in many of the dust source regions^{26,27} that likely reacts with HNO₃ or NO_x instead of H₂SO₄ or SO₂ due to faster reactions^{20,25,32,33,36} (Supplementary Discussion and Supplementary Fig. 4). Our conclusion that the residual $nssSO_4^{2-}$ flux decreases during cold periods does not change, although the correlation between residual sulphate and temperature proxy changes slightly (Fig. 4a, b, Supplementary Fig. 5). We also change the $nssSO_4^{2-}/nssCa^{2+}$ ratio (R_1) assuming that part of CaSO₄ originates from the reaction of CaCO₃ with marine biogenic sulphate. When we change R_1 values, we consider only CaSO₄ and ignore other minerals. The same conclusion remains if $R_1 > 1.2$, but fails if $R_1 < 1.2$. For EDC and EDML cores, we consider only the CaSO4 contribution because neither Mg²⁺ nor K⁺ data are available.

We calculate the marine biogenic/total nss SO_4^{2-} ratio (R_2) for different terrestrial gypsum contributions (Supplementary Discussion and Supplementary Fig. 6). If we assume that Ca^{2+} and Mg^{2+} are major evaporite-originated cations that form sulphate in DF core and that the carbonate hosts of these ions react with HNO₃ or NO_x rather than H₂SO₄ or SO₂, R_2 for the LGM is 0.46. This value is consistent with that estimated from sulphur isotopes



Fig. 3 Variability of residual $nssSO_4^{2-}$ flux at Dome Fuji (DF), Dome C (EDC), and Dronning Maud Land (EDML). **a** Residual $nssSO_4^{2-}$ flux at DF and EDC for the past 720,000 years, calculated by subtracting the terrestrial CaSO₄ contribution from the $nssSO_4^{2-}$ flux. The EDC flux is plotted on the AICC12 timescale^{53,54} using previously published ion data^{7-9,16} and accumulation rates^{53,54}. **b** $\delta^{18}O$ at DF over the past 720,000 years^{14,15}. Gray bar indicates the thresholds (Fig. 2a). Marine isotope stage numbers for interglacials are also shown. **c** Residual $nssSO_4^{2-}$ at DF, EDC, and EDML calculated by subtracting the terrestrial CaSO₄ contribution from the $nssSO_4^{2-}$ flux. The EDC and EDML fluxes are plotted on the AICC12 timescale^{53,54}. **d** The $\delta^{18}O$ values at DF¹⁴ for the past 150,000 years. All ion and $\delta^{18}O$ values are averages over 1000 years

 $(R_2 \sim 0.5)$ assuming no isotopic fractionation¹¹. However, R_2 values for interglacials exceed 1, which is implausible. This most likely suggests an overestimation of the NO₃⁻ derived from the reaction between carbonates and HNO₃ or NO_x, because NO₃⁻ can also exist as HNO₃. If we consider only terrestrial gypsum as a major contributor to terrestrial nssSO₄²⁻, $R_1 = 2.4$, 1.5, and 1.3 yield $R_2 = 0.24$, 0.52, and 0.59, respectively (Supplementary Fig. 6) for the LGM. The same R_1 values yield $R_2 = 0.24$, 0.56, and 0.60, respectively, for EDC core, and $R_2 = 0.24$, 0.56, and 0.60, respectively, for EDML core. Larger dust input at DF and



Fig. 4 Relationship between residual $nssSO_4^{2-}$ flux and $\delta^{18}O$ at Dome Fuji (DF). **a** Residual $nssSO_4^{2-}$ flux, considering only the terrestrial CaSO₄ contribution, plotted against $\delta^{18}O^{14,15}$. **b** Residual $nssSO_4^{2-}$ flux considering the contributions of CaSO₄, MgSO₄, Ca(NO₃)₂, and Mg(NO₃)₂ plotted against $\delta^{18}O^{14,15}$. Residual $nssSO_4^{2-}$ flux and $\delta^{18}O$ are averages over 1000 years. Before averaging, the $\delta^{18}O$ depths that differ from the ion data depths have been interpolated to match. Straight lines in **a** and **b** display results of linear regressions. Correlation coefficients (*r*) were calculated with sample size (*n*) = 681 and for significance level (*a*) = 0.05. **c** Normalized power spectra of residual $nssSO_4^{2-}$ flux and $\delta^{18}O$ at DF. The residual $nssSO_4^{2-}$ flux was calculated in the same manner as **b**. Power spectra were calculated with the Blackman-Tukey method (30% lag) using the Analyseries software package⁵⁵ (see Methods). To use the software, the raw data were resampled to a 200-yr interval using linear interpolation

EDML likely yields smaller R_2 values compared with EDC. R_2 values for the LGM might be underestimated for large R_1 values (~2.4) owing to contribution of marine biogenic sulphate. In any case, a contribution of terrestrial sulphate during glacials is likely much larger than previously assumed, consistent with that estimated from sulphur isotope mass balance¹¹. This leads to a conclusion that DMS-derived sulphate decreases in glacials, although the degree of decrease remains uncertain depending on glacial/interglacial changes in R_2 values.

Reduced DMS emissions in the AZ of the SO during glacials. Sulphate aerosol observations at EDC and coastal Antarctic sites display a clear seasonal pattern with a maximum in austral summer³⁷. High surface DMS concentrations and emission fluxes over the modern SO in austral summer have also been reported^{38,39}. The dominant source of biogenic sulphate in the Antarctic interior is thus most likely DMS emitted from the SO. The flux of marine biogenic sulphate deposited in the Antarctic interior would then be controlled by DMS emissions in the source regions, the location of these source regions (i.e., distance to Antarctic interior sites), DMS oxidation chemistry, and depositional processes. As glacial/interglacial changes in oxidation chemistry and deposition are likely to be small, the decreased biogenic sulphate flux during glacials would be caused by reduced DMS emissions and/or longer transport distances⁴⁰ (Supplementary Discussion). Transport distances depend strongly on the summer sea ice extent around Antarctica⁴⁰ (Supplementary Discussion), but only limited information is available for glacials. In the Indian Ocean sector, the summer sea ice extent at the LGM was only slightly greater than the present day⁴¹, whereas in the Atlantic Ocean sector, the sporadic occurrence of summer sea ice considerably farther north is indicated⁴¹ (Supplementary Discussion). Although data from other oceanic sectors are very sparse, Gersonde et al.⁴¹ speculate that the summer sea ice field around Antarctica changed from 4×10^6 km² (present day) to $5-6 \times 10^6 \text{ km}^2$ (LGM).

DF and EDC display similar residual nssSO₄²⁻ fluxes with glacial/interglacial ratios of 1/3 to 1/4 (Fig. 3). The LGM/ Holocene ratios (~1/3) at DF, EDC, and EDML are consistent with the MSA flux at Siple Dome (West Antarctica, Supplementary Fig. 1) where MSA can be used as a proxy for marine biogenic sulphur deposition because its post-depositional loss is minimal⁴². In other words, the four sites facing different sectors of the SO, which includes the Indian sector where summer sea ice extent increased only slightly at the LGM, display similar glacial/ interglacial ratios of biogenic sulphur species. The similar ratios would be mainly associated with glacial-interglacial changes in DMS emissions in the SO, and specifically the AZ because it is a major DMS source region for biogenic sulphate in the presentday Antarctic interior^{38,43} (Supplementary Discussion). The reduced biogenic sulphate fluxes at the LGM could be partly due to the increased transport distances. However, the LGM increase in the summer sea ice extent around Antarctica by 1.25 to 1.50 times⁴¹ would only slightly increase the transport distances to the Antarctic interior sites, which are affected by a mixture of air masses from different oceanic sectors 44,45 (Supplementary Discussion and Supplementary Fig. 7). Thus, lower biogenic nssSO₄²⁻ fluxes during glacials indicate reduced DMS emissions in the AZ, suggesting that primary production, as well as export production, decreases during glacials, which is consistent with marine sediment records⁴.

Discussion

Sea surface temperature (SST), solar radiation, sea ice extent, and nutrient and iron supply can affect DMS emissions^{1,43,46,47} in the

AZ. Power spectra of residual $nssSO_4^{2-}$ show strong powers in the 41-kyr and 93-kyr bands (Fig. 4c). Powers in similar bands (41-kyr and 98-kyr) are also observed in the δ^{18} O record, which is closely linked to SST and sea ice extent in the AZ. To our knowledge, the relationship between DMS emissions and SST has not been directly investigated. The growth rate of phytoplankton (unicellular algae), however, shows little dependence on SST near the melting point of sea ice⁴⁸, which is the major source of DMS^{46,49}. Hence, covariance of the residual $nssSO_4^{2-}$ flux and $\delta^{18}O$ record at DF (Figs. 3, 4, Supplementary Fig. 5) does not imply that decreased summer SST is a major cause of reduced DMS emissions. Although the integrated summer insolation at 55°S, the latitude of a major source region of DMS, shows strong spectral power in the 41-kyr band, variability in solar radiation could not be a major cause of the reduced DMS emissions during glacials because it is less than 3% (Supplementary Discussion). The large seasonal difference in sea ice extent during glacials implies large areas of melting sea ice in summer, which would lead to enhanced DMS emissions because melting sea ice is an important DMS source^{46,49}. However, this is not the case because DMS-derived sulphate decreases in glacials (Figs. 3, 4, Supplementary Fig. 5). Thus, the change in winter sea ice extent does not directly affect overall DMS emissions in the AZ on orbital timescales.

Vertical mixing and upwelling appear to dominate the nutrient and iron supply in Antarctic surface waters⁴. Expanded winter sea ice during glacials would enhance AZ stratification, weaken mixing and upwelling, and decrease the supply of nutrients and iron in winter⁴. This would decrease the nutrient/iron abundance and thus DMS emissions in summer. Reduced vertical mixing and upwelling during glacials should also reduce the CO₂ exchange between the ocean interior and atmosphere, thereby sequestering CO₂ into the ocean and leading to decreased atmospheric CO₂ concentrations, as is proposed by⁴. This study also implies that reduced DMS emissions during glacials may reduce cloud albedo, resulting in a negative feedback by biogenic sulphate aerosol-cloud interaction^{1,2}. Although an improved understanding of the precise mechanisms controlling nssSO₄²⁻ flux variations and their links to climate change is needed, the data provided here can be used to constrain the sulphur cycle and climate models. Ongoing analyses of sulphur isotopes of SO₄²⁻ $(\delta^{34}S)$ in DF core will reduce the estimation uncertainty of DMSderived sulphate, and enable more quantitative discussion on the interaction between DMS-derived sulphate and climate.

Methods

lon data. We use ion data from DF1 and DF2 cores after and before 300,000 BP, respectively¹⁴. Na⁺, Ca²⁺, Mg²⁺, NO₃⁻, and SO₄²⁻ were measured from both cores using ion chromatography. In addition, K⁺ was measured from DF2 core. For DF1 core, we use previously published data⁵⁰ after re-examination and removal of some data points because of large measurement errors. Fifty-nine samples were newly cut from DF1 core, re-measured, and the new data were added to the earlier dataset. Measurement errors were generally less than 10% but may be higher for low concentrations. For DF2 core, 10-cm-long samples were cut every 0.5 m and measured on two Dionex DX-500 ion chromatographs: one for anions and the other for cations. Measurement errors were estimated to be less than 3%. Sea salt (ss) Na⁺ and non-sea-salt (nss) Ca^{2+} concentrations were calculated from Na⁺ and Ca^{2+} concentration data using the weight ratios of Ca²⁺/Na⁺ for seawater (0.038) and average crust (1.78), as described in previous studies^{7-9,16,51}. The nssSO₄²⁻ concentrations were calculated assuming a sea ice source^{7,8} of ssNa⁺. Similar values are obtained if we assume an open ocean source^{7,8} of ssNa⁺. Fluxes of nssCa²⁺ and nssSO₄²⁻ were calculated by multiplying concentrations by estimated accumulation rates¹⁴.

Chronology and accumulation rate estimation. We use the DFO-2006⁵² timescale for the past ~342,000 years and the AICC2012⁵³ timescale for the period older than ~344,000 years¹⁴. The AICC2012^{53,54} chronology is used for EDC and EDML. The accumulation rates at DF were deduced from the δ^{18} O record by Dome Fuji Community members¹⁴, and those at EDC and EDML were taken from [53,54]. **Spectral analysis.** Spectral analyses were carried out with the Analyseries software package⁵⁵ (Fig. 4c). Blackman-Tukey spectra (30% lag) using a Bartlett window with a bandwidth of 0.00702905 are shown in Fig. 4c. The amplitudes of the spectra were normalized. The δ^{18} O and residual nssSO₄²⁻ data used for the spectral analysis were resampled at a 200-yr interval using linear interpolation. For resampling, δ^{18} O data from¹⁴ and residual nssSO₄²⁻ data provided in the Source Data file were used.

Data availability

The source data underlying Figs. 1–4 and Supplementary Figs. 2–7 are provided as a Source Data file. The data are also available in the Arctic and Antarctic Data Archive System at the National Institute of Polar Research [https://ads.nipr.ac.jp/dataset/A20190607-001].

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Author contributions

H.M. and Y.F. recovered the Dome Fuji cores. K.G.-A., M.H., T.M., T.K., R.U., K.S., Y.I, T. Suzuki, S. Horikawa, and K.F. processed the cores. M.H. and M.I. performed ion analyses. R.U. and H.M. obtained stable isotope data. T.K., M.H., and K.G.-A. were responsible for quality control of the ion data. K.G.-A. led the manuscript preparation. R.U., T. Suzuki, T. Sakurai, and K.F. contributed to the discussion on the ice core data. Y.K. contributed to the discussion on DMS and overall manuscript preparation. S. Hattori contributed to the discussion on sulphur isotopes.

Additional information

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Supplementary Information

Reduced marine phytoplankton sulphur emissions in the Southern Ocean

during the past seven glacials

K. Goto-Azuma et al.

Supplementary Figures



Supplementary Figure 1. Location of Dome Fuji (DF) in East Antarctica. The map is

modified after [1]. Additional deep ice core sites referred to in the text are marked.



Supplementary Figure 2. Variability in ion concentrations and accumulation rates at Dome Fuji (DF). a Na⁺, b Ca²⁺, and c SO4²⁻ concentrations (see Methods). d Accumulation rates together with δ^{18} O at DF¹. All ion and δ^{18} O data are averages over 1000 years.



Supplementary Figure 3. Variability in nssCa²⁺ and nssSO4²⁻ fluxes for the past 150,000 years at Dome Fuji (DF), Dome C (EDC), and Dronning Maud Land (EDML). a nssCa²⁺ at DF, EDC, and EDML, b nssSO4²⁻ at DF, EDC, and EDML, and c δ^{18} O at DF¹. See Methods for the DF chronology and flux calculations. The EDC and EDML fluxes are plotted on the AICC12 timescale^{2, 3} using previously published ion data⁴⁻⁷ and accumulation rates^{2,3}. All ion and δ^{18} O data are averages over 1000 years.



Supplementary Figure 4. Correlation between ion fluxes at Dome Fuji (DF). a $nssSO_4^{2^-}$ flux (black), NO_3^- flux (red), and $[NO_3^- + nssSO_4^{2^-}]$ flux (blue) plotted against $nssCa^{2+}$ flux. b $nssSO_4^{2^-}$ flux (black), NO_3^- flux (red), and $[NO_3^- + nssSO_4^{2^-}]$ flux (blue) plotted against $[nssCa^{2+} + nssMg^{2+}]$ flux. Black lines represent a stoichiometric ratio of 1. All data are averages over 1000 years. The strong correlation between $[NO_3^- + nssSO_4^{2^-}]$ flux and $[nssCa^{2+} + nssMg^{2+}]$ flux during cold periods supports the assumption that the majority of terrestrial CaCO₃, MgCO₃, and CaMg(CO₃)₂ are converted to Ca(NO₃)₂ and Mg(NO₃)₂ by HNO₃ or NO_x (see Supplementary Discussion).



Supplementary Figure 5. Different estimates of marine biogenic nssSO₄^{2–} flux (residual nssSO₄^{2–} flux) at Dome Fuji (DF). a Residual nssSO₄^{2–} flux considering (i) only terrestrial CaSO₄ contributions to nssSO₄^{2–} flux (red), and (ii) terrestrial CaSO₄ and MgSO₄ contributions along with Ca(NO₃)₂ and Mg(NO₃)₂ (blue). b δ^{18} O at DF¹. All ion and δ^{18} O data are averages over 1000 years.



Supplementary Figure 6. Marine biogenic/total nssSO₄²⁻ ratios at Dome Fuji (DF) for different estimations of marine biogenic sulphate. a Ratios (R_2) calculated based on different estimations. Marine biogenic sulphate was estimated considering (i) only terrestrial CaSO₄ contributions to the nssSO₄²⁻ flux with terrestrial nssSO₄²⁻/nssCa²⁺ ratio (R_1) = 2.4 (red), (ii) same as (i) but with R_1 = 1.5 (yellow), (iii) same as (i) but with R_1 = 1.3 (black), and (iv) terrestrial CaSO₄ and MgSO₄ contributions along with Ca(NO₃)₂ and Mg(NO₃)₂ (blue). **b** δ^{18} O¹. Ratios and δ^{18} O data are averages over 1000 years. Marine isotope stage numbers for interglacials are also shown.



Supplementary Figure 7. Comparison of ssNa⁺ fluxes at Dome Fuji (DF), Dome C (EDC), and Dronning Maud Land (EDML). a Flux of ssNa⁺ at DF and EDC over the past 720,000 years. b $\delta^{18}O^1$ at DF over the past 720,000 years. c Flux of nssNa⁺ at DF, EDC, and EDML over the past 150,000 years. d $\delta^{18}O^1$ at DF over the past 150,000 years. The EDC and EDML fluxes are plotted on the AICC12 timescale^{2,3} using previously published ion data^{4,5,7} and accumulation rates^{2,3}. All data are averages over 1000 years. The similarity between ssNa⁺ flux at DF and EDC suggests that both sites are affected by inland air masses, which are likely a mixture of air masses from different oceanic sectors^{8,9}.

Supplementary Discussion

Different estimations of residual nssSO42-

We examine the contributions of terrestrial cations other than Ca^{2+} . NssK⁺ and nssMg²⁺ could originate from sulfate-containing mineral dust. We calculate equivalent concentrations of nssK⁺ and nssMg²⁺ where [nssK⁺] = [K⁺] - 0.02 · [ssNa⁺], and [nssMg²⁺] = [Mg²⁺] - 0.11 · [ssNa⁺], using equivalent seawater ratios of K⁺/Na⁺ = 0.02 and Mg²⁺/Na⁺ = 0.11. We use [ion] for the equivalent concentration/flux of each ion. Much lower equivalent concentrations of nssK⁺ compared with nssCa²⁺ (less than 5% for most of DF2 core, not measured for DF1 core) suggest that contributions of K-containing minerals are much lower than those of CaSO₄. Equivalent concentrations of nssMg²⁺ are correlated with those of nssCa²⁺, with the former being about 35% of the latter. This suggests that during cold periods in glacials, a major part of nssMg²⁺ could also originate from evaporites in the form of MgSO₄ or CaMg(CO₃)₂, as deduced from the strong correlation between the Mg²⁺ and SO₄²⁻ fluxes. To remove terrestrial MgSO₄ contributions from the nssSO₄²⁺ flux, we should subtract the nssMg²⁺ only associated with nssSO₄²⁻.

It should be noted that South American dust source areas include CaCO₃-rich sources¹⁰, as well as gypsum-rich sources^{11,12}. Because CaCO₃ is not a major chemical form of Ca²⁺ in ice cores from Antarctic interior sites¹³, previous studies assume that CaCO₃ reacts with H₂SO₄ or SO₂ and forms CaSO₄^{14,15}. Ca²⁺, however, has also been reported to be associated with NO₃⁻ in the Antarctic interior during cold periods in glacials when dust concentrations increases¹⁶⁻¹⁸. Supplementary Fig. 4a displays a strong correlation between the NO₃⁻ flux and nssCa²⁺ flux at DF, which indicates the presence of Ca(NO₃)₂ at DF. Recent studies show that CaCO₃ reacts more readily with HNO₃ or NO_x than with SO₂ or H₂SO₄ and that the reaction with SO₂ or H₂SO₄ is very slow^{16,19-22}. We therefore deduce that primary continental gypsum is a major

contributor to the CaSO₄ flux and that secondary CaSO₄, formed by the reaction between CaCO₃ and H₂SO₄/SO₂, is only a minor contributor. Here, we assume that CaCO₃ completely reacts with HNO₃/NO_x and that CaSO₄ originates solely from continental gypsum. Similarly, some nssMg²⁺ would be associated with NO₃⁻ because MgCO₃ and CaMg(CO₃)₂, as well as CaCO₃, react readily with HNO₃/NO_x and form Mg(NO₃)₂¹⁹. A strong correlation between nssMg²⁺ flux and NO₃⁻ flux at DF provides evidence of this reaction. Using the following equation, we can better estimate residual nssSO₄²⁻ concentrations [nssSO₄²⁻]_{res}, a revised proxy for marine biogenic sulphate, because nssCa²⁺ and nssMg²⁺ are both associated with NO₃⁻.

$$[nssSO_4^{2^-}]_{res} = [nssSO_4^{2^-}] - ([nssCa^{2^+}] + [nssMg^{2^+}] - [NO_3^{-}])$$

Here we assume that the majority of terrestrial CaCO₃, MgCO₃, and CaMg(CO₃)₂ are converted to Ca(NO₃)₂ and Mg(NO₃)₂ by HNO₃/NO_x. This assumption is supported by a strong correlation between the [NO₃ + nssSO₄^{2–}] flux and [nssCa²⁺ + nssMg²⁺] flux at DF during cold periods with increased dust flux and by the slope (~1) of the lower bound of the scatter plot (Supplementary Fig. 4b).

Although residual nssSO₄²⁻ fluxes calculated with different assumptions give different r² values (Fig. 4), both decrease during cold periods in glacials. Interestingly, the first-order approximation, assuming that nssCa²⁺ is associated only with nssSO₄²⁻ and that nssSO₄²⁻ is associated only with nssCa²⁺ during cold periods in glacials, is similar to the estimation of residual nssSO₄²⁻ flux using the equation above. Although nssMg²⁺ and NO₃⁻ data are not available for EDC and EDML cores, it is expected that the calculation of residual nssSO₄²⁻ using only nssCa²⁺ and nssSO₄²⁻ would be fairly reasonable.

Causes of reduced biogenic sulphate flux during glacials

A tracer transport model using the DMS concentration data of [23] shows that in austral summer, more than 60% (80%) of the geographic origin of DMS leading to sulphate at Vostok (Supplementary Fig. 1), an East Antarctica interior site, is located south of 55° S (50° S)²⁴. Although the climatology of summer DMS concentrations has been recently revised, mean summer DMS concentrations in the SO are close to the original estimates^{23,25}. The Antarctic Polar Front, the northern edge of the AZ, lies roughly between 50° S and 60° S²⁶. These studies suggest that a major source region of DMS for the Antarctic interior is the AZ. A study of sulphur cycling at the LGM based on atmospheric general circulation and sulphur chemistry models indicates that biogenic sulphate flux on the Antarctic ice sheet is sensitive to both oceanic DMS concentration and spatial distribution²⁷. The latter strongly depends on the extent of summer sea ice²⁷. The model study also shows that the flux is almost proportional to oceanic DMS concentrations, provided that the summer sea ice extent does not change. The proportion of DMS oxidized to SO_4^{2-} or MSA can vary with time, but SO_4^{2-} likely remains the dominant product^{4,27}. Changes in atmospheric circulation and DMS oxidation chemistry have minor impacts on the model results. Depositional processes do not change substantially under different climate conditions because dry deposition remains the dominant process at the Antarctic interior sites discussed here.

The lid effect of sea ice could move the source region north during glacials as a result of sea ice expansion²⁷, which would lead to a larger transport distance and lower flux of DMS-derived sulphate. Sea ice reconstructions based on ocean sediment cores suggest that while the winter LGM sea ice extent is about two times greater than the present day, the LGM summer extent appears to be only slightly greater, except for the Weddell Sea area, where the occurrence of

sporadic sea ice is observed around the present-day winter sea ice edge²⁸. DMS-derived sulphur species in EDC, EDML, and Siple Dome ice cores have been traditionally assumed to be dominated by those from the nearby Indian, Atlantic, and Pacific Ocean sectors of the SO, respectively^{4-6,29}. Accordingly, DF should be mainly affected by the Atlantic and Indian Ocean sectors. The large difference in summer sea ice extent between the Atlantic and Indian Ocean sectors would lead to differences in the marine biogenic sulphate flux between DF and EDC. However, this is not the case. DF and EDC show rather similar fluxes and variations in the marine biogenic sulphate flux (Fig. 3a).

According to recent back-trajectory studies, the Antarctic interior sites (e.g. DF and EDC) are affected by inland air masses, which are likely a mixture of air masses from different oceanic sectors, as well as by air masses from the ocean sectors they face^{8,9}. Thus, the marine biogenic sulphate fluxes at DF and EDC reflect variations in the overall DMS emissions in the AZ. This result is supported by the similarity between ssNa⁺ fluxes at DF and EDC, which likely originates from the sea ice surface^{4,5,7,29} (Supplementary Fig. 7). Overall, the summer sea ice field around Antarctica at the LGM is estimated to be about 1.25 to 1.50 times that of today, although data remain sparse²⁸. This finding points to similar or only slightly more distant source areas for DMS during glacials compared to interglacials. Hence, the large glacial/interglacial variability in the marine biogenic sulphate flux at DF and EDC would be dominated by glacial/interglacial variability in DMS emissions in the AZ, rather than changes in transport distance.

EDML, a site close to the Weddell Sea where summer sea ice during glacials seems to have expanded much farther compared to other ocean sectors²⁸, shows higher biogenic sulphate fluxes than DF and EDC (Fig. 3c), as well as higher ssNa⁺ fluxes (Supplementary Fig. 7c). This can be

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explained by more efficient transport of marine air masses to EDML than to the sites located farther inland (DF and EDC)^{8,9}. Reduced marine biogenic sulphate flux at EDML during glacials could be a result of the longer transport distance from the summer sea ice edge. Reduced DMS emissions during glacials should also play a role considering the strong DMS emissions from leads and polynyas in the present-day summer sea ice zone²⁹. Although we cannot yet conclude which of the two causes is more important, the coherent variability in marine biogenic sulphate fluxes at EDML, DF, EDC, and Siple Dome suggests reduced DMS emissions in the Atlantic Ocean sector, as well as in other ocean sectors.

To evaluate the effect of solar irradiance on DMS emissions, we calculated the integrated summer insolation at 55°S, the latitude of a major source region of DMS²⁴. Since the modern daily insolation at the spring and autumnal equinox at 55°S is about 250 W/m² ³⁰, we integrated daily insolation >250 W/m² over the year³¹. We calculated power spectra with the Blackman-Tukey method (30% lag) using the Analyseries software package³². Although strong powers were found in the 41-kyr and 98-kyr bands, similar to those for δ^{18} O, the variability was less than 3%. Integrated summer insolations at 50°S, 60°S, 65°S, and 70°S give similar power spectra as 55°S. Variability of the integrated summer insolation from 50°S to 70°S was 3%–10%, depending on the latitude. This small variability would not be a major cause of the variability in DMS emissions³³.

Supplementary References

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