



HOKKAIDO UNIVERSITY

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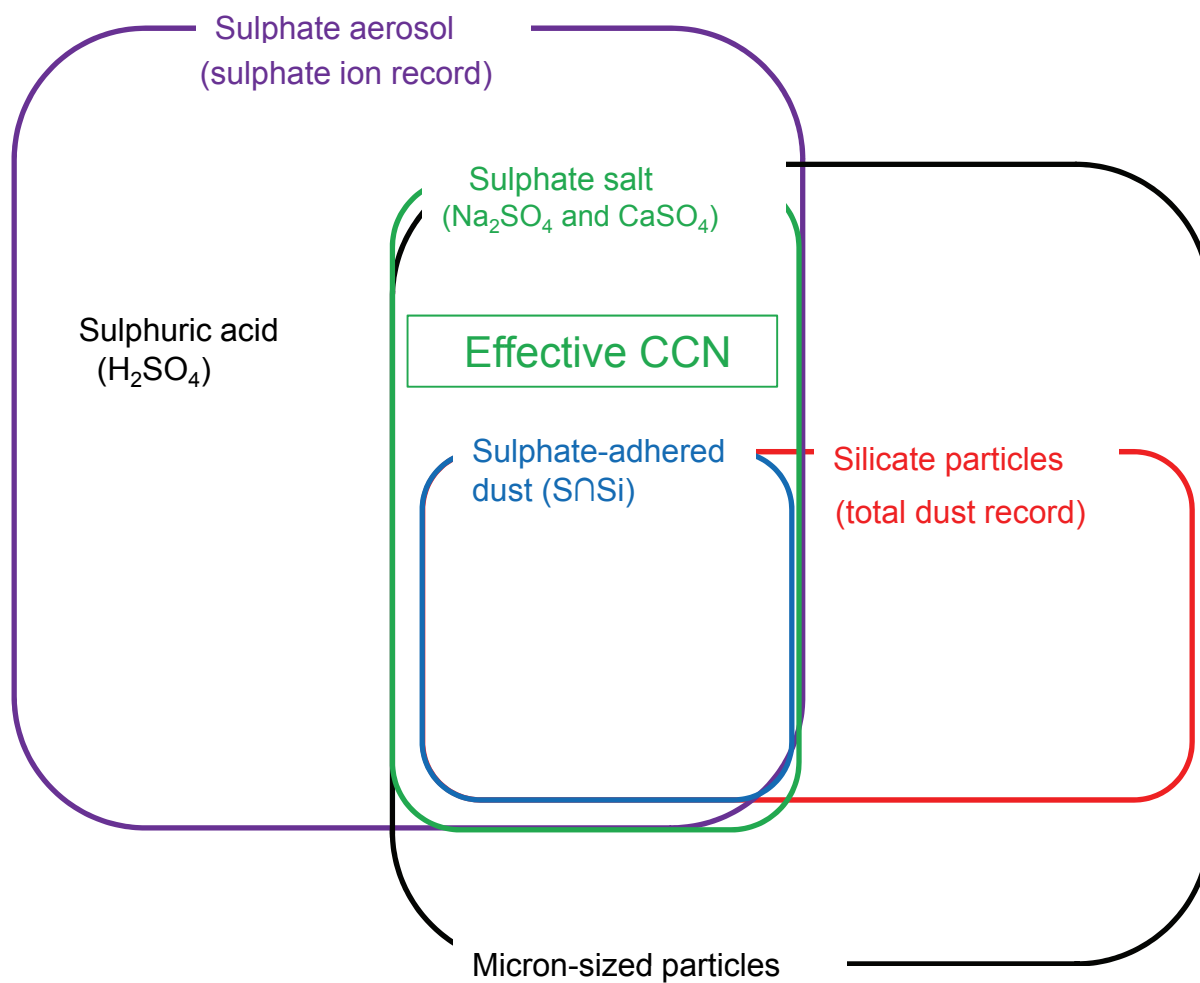


Figure S1 | Relation of cloud condensation nuclei (CCN) to compounds and particles detected in ice cores.

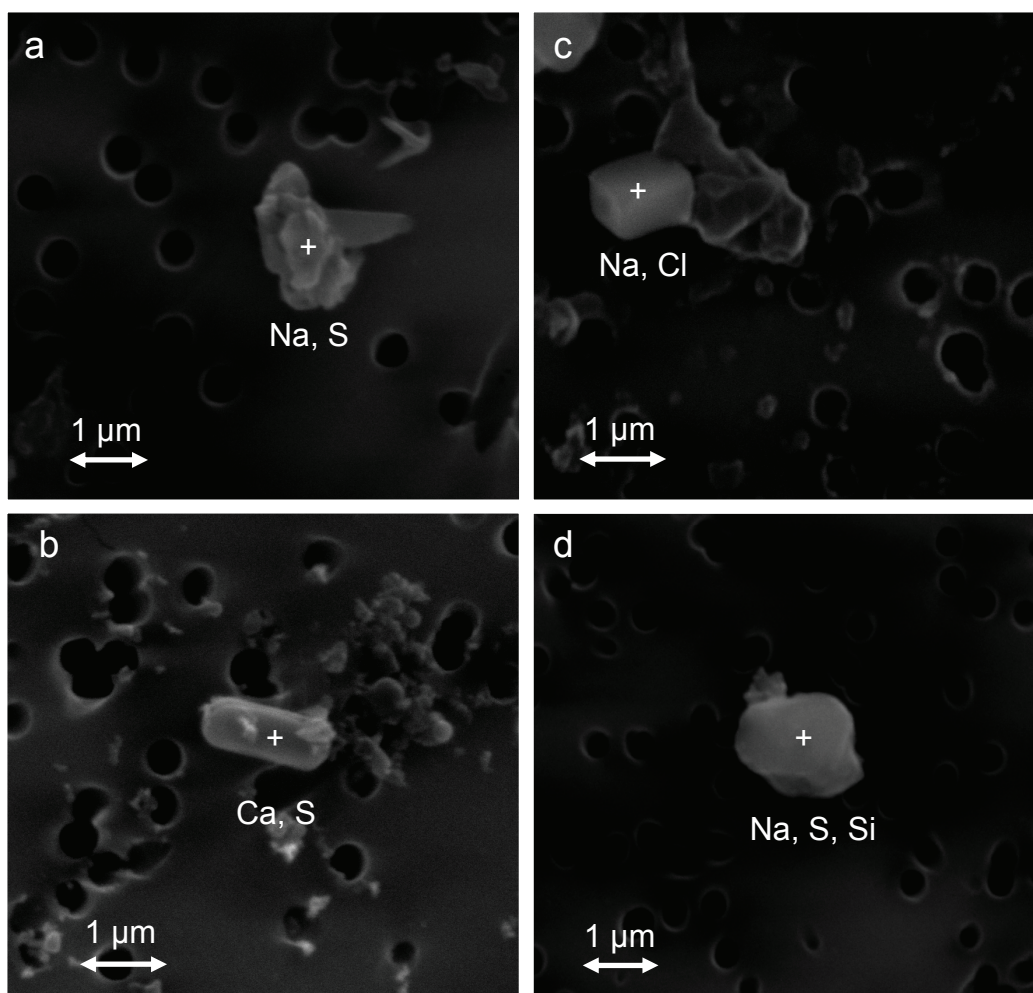


Figure S2 | Electron photomicrographs of typical particles in the filter samples. **a**, Sodium sulphate from the 1573.5 m section. **b**, Calcium sulphate from 2410.0 m. **c**, Sodium chloride from 2150.1 m. **d**, Sulphate-adhered dust particles from 1573.5 m. The filter is 13 mm in diameter, made from polycarbonate, with a pore size of 0.4 μm (ADVANTEC, K040A013A). All filters were coated by platinum for 30 s with a thickness of 10 nm using magnetron sputtering (VACUUM DEVICE, MSP-10). The images were taken with the following settings; scanning time : 80 s; space resolution: 1280 x 960 pixels; spot size: 45.

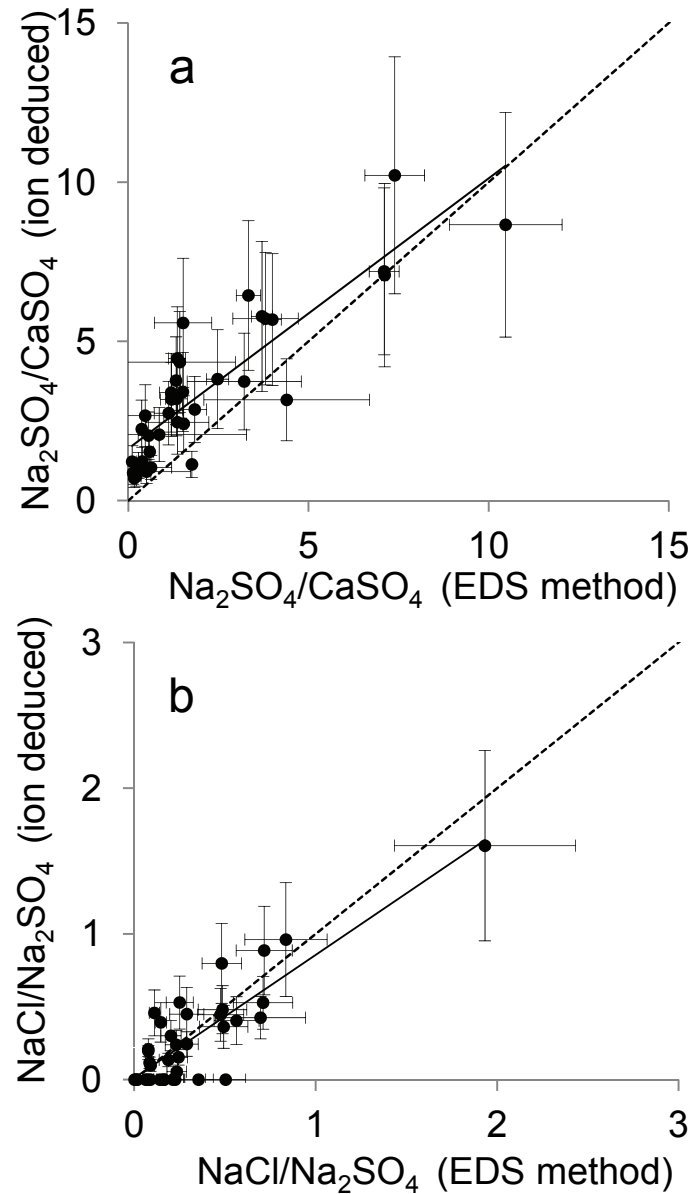


Figure S3 | Test of the ion-method for deducing salt ratios by comparison to the EDS method. **a**, Mass ratios Na_2SO_4 to CaSO_4 calculated from single-particle analysis (EDS method) on 37 filter samples (not 38 because one EDS datum has no corresponding ion measurement at the same depth), and deduced from either the ion concentration of the nearest age or from the average ion concentration of the ages immediately before and after (values in Supplementary Data). The linear fitting line is $\text{Ratio}_{(\text{ion})} = 0.85 \text{ Ratio}_{(\text{EDS})} + 1.63$ with $r^2 = 0.76$. The correlation's P value is below 0.001. The dotted line marks 1:1 relation. **b**, The same as (a) except for NaCl to Na_2SO_4 . The solid line is the linear fitting line $\text{Ratio}_{(\text{ion})} = 0.84 \text{ Ratio}_{(\text{EDS})} + 0.01$ with $r^2 = 0.73$. The P value is below 0.001. The vertical error bars are the coefficient of variation in ion-deduced salt fluxes. The horizontal error bars are the coefficient of variation in EDS mass ratios (values in the Supplementary Data).

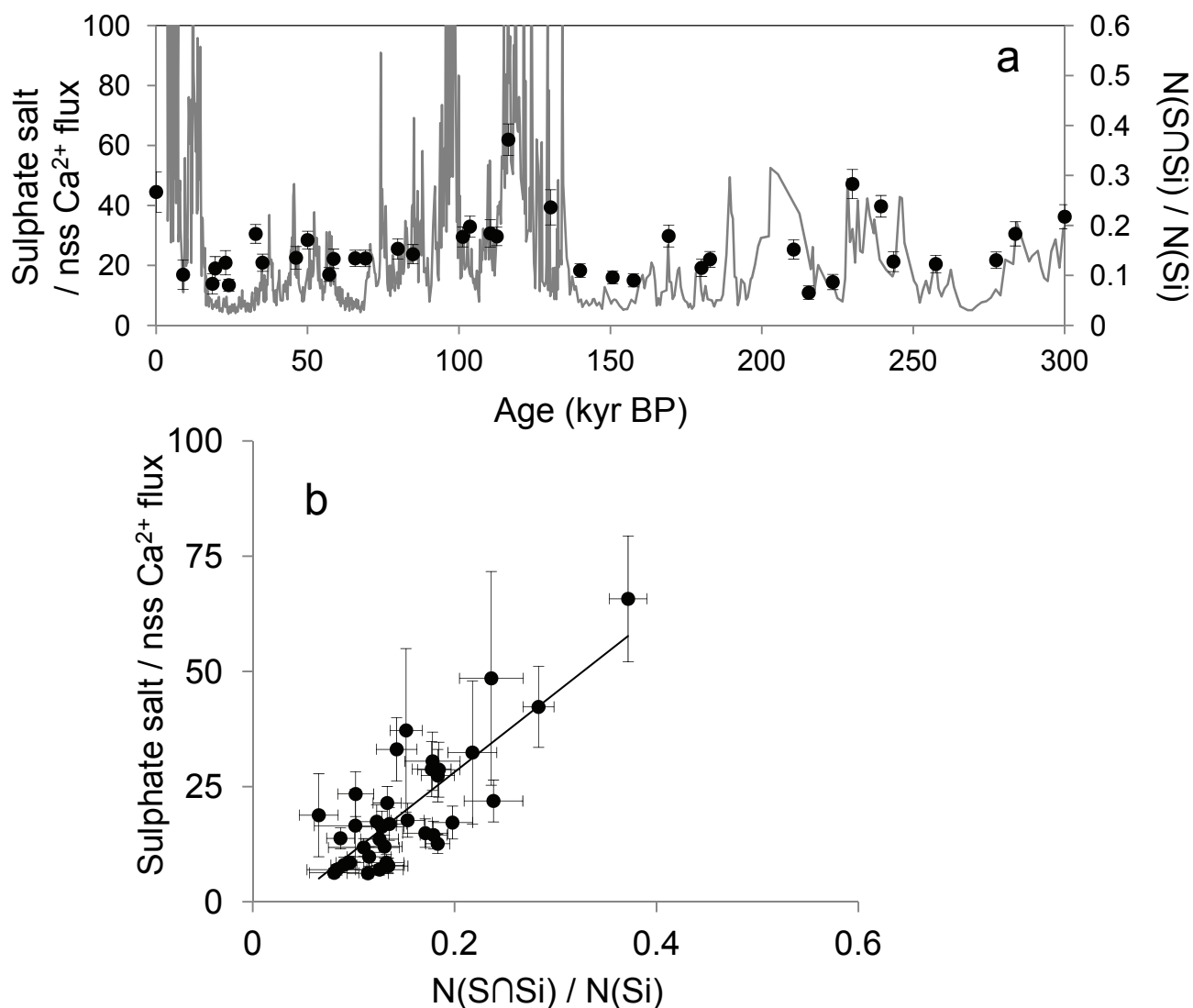


Figure S4 | Correlation between the number ratio of sulphate-adhered dust particles to the flux ratio of total sulphate salts to non-sea-salt calcium ion (nss-Ca²⁺). **a**, The number ratios of sulphate-adhered dust $N(S \cap Si)/N(Si)$ ($n = 38$) and the flux ratio of sulphate salt (Na_2SO_4 and $CaSO_4$) to nss-Ca²⁺ deduced from ion measurements (ref. 27) ($n = 691$) over the past 300 kyr in the Dome Fuji ice core. The coefficient of variation in the mass ratios are shown as the vertical error bars (values in Supplementary Data). **b**, Correlation between the number ratios of plot a above. The linear fitting line is $Ratio_{(flux)} = 172 Ratio_{(number)} - 6.17$ with $r^2 = 0.64$ ($n = 37$; $P < 0.001$). The vertical error bars are uncertainties in ion-deduced salt fluxes, which range from 25 to 51% for average glacial and interglacial conditions, respectively. The horizontal error bars are the coefficient of variation in the number ratio (values in the Supplementary Data).

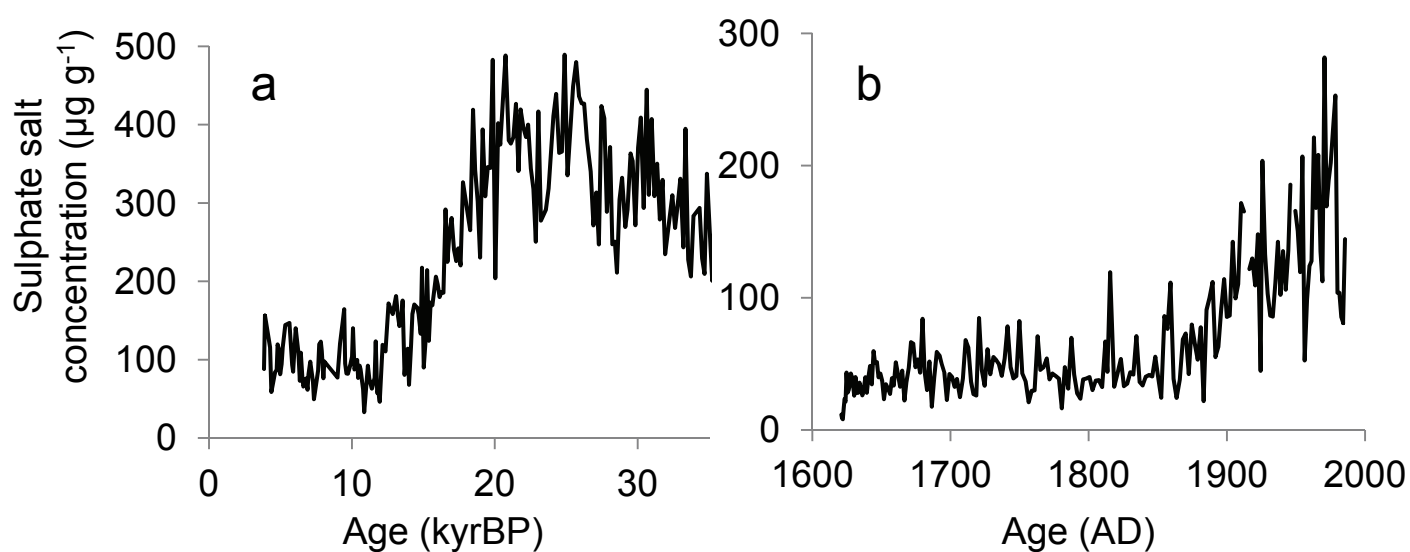


Figure S5 | Comparison of sulphate-salt trends between this study and a recent period in Greenland. **a**, This study, for the period between the last glacial maximum (LGM) to the Holocene. **b**, From the Site J firn core in Greenland from pre-industrial times to the present. The sulphate salts of the firn core data are calculated from ion concentrations provided from Y. Fujii ²² by the same method ⁹ used in this paper. The uncertainties in the salt fluxes are less than 17%.

Supplementary Methods

Measurement of particles by the SEM-EDS

The Dome Fuji (DF) ice cores used here were drilled in 1995–1997^{27, 28} and preserved below -50 °C at the Institute of Low Temperature Science, Hokkaido University. The DFO2006 timescale²⁹ is used for dating the ice cores. Our analyses used new data from analysis of 16,821 micron-sized particles plus previous data collected from the same core. For the particle analysis, we pulverized a 1-g ice sample and sublimated the ice on a polycarbonate filter at -45 °C using clean, dry air. (Refs. 11 and 14 have further details.) The sublimation removes volatiles such as H₂O, HCl, HNO₃, and H₂SO₄. We sublimated 38 filter sample sections over the 300-kyr period and analysed them using scanning electron microscopy/energy dispersive spectroscopy (SEM-EDS: JSM-6360LV (JEOL) SEM & JED2201 (JEOL) EDS). Each filter yielded several hundred particles exceeding 0.4-μm diameter (total: 16,821) whose constituent elements were determined by SEM-EDS at 20 keV (Supplementary Data). The elements detected were O, Si, Al, S, Cl, Na, Mg, and Ca.

Determination of sulphate, chloride, and mineral components

To determine the sulphate, chloride, and mineral components, we used the scheme in ref. 14 for identifying the non-volatile particles and separating the nonvolatiles into soluble and insoluble components. For calculating the mass ratio of

soluble components, we used the method in ref. 11. Particles containing Si were assumed to have silicate material. As such, silicate material was in 88% of the particles in glacial maxima, compared to only about 52% in interglacials. If a particle contained S or Cl, but its soluble component had neither (nearly all soluble components), then we assumed that the particle had contained a soluble S or Cl compound. As the sublimation removed the HCl and H₂SO₄, then the S and Cl in nonvolatile particles were assumed to be from sulphate and chloride salts. After considering the possible remaining compounds, we could assume that Na and S in a given particle came from Na₂SO₄, whereas Na and Cl came from NaCl, and Ca and S from CaSO₄.

Calculation of mass ratios

We calculated the mass ratios of Na₂SO₄ to NaCl and of Na₂SO₄ to CaSO₄ following the method described in ref. 11. To determine the mass of NaCl (m_{NaCl}), we used our measure of m_{Na} and m_{Cl} to determine the number of ions N of each component. Then we assumed that the number of NaCl molecules equalled the minimum of N_{Na} and N_{Cl} . We followed the same method for the other salts; for Na₂SO₄, we used the minimum of N_{S} and $1/2 N_{\text{Na}}$; for CaSO₄, we used the minimum of N_{S} and N_{Ca} . Although it seldom occurred, if we found Na, Ca, and S in a single particle, we first determined the number N_{S} for CaSO₄, and then the number for Na₂SO₄ as the residual N_{S} . Similarly, if we found Na, Cl, and S in a single particle, we first determined the number N_{Na} for

Na_2SO_4 , and then the number for NaCl as the residual N_{Na} (ref. 11). We similarly calculated m_{MgSO_4} and m_{MgCl_2} , but found them to be an order of magnitude lower than those of the two sodium salts. To compare with mass ratios from the IC analyses, we included m_{MgSO_4} with $m_{\text{Na}_2\text{SO}_4}$ and m_{MgCl_2} with m_{NaCl} . For the H_2SO_4 concentration in equivalent per liter, we subtracted the sulphate-salt concentration (Na_2SO_4 and CaSO_4) from the SO_4^{2-} concentration.

Uncertainty of mass ratios

The calculated uncertainty of the single-particle mass ratios follows the method described in ref. 11. Also, the calculated uncertainty from using the spherical approximation averages 0.05 over all particles, with 95% of the particles having uncertainty below 0.20. For the ratio of Na_2SO_4 to NaCl, the average value of CV_{ratio} over all depths is 0.260, and the standard deviation of CV_{ratio} over all depths is 0.050. (We summarize the CV_{ratio} for each filter in Supplementary Data.) The same procedure was followed for the ratio of Na_2SO_4 to CaSO_4 with the corresponding result being 0.223 with a standard deviation of 0.023.

Uncertainty of sulphate-salt flux

The ion and salt fluxes F ($\text{mg m}^{-2} \text{yr}^{-1}$) were calculated from $F = \rho CA$, where ρ is the ice density (917 kg m^{-3}), C is the measured concentration ($\mu\text{g g}^{-1}$), and A is the ice

accumulation rate³⁰ (m yr^{-1}) as deduced from the ice $\delta^{18}\text{O}$ record²⁷. Uncertainty of the reconstructed accumulation rates is 17% for glacial times and 5.3% for interglacial³⁰. Uncertainties of the ion concentrations were estimated from blank data³¹ as follows. The average blank contribution for the DF ion flux ranges from 5 to 38% of the Ca^{2+} concentration for the average glacial and interglacial conditions, respectively. Comparing to the Ca^{2+} concentration, the corresponding values for Na^{+} range from 2.8 to 7.4%; for SO_4^{2-} , from 1.3 to 2.1%; and for Cl^{-} , from 0.5 to 1.8%. Considering error propagation in flux and ion concentrations, the uncertainties of ion-deduced fluxes range from 19 to 39% of the CaSO_4 concentration. For both Na_2SO_4 and NaCl , the values are 17 and 10%. Ultimately, the uncertainty in total sulphate-salt flux (CaSO_4 plus Na_2SO_4) ranges from 17 to 12% for average glacial and interglacial conditions. Due to the $\text{Na}_2\text{SO}_4/\text{CaSO}_4$ slope of 0.85 (Fig. S3), our ion-deduced methods may underestimate the Na_2SO_4 salt fluxes by 15%. However, such systematic underestimate does not change the Holocene/LGM ratio of sulfate-salt, which is the only quantitative values we used to calculate radiative forcing impact.

Calculation and uncertainty of sulphate-adhered dust flux

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 ($N(\text{S} \cap \text{Si})$) by the total number of particles with Si. (Here, $N(\text{Si})$

equals the insoluble particle number.) These number ratios range from 0 to 1. The minimum relative uncertainty on any calculation using particle number should be less than $N^{1/2}/N$, assuming a Poisson distribution as described in ref. 14. Over all depths, the average uncertainty was 0.142 for $N(S \cap Si)/N(Si)$. Supplementary Data file lists the uncertainty for $N(S \cap Si)/N(Si)$ in each filter. To calculate the sulphate-adhered dust flux, we first used the above formula to calculate the number ratio using the correlation in Fig. S4 and then converted the result to the sulphate-adhered dust flux from total dust flux (i.e., by multiplying the amount by the ratio of the sulphate-salt flux to the $nss-Ca^{2+}$ flux).

$\delta^{18}O$ of ice

A recent report³² found a systematic offset of 0.24‰ in $\delta^{18}O$ between DF1 and the new DF core (Dome Fuji 2nd). For consistency with the latest data, the $\delta^{18}O$ of the 1st DF core used in this study was corrected by the above offset.

Equipment and settings

All raw data used in figures are in the Supplementary Data. Figures were created as vector images by using Illustrator CS3 and Igor Pro 6.22J.

Supplementary References

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