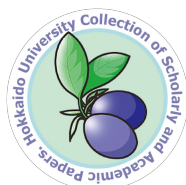




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Sulphate-climate coupling over the past 300,000 years in inland Antarctica

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Sulphate aerosols, particularly micron-sized particles of sulphate salt and sulphate-adhered dust, can act as cloud condensation nuclei (CCN), leading to increased solar scattering that cools Earth's climate¹⁻². Global climate, according to the "CLAW" hypothesis³, may be regulated by marine phytoplankton in a negative feedback loop composed of temperature, cloud albedo, and sulphate production. Evidence for such sulphate-climate coupling in the current era has not been found⁴, but may be revealed in the long-term sulphate record from polar ice cores. Melted ice-core samples have previously provided only sulphate-ion concentrations, which may be due to sulphuric acid⁵. Here we present profiles of sulphate-salt fluxes over the past 300,000 years from the Dome Fuji ice core in inland Antarctica. Results show a nearly constant flux of sulphate-adhered dust through glacial and interglacial periods despite large increases of dust flux during glacial maxima⁶. The sulphate-salt flux, however, correlates inversely with temperature, suggesting a climatic coupling between particulate sulphur and temperature. For example, the total sulphate-salt flux during the last glacial maximum averages $5.78 \text{ mg m}^{-2} \text{ yr}^{-1}$, twice that of the $2.93 \text{ mg m}^{-2} \text{ yr}^{-1}$ during the present Holocene. Although based on a model with serious uncertainties when applied to the ice core record, this analysis indicates that the glacial-to-interglacial decrease in sulphate would lessen the aerosol indirect effects on cloud albedo, leading to an Antarctic warming of 0.1 to 5.2 K. Our results provide further evidence against the CLAW hypothesis: although marine sulphur production does influence sulphate-salt flux during glacial maxima, SO_4^{2-}

remains constant when, according to CLAW, it should decline.

Climate of the last 430 kiloyear (kyr) is guided by large-amplitude 100-kyr glacial-interglacial cycles⁷. The glacial-interglacial cycles are triggered by the Earth's orbital changes, and then amplified by various land-atmospheric responses¹. Of these responses, the influence from aerosol radiative forcing¹ is particularly hard to accurately quantify. The low aerosol concentrations of the southern high-latitude region makes the direct effect of aerosol radiative forcing negligible, but the indirect effect, in which the aerosol acts as CCN, could be significant^{8,9}. Many CCN consist of sulphate salt, either by itself or mixed with silicate materials (Fig. S1)⁸, which can be preserved in the ice after precipitating to the ground.

Aerosols in the Antarctic region contain little anthropogenic and ammonium sulphates¹⁰, instead being dominated by sulphuric acid (H_2SO_4), sodium sulphate (Na_2SO_4), and calcium sulphate (CaSO_4)¹¹. The Na_2SO_4 arises mostly from the reaction of sodium chloride (NaCl) with H_2SO_4 that comes mainly from marine biological activity¹². The CaSO_4 arises from terrestrial gypsum and also from a reaction in aerosol between H_2SO_4 and calcium carbonate¹². These salts primarily form during their transport through the atmosphere¹³. Once in the ice, sulphate salts are good proxies for past atmospheric chemistry because, unlike the more mobile, volatile compounds such as HNO_3 (ref. 14) and liquid H_2SO_4 (ref. 10), they are largely unaffected by post-depositional processes.

Analyses^{5, 15} of the sulphate-ion (SO_4^{2-}) record in Antarctic ice cores show that almost all non-sea-salt sulphate ions in inland Antarctic ice cores come from marine biological activity¹⁵. However, because the ice samples were melted before measurement, those studies could not definitively separate the sulphuric-acid (H_2SO_4) flux from the sulphate-salt (Na_2SO_4 and CaSO_4) flux. Even less is known about how much of the sulphate salt mixed with silicate mineral dust. Here, we present a complete record of the sulphate salt and sulphate-adhered dust fluxes to inland Antarctica over the past 300 kyr.

To determine the sulphate-salt and sea-salt (NaCl) fluxes, we combined two methods: i) an ion-analysis method¹¹, here applied to the 300-kyr record in the Dome Fuji ice core, and ii) elemental and compositional analysis of single particles extracted from the same ice record, using a sublimation method^{13, 16}.

We found that particles (Fig. S2) in glacial inceptions and interglacial periods can be distinguished from those in glacial maxima by their values of $\text{Na}_2\text{SO}_4/\text{CaSO}_4$ and $\text{NaCl}/\text{Na}_2\text{SO}_4$. During glacial maxima, $\text{Na}_2\text{SO}_4/\text{CaSO}_4$ values are particularly low, whereas $\text{NaCl}/\text{Na}_2\text{SO}_4$ values are high (Fig. 1). With $r^2 = 0.76$ and a regression slope close to 1 (0.85 ± 0.17 in Fig. S3), the $\text{Na}_2\text{SO}_4/\text{CaSO}_4$ mass ratio correlates well to that from the ion chromatograph (IC) analyses. Since the ion-deduced CaSO_4 flux is well-confirmed from the relation between Ca^{2+} and particle components^{16, 17} in the Dome Fuji ice core, we can confidently use the ion-deduced Na_2SO_4 and CaSO_4 fluxes.

The regression slope of $\text{NaCl}/\text{Na}_2\text{SO}_4$ equals 0.84 (Fig. S3), which, considering the $\text{Na}_2\text{SO}_4/\text{CaSO}_4$ slope of 0.85, indicates that the IC method underestimated the NaCl flux by up to 29% ($1 - 0.85 \times 0.84$). This underestimate may be due to a poor understanding of mixed nitrate and chloride salt formation. Nevertheless, the high correlation ($r^2 = 0.73$) suggests that the NaCl variations during the 300-ka time-series can be reconstructed well.

The resulting IC-derived CaSO_4 and NaCl fluxes to the ground surface vary significantly over the past 300 kyr, both showing high values during glacial maxima (Fig. 2). The high CaSO_4 flux agrees with the high dust flux from South America during these stages^{6, 18}, which suggests that the higher dust flux increases Ca^{2+} sulphatization, and thus consumes more H_2SO_4 in the atmosphere¹⁹.

During interglacials, both the NaCl and the Na_2SO_4 fluxes are low, probably because the reaction between NaCl and H_2SO_4 to produce Na_2SO_4 was limited by the low NaCl flux^{10, 19}. Moreover, the $\text{NaCl}/\text{Na}_2\text{SO}_4$ ratio is low during interglacials and glacial inceptions, but high in glacial maxima (Fig. 1), a trend predicted by the NaCl– H_2SO_4 reaction¹⁹. A low ratio in interglacials and glacial inceptions indicates excess H_2SO_4 in the Antarctic atmosphere (Fig. 2), causing the sulphate-salt flux to be controlled mainly by sea-salt flux^{10, 11}. In contrast, a high ratio in glacial maxima indicates excess sea-salt flux¹¹, causing the sulphate-salt flux to be controlled mainly by H_2SO_4 flux. Consistent with this interpretation, we measured very little H_2SO_4 during

glacial maxima (Fig. 2), as nearly all SO_4^{2-} was associated with sulphate salt. In contrast, during interglacial periods and glacial inceptions, the H_2SO_4 contribution is relatively high, meaning that the SO_4^{2-} flux is not a good measure of the sulphate-salt flux during these periods.

We also estimated the flux of “sulphate-adhered dust”, which are particles with both Si and sulphate. Such particles likely act as cloud condensation nuclei (CCN)^{8, 20}, and thus influence climate. We refer to all particles containing Si as “total dust”, which are often measured in ice-core studies^{6, 18}. Since the total dust flux correlates to the non-sea-salt calcium-ion flux^{5, 6}, we examined the time variation of the ratio of sulphate-adhered dust to total dust versus the ratio of sulphate-salt flux to non-sea-salt calcium-ion flux (Fig. S4). These ratios correlate, both being high during glacial inceptions but low during glacial maxima. We use this correlation together with the measured total-dust flux from the melt samples to obtain the sulphate-adhered dust flux.

The sulphate-adhered dust flux averages $0.10 \text{ mg m}^{-2} \text{ yr}^{-1}$ through glacial and interglacial periods (Fig. 3a). This constant trend occurs despite the total dust flux increasing by a factor of 50 (up to $\sim 5 \text{ mg m}^{-2} \text{ yr}^{-1}$) between interglacials and glacial maxima. Because of the constant trend, no significant correlation occurs between temperature and sulphate-adhered dust flux, suggesting that the sulphate-adhered dust has little influence on the glacial and interglacial temperature changes via the indirect effect of CCN.

In contrast to the sulphate-adhered dust, the sulphate-salt flux (another measure of CCN) correlates inversely to $\delta^{18}\text{O}$, a temperature proxy (Fig. 3b). This correlation suggests a coupling between temperature and particulate sulphur (through Na_2SO_4 and CaSO_4). The higher sulphate-salt flux at lower temperature also contrasts with the SO_4^{2-} flux, which shows no clear correlation to temperature⁵. For the relatively warm interglacial periods, including the present Holocene, the evidence here suggests that Na_2SO_4 is generally controlled by the flux of sea salt from the ocean, which is relatively low. But in glacial maxima, the sea-salt and dust fluxes increase, leading to greater particulate sulphur flux. (The flux of sulphate salt exceeds that of SO_4^{2-} because the salt has a higher molar weight). During such cold periods, the amount of particulate sulphur is limited by the amount of SO_4^{2-} . This SO_4^{2-} comes from marine biogenic sulphur¹⁵, and thus marine biological activity influences the amount of sulphate salt.

The coupling shown here between temperature and sulphate-salt flux provides new evidence to examine the long-debated⁴ CLAW hypothesis³. In the CLAW hypothesis, marine biogenic sulphur provides a negative feedback to climate change. As such, the CLAW feedback requires both a controlling effect of this sulphur on CCN production and a response of the biogenic sulphur production to climate. Concerning the first requirement, a recent review⁴ shows that sulphur does not control CCN in the present interglacial period. Our evidence from the three most recent interglacials agrees with this view because our data indicates that sea salt rather than marine sulphur

controls particulate sulphate flux. On the other hand, during glacial maxima, the greater sulphate-salt flux is determined by the marine-sulphur flux, which agrees with the first requirement. However, the CLAW negative feedback requires that the greater sulphate-salt flux decreases marine sulphur emissions as a consequence of changes in cloud albedo and surface temperature, which is inconsistent with our finding that SO_4^{2-} flux does not decrease during glacial maxima (Fig. 3). Thus, the CLAW requirement appears to fail even during glacial maxima.

The correlation between temperature and sulphate salts suggests that the sulphate salts have an indirect aerosol effect on glacial-interglacial temperature changes. To obtain a rough estimate of the radiative forcing caused by the flux change of sulphate salt, we use recent radiative modelling results. To use the results, we i) note that the Holocene-to-LGM sulphate-concentration ratio roughly equals the corresponding ratio of the pre-industrial-to-present anthropogenic sulphate emissions^{21, 22} (see Fig. S5), and ii) assume that the sulphate-salt concentration changes globally. This assumption is consistent with the finding that the change of dust flux in Antarctica correlates strongly to global dust flux²³.

The resulting model gives a net radiative cooling in the LGM from the sulphate of -1.85 (ref. 24) and -2.57 (ref. 25) W/m^2 , producing a global climate cooling of 0.10 and 2.24 K. By applying the polar-amplification factor²⁶ (1.3–2.3), the resulting cooling in Antarctica ranges from 0.1 to 5.2 K just due to the indirect aerosol effect. The value

5.2 K is likely overestimated because other reports² suggest lower radiative cooling. Considering that the temperature change between the LGM and Holocene in Antarctica is $\sim 8\text{ }^{\circ}\text{C}$ ²⁶, our estimate highlights the large uncertainty in the climatic impact of indirect aerosol effects from sulphate salts. Thus, the role of sulphate salts and sulphate-adhered dust as the indirect effect should be quantified using paleoclimate models with our new aerosol data and other proxies (e.g., temperature, CO₂, CH₄, total dust) archived in the ice core.

Methods Summary

To determine the amount of sulphate, chloride, and mineral particles in the Dome Fuji ice core, we used our recently developed low-temperature sublimation and particle-analysis method^{13, 16} and compared the results to analysis¹¹ on ion chromatography (IC) data obtained earlier²⁷. The analysis of the IC data determines the salt fluxes of CaSO₄, Na₂SO₄ plus MgSO₄, and NaCl plus MgCl₂ from ion concentrations. Results from the two methods agreed well for CaSO₄ and the Na₂SO₄ plus MgSO₄ fluxes (Fig. S3).

The sublimation method removes volatiles such as H₂O, HCl, HNO₃, and H₂SO₄^{13, 16}. In all, we sublimated 38 sampled sections over the 300-kyr period and analysed them using scanning electron microscopy (SEM) / energy dispersive spectroscopy (EDS). Each sample yielded several hundred particles exceeding 0.4- μm

diameter (total: 16,821). To determine if the particles had a mineral, a sulphate, or a chloride component, we used a scheme from previous studies^{13, 16} that divides nonvolatile particles into insoluble and soluble components. We assumed that Na and S in a given particle came from Na₂SO₄, whereas Na and Cl came from NaCl, and Ca and S from CaSO₄. Then, we calculated the mass ratios of Na₂SO₄ to NaCl and of Na₂SO₄ to CaSO₄ following the method described in ref. 16. To obtain the number ratio of sulphate-adhered dust to total silicate dust particles, we assumed that a particle with both S and Si was sulphate-adhered dust and divided the number ($N(S \cap Si)$) by the total number of particles with Si ($N(Si)$). Supplementary Data file lists the uncertainties.

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Author Contributions

Y.I. ran the experiments and analyzed data on statistical methods. Y.I., R.U., T.S, H.M., and T.H. discussed the results and commented on the manuscript. T.M. and M.H. provided the dust and ion data. Y.I. and R.U. wrote the paper. Y.I., H.M., and T.H. supported financial resources.

Author Information

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Figure Legends

Figure 1 | Oxygen isotope and salt mass ratios of the past 300 kyr before present

(AD 2,000) in the Dome Fuji ice core. a, Oxygen isotope ratio of ice (expressed as $\delta^{18}\text{O}$ with VSMOW reference) from ref. 27 ($n = 691$, uncertainty below 0.1‰). Gray bars indicate glacial maxima (the Marine Isotope Stages of 2, 4, 6b, 6d, 6f, 8d). **b,** Salt mass ratio $\text{Na}_2\text{SO}_4/\text{CaSO}_4$ from the EDS method (single-particle analysis) on 38 filter samples (solid circles) and measured from ion concentrations (ref. 27) of 691 melt samples (line). Vertical error bars are uncertainties (i.e., coefficient of variation) in the EDS ratios. Numerical values are in Supplementary Data. Uncertainty in the ion-deduced ratios ranges from 36 to 49% for average glacial and interglacial conditions. **c,** Same as **b** except for the $\text{NaCl}/\text{Na}_2\text{SO}_4$ salt mass ratio. Uncertainty in the ion-deduced ratios ranges from 34 to 19% for average glacial and interglacial conditions.

Figure 2 | Sulphate ion and salts fluxes. a, Isotopic data as in panel **a** of Fig. 1. The Marine Isotope Stages 1–8e are indicated at top. Open boxes (1, 5e, 7e) are interglacials, arrows (5d, 7d) are glacial inceptions, and filled boxes (2, 4, 6b, 6d, 6f, 8d) are glacial maxima. **b,** NaCl flux from ion concentration measurements (ref. 27) after being verified by the single-particle (EDS) measurements. Uncertainty of the NaCl flux is 17% for average glacial conditions and 10% for interglacial conditions. **c,** Cumulative salt fluxes from ion concentration measurements (ref. 27) after being verified by EDS measurements. Na_2SO_4 is blue and CaSO_4 orange. The Na_2SO_4 flux

uncertainty ranges from 17 to 10% for average glacial and interglacial conditions; the corresponding values for CaSO_4 range from 19 to 39%. **d**, The sulphate-ion (SO_4^{2-}) flux (from ref. 27). Uncertainty in the SO_4^{2-} flux ranges from 17 to 5.7% for average glacial and interglacial conditions. **e**, Fractional contribution of sulphuric acid (H_2SO_4) and sulphate salt (Na_2SO_4 plus CaSO_4) to the total sulphur flux.

Figure 3 | Correlations of relevant fluxes to the temperature proxy $\delta^{18}\text{O}$. **a**, Sulphate-adhered and total dust fluxes (from ref. 28). The uncertainty of the sulphate-adhered dust flux ranges from 31 to 58% for average glacial and interglacial conditions; the corresponding values for the total dust flux are 17 to 14%. **b**, Sulphate-ion and sulphate-salt fluxes. The linear fitting line for the salt is $F_{\text{SALT}} = -0.44 \delta^{18}\text{O} - 20.9$ with $r^2 = 0.42$ ($n = 691$). The correlation is significant with a P value below 0.001. (For the ion, a linear fit gives an R^2 of only 0.005). Uncertainty of the sulphate-ion flux ranges from 17 to 5.7% for average glacial and interglacial conditions; for the sulphate-salt flux, the range is 17 to 12%.

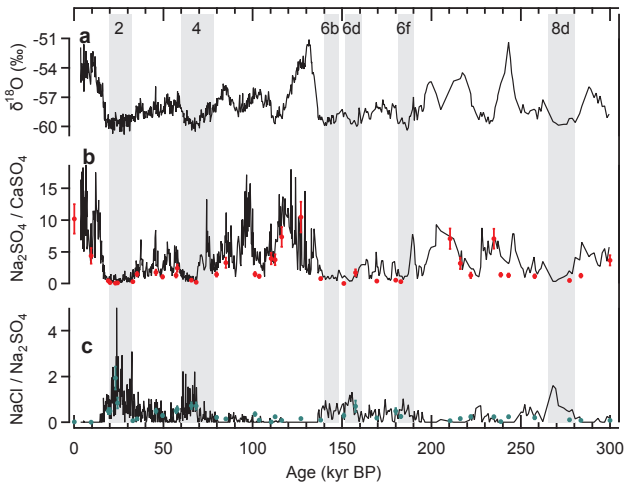


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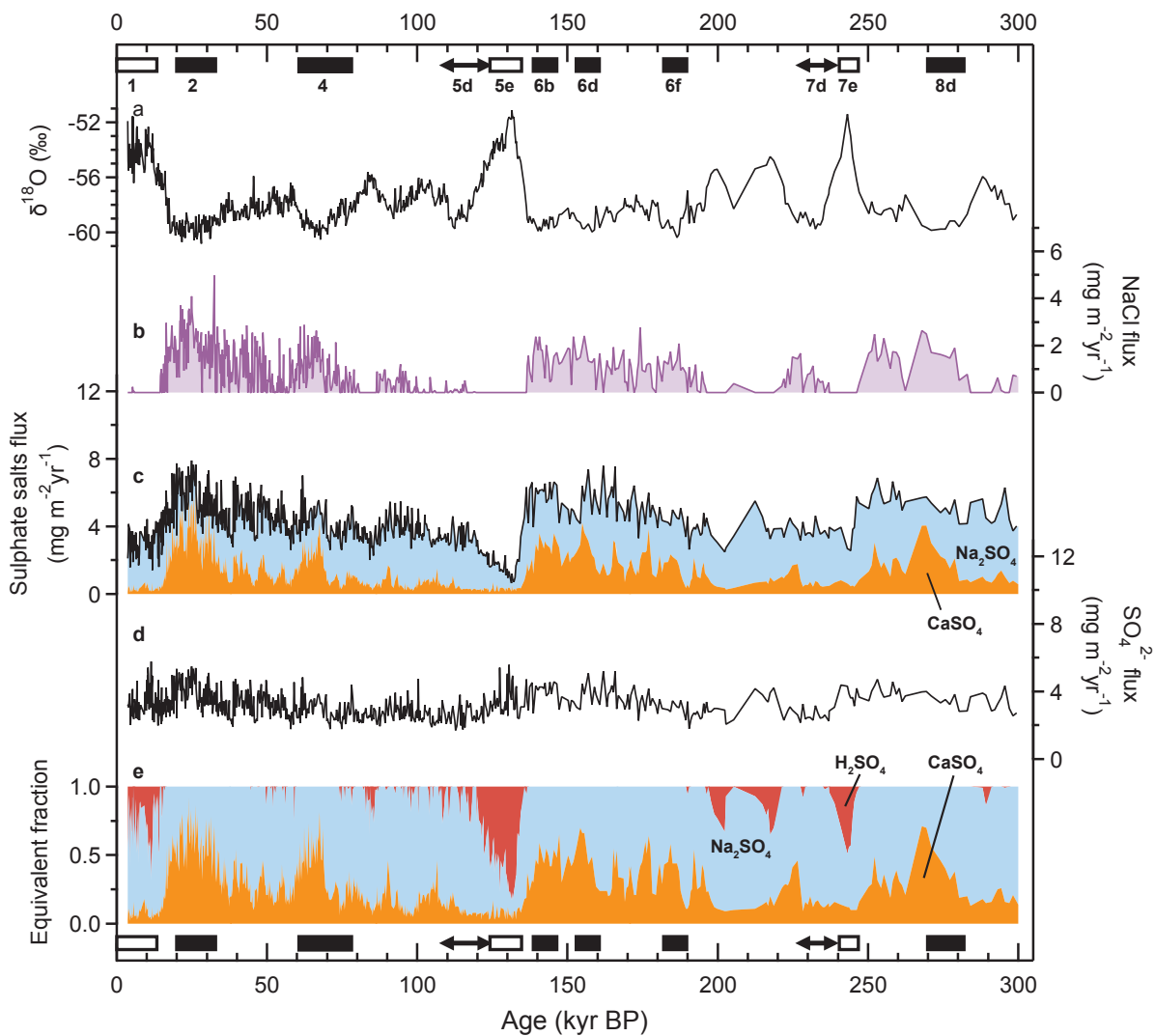


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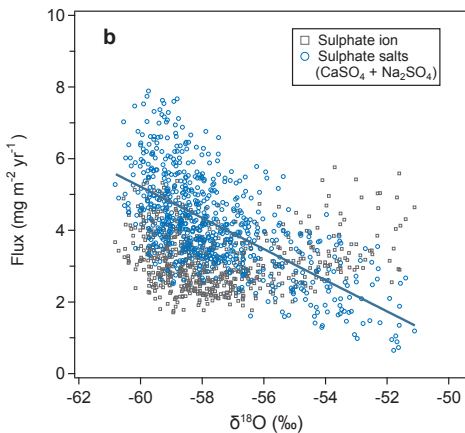
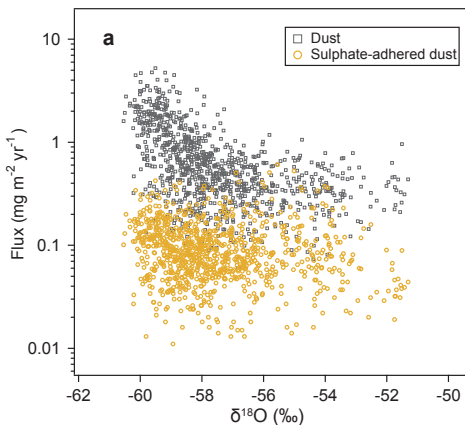


Fig. 3, Nature manuscript 2012-01-01306C