Supplementary Discussion

Concentrations and fluxes

For aerosol species that are stable (non-volatile) once deposited to snowpack, the deposition flux of a chemical is the sum of the wet deposition (deposited with snowfall) and the dry deposition (deposited continually to the surface). In the simplest formulation, both are proportional to the concentration of the chemical in the air. The flux, J, is given by:

$$J = v_d \bullet C_{air} + K \bullet P \bullet C_{air}$$

where C_{air} is the concentration of the chemical in air, P is the snow precipitation rate, v_d and K are constants of proportionality (v_d is known as the dry deposition velocity, and K is related to a mass-based scavenging ratio). The first term is the dry deposited flux and the second term is the wet deposited flux. The concentration in ice, C_{ice} is simply the flux divided by the average precipitation rate for the period represented by the ice sample, thus:

$$C_{ice} = v_d \bullet C_{air} / P + K \bullet C_{air}$$

where C_{air} is now a time-averaged value.

It is thus immediately obvious that, if the precipitation rate is low, the first term (dry deposition) in each equation dominates, and it is the flux that is directly proportional to the concentration in air (assuming v_d remains constant). If the precipitation rate is high, then the second term (wet deposition) dominates, and it is the concentration in ice that is directly proportional to the concentration in air (assuming K remains constant). There has been much debate in the ice core chemical literature about whether to use concentrations or fluxes in different situations, and about what precipitation rate is low enough that dry deposition dominates.

This can be tested by comparing the flux in individual years in a single core, or by comparing the flux at different sites that are believed to have similar atmospheric concentrations but that have different precipitation rates. Such tests show that wet deposition remains the dominant mechanism at snow accumulation rates of 100 kg m^{-2}yr^{-1}or more[1], but that dry deposition is the dominant mechanism at rates of 30 kg m^{-2}yr^{-1}or less[2]. Using spatial variations in ice core chemistry data from Dronning Maud Land in the Atlantic sector of Antarctica, it was estimated that 75% of the sulfate flux is dry deposited[3] at sites with double the snow accumulation rate of Dome C. For Dome C itself, it has been estimated that, in the present-day, 60% of sea salt and 80% of nssSO$_4^{2-}$ was dry deposited[2]; at the lower snow accumulation rates of colder periods, these percentages will increase. This implies that the flux is the better analogue for atmospheric concentration at Dome C, although its use could induce an error in the change in concentration between glacial and interglacial of 10-20%.

For completeness, we present in Supplementary Fig. 1 the concentration of selected chemical species on a time scale; this is the concentration equivalent of Fig. 2 from the main paper.

Sea salt and sea ice

As indicated in the main text, there are two principal interpretations of sea salt in ice cores. In the classic interpretation, the source of sea salt to ice cores is bubble bursting from open water. Since water within the sea ice zone is generally rather calm and limited, it must be assumed that the source is beyond the ice edge. One control on the concentration reaching Antarctica should be the distance it has to travel, since it is well-known that the concentration of sea salt over continents falls off rapidly with distance from the coast[4-6]. If this was the main control on sea salt concentrations, then concentrations would be lowest in winter, and lower in glacials than in interglacials.

Since the opposite is the case, it has been instead postulated that higher wind speeds, either at the source (more salt mobilised), or on the transport route (more efficient transport), combined with less efficient scavenging due to lower precipitation rates, compensate for the greater distances. If that is the case, then sea salt is a proxy for storminess over the Southern Ocean and/or the strength of higher-level transporting winds. However, modelling studies[7] contradict this interpretation: based on an open water source, sea salt concentrations in Antarctica would be much lower in the last glacial maximum (LGM) than the present.

In the more recent interpretation[8], the sea ice surface is the main source of sea salt to Antarctica. Sea ice surfaces can be very salty, and frequently has an interesting chemical composition, with a very low SO_4^{2-}/Na ratio compared to that of sea water, because mirabilite ($Na_2SO_4.10H_2O$) precipitates out of brines at low temperatures. Frost flower crystals are one manifestation of these salty surfaces (common on new ice) but a brine slush, or a brine-soaked snowpack are also possible. There is now strong evidence, based on low SO_4^{2-}/Na ratios in aerosol and snow, as well as combined satellite and back trajectory work, that sea ice surfaces are the main contributor to sea salt at many coastal Antarctic sites. The new evidence of low SO_4^{2-}/Na ratios at an inland site[9] is the first direct evidence for their importance at sites such as Dome C, adding to other circumstantial evidence. Although mirabilite should precipitate from sea salt aerosol at cold temperatures also, this does not lead to fractionation unless the solid and liquid parts of the aerosol droplet can be separated. In laboratory experiments, such a separation was not observed[10]. Until another plausible mechanism for fractionation is found, it is reasonable to interpret them as evidence for sea ice surfaces as the source of sea salt throughout the continent.

If this is the case, then it becomes important to consider what a change in sea salt concentration in an ice core implies about sea ice. It is new sea ice production that leads

to a brine surface on top of the ice. On the assumption that the sea ice source is dominant, we now consider two possibilities about what controls sea salt in ice cores.

If we firstly assume that all new sea ice surfaces contribute to the sea salt source, then the annual source is proportional to the amount of new ice production. This should be equivalent to the seasonality of the ice area: the difference between the winter maximum and the summer minimum. In most regions of Antarctica in the present-day, and in the Indian Ocean sector in the LGM[11], the summer ice extent is very small, so that the seasonality is equal to the extent. This will not be the case for regions with a significant residual summer ice extent. Although additional ice production will lead to additional salt aerosol production, the amount reaching the continent will be modulated by a number of factors. The location of production is the first variable. Much production takes place in shore leads and polynyas relatively close to the continent. We have no reason to expect that to alter, but clearly additional production further from the continent will lead to non-linearities in the relationship between production and sea salt concentrations inland. Changes in meteorology over the sea ice zone would affect the ability of salt to be mobilised and transported inland. We cannot yet estimate the effect of this: experimental flux studies, and modelling studies in which the source is parameterised more realistically, are needed. However, the modelling studies done so far imply that transport at least is not decisive.

A second possibility is that only frost flower surfaces really contribute sea salt aerosol, because the salt on other surfaces cannot easily be mobilised into the atmosphere. Based on laboratory experiments on frost flower growth[12], an algorithm for estimating the surface coverage of frost flowers was recently proposed[13]. Essentially, the areal coverage depends on the area of open water within the sea ice zone, and the air temperature. A larger sea ice zone implies a larger area of open water within it, although this may be less relevant if much of the production takes place close

to the continent. Colder temperatures lead to faster frost flower growth, and to greater areal coverage. Of course the colder temperatures within the sea ice zone also lead to more sea ice production. If sea salt in Antarctic ice is controlled by frost flower areal coverage alone (and with all the caveats about transport in the previous paragraph), then the sea salt concentration is probably mainly a function of temperature in the sea ice zone, which in turn controls sea ice production. The argument is less direct, but leads to the same conclusion: that sea salt in Antarctic ice cores is an indicator of sea ice production and, if summer extent is low, an indicator of winter extent.

In either case, there is not yet a parameterisation or model simulation that would allow us to quantify the relationship between sea ice production or extent and sea salt concentrations in ice cores. Instead we can try to calibrate the ice core signal from other information[11]. The likely non-linearity of the relationship implies that we must seek further calibration points in the future.

Finally, we accept that the dominance of the sea ice source is not yet fully proven, and its consequences not fully explored. Although our interpretation is plausible, it will remain tentative for some time to come. In addition, although we expect sea ice to be the main control on ssNa on the millennial timescales shown here, changes in transport from year-to-year are likely to dominate variability on annual and even decadal timescales[14,15].

Sea level and exposure of the Argentine continental shelf

If the Argentine continental shelf does play a role as a source of dust to Antarctica, then the exposed area is more relevant than sea level itself. Relative sea level (RSL) on the Argentine continental shelf at the LGM is estimated to have been at about 150 m (eustatic and hydroisostatic components plus a small correction for tectonic uplift) below present sea level[16]. This corresponds to a eustatic level of about −110 m. Using

gridded bathymetric data[17] (Supplementary Fig. 2), we find that over 50% of the shelf

area south of 45ºS becomes flooded between an RSL of -150 and -100 m, and 70% is

flooded by the time RSL reaches –80 m. On the Argentine Shelf, the RSL change from

–150 to –100 m occurs between 17 and 14 kyr BP, and 80 m is reached by 13 kyr BP[16].

This pattern is in agreement with other measures of sea level[18]. The flux of nssCa flux

has already halved from its LGM maximum by 17 kyr BP, confirming that the flooding

of the shelf cannot be the sole cause of changes in nssCa flux. However, the changing

exposure of continental shelf could play a role whenever the RSL varies between about

80 and 150 m.

1. Alley, R. B. et al. Changes in continental and sea-salt atmospheric loadings in central Greenland during the most recent deglaciation: model-based estimates. *Journal of Glaciology* **41**, 503-514 (1995).

2. Legrand, M. Chemistry of Antarctic snow and ice. *Journal de Physique* **48**, C1/77-C1/86 (1987).

3. Goktas, F. et al. A glacio-chemical characterization of the new EPICA deep-drilling site on Amundsenisen, Dronning Maud Land, Antarctica. *Annals of Glaciology* **35**, 347-354 (2002).

4. Guelle, W., Schulz, M., Balkanski, Y. & Dentener, F. Influence of the source formulation on modeling the atmospheric global distribution of sea salt aerosol. *Journal of Geophysical Research-Atmospheres* **106**, 27509-27524 (2001).

5. Mulvaney, R. & Wolff, E. W. Spatial variability of the major chemistry of the Antarctic ice sheet. *Annals of Glaciology* **20**, 440-447 (1994).

6. Minikin, A., Wagenbach, D., Graf, W. & Kipfstuhl, J. Spatial and seasonal variations of the snow chemistry at the central Filchner-Ronne Ice Shelf, Antarctica. *Annals of Glaciology* **20**, 283-290 (1994).

7. Reader, M. C. & McFarlane, N. Sea-salt aerosol distribution during the Last Glacial Maximum and its implications for mineral dust. *Journal of Geophysical Research* **108**, 4253, doi:10.1029/2002JD002063 (2003).

8. Wolff, E. W., Rankin, A. M. & Rothlisberger, R. An ice core indicator of Antarctic sea ice production? *Geophysical Research Letters* **30**, 2158, doi:10.1029/2003GL018454 (2003).

9. Hara, K. et al. Chemistry of sea-salt particles and inorganic halogen species in Antarctic regions: Compositional differences between coastal and inland stations. *Journal of Geophysical Research* **109**, D20208, doi:10.1029/2004JD004713 (2004).

10. Wagenbach, D. et al. Seasalt aerosol in coastal Antarctic regions. *Journal of Geophysical Research* **103**, 10961-10974 (1998).

11. Gersonde, R., Crosta, X., Abelmann, A. & Armand, L. Sea-surface temperature and sea ice distribution of the Southern Ocean at the EPILOG Last Glacial Maximum - a circum-Antarctic view based on siliceous microfossil records. *Quaternary Science Reviews* **24**, 869-896 (2005).

12. Martin, S., Yu, Y. & Drucker, R. The temperature dependence of frost flower growth on laboratory sea ice and the effect of the flowers on infrared observations of the surface. *Journal of Geophysical Research* **101**, 12111-12125 (1996).

13. Kaleschke, L. et al. Frost flowers on sea ice as a source of sea salt and their influence on tropospheric halogen chemistry. *Geophysical Research Letters* **31**, L16114, doi:10.1029/2004GL020655 (2004).

14. Fischer, H., Traufetter, F., Oerter, H., Weller, R. & Miller, H. Prevalence of the Antarctic Circumpolar Wave over the last two millenia recorded in Dronning Maud Land ice. *Geophysical Research Letters* **31**, art. no.-L08202 (2004).

15. Kreutz, K. J. et al. Sea level pressure variability in the Amundsen Sea region inferred from a West Antarctic glaciochemical record. *Journal of Geophysical Research-Atmospheres* **105**, 4047-4059 (2000).

16. Guilderson, T. P., Burckle, L. H., Hemming, S. & Peltier, W. R. Late Pleistocene sea level variations derived from the Argentine Shelf. *Geochemistry Geophysics Geosystems* **1**, doi:10.1029/2000GC000098 (2000).

17. ETOP02. 2-minute Gridded Global Relief Data, www.ngdc.noaa.gov/mgg/fliers/01mgg04.html. (U.S Department of Commerce, National Oceanic and Atmospheric Administration, National Geophysical Data Center, 2001).

18. Siddall, M. et al. Sea-level fluctuations during the last glacial cycle. *Nature* **423**, 853-858 (2003).
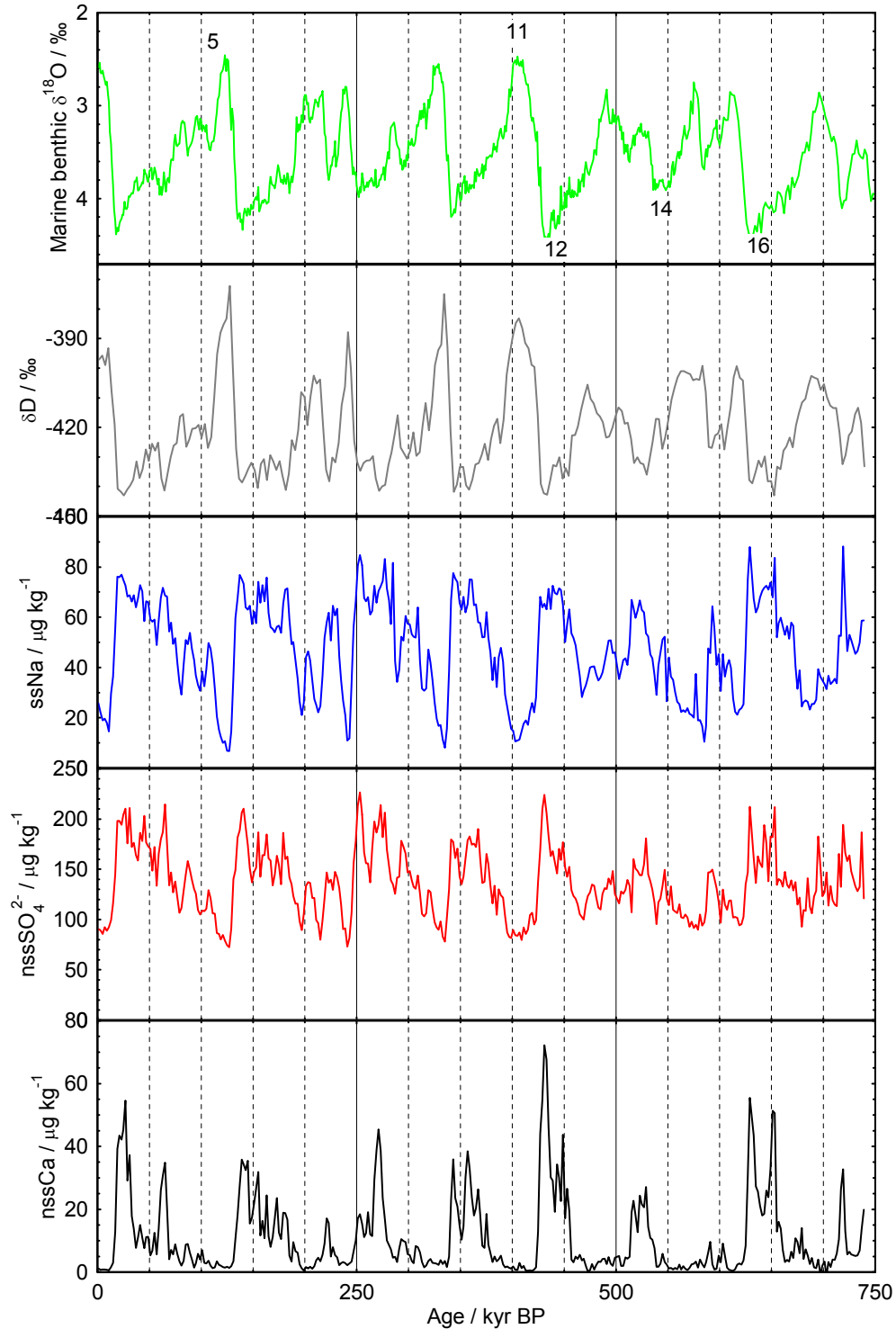
Concentrations of selected chemical components, on an age scale, along with δ*D* from the EDC core, and the oxygen isotope values of the new marine benthic stack[1]. The chemical fluxes are averaged over 2 kyr intervals, δ*D* over 3 kyr intervals[2], benthic δ^{18}O over 1 kyr intervals. The benthic record is annotated with selected MIS numbers. The obvious timing mismatch between EDC and the benthic stack around MIS14 has yet to be resolved[1]. This is the concentration equivalent of Fig. 3 (using fluxes) in the main text.

1. Lisiecki, L. E. & Raymo, M. E. A Pliocene-Pleistocene stack of 57 globally distributed benthic delta O-18 records. *Paleoceanography* **20**, PA1003; doi:10.1029/2004PA001071 (2005).
2. EPICA Community Members. Eight glacial cycles from an Antarctic ice core. *Nature* **429**, 623-628 (2004).
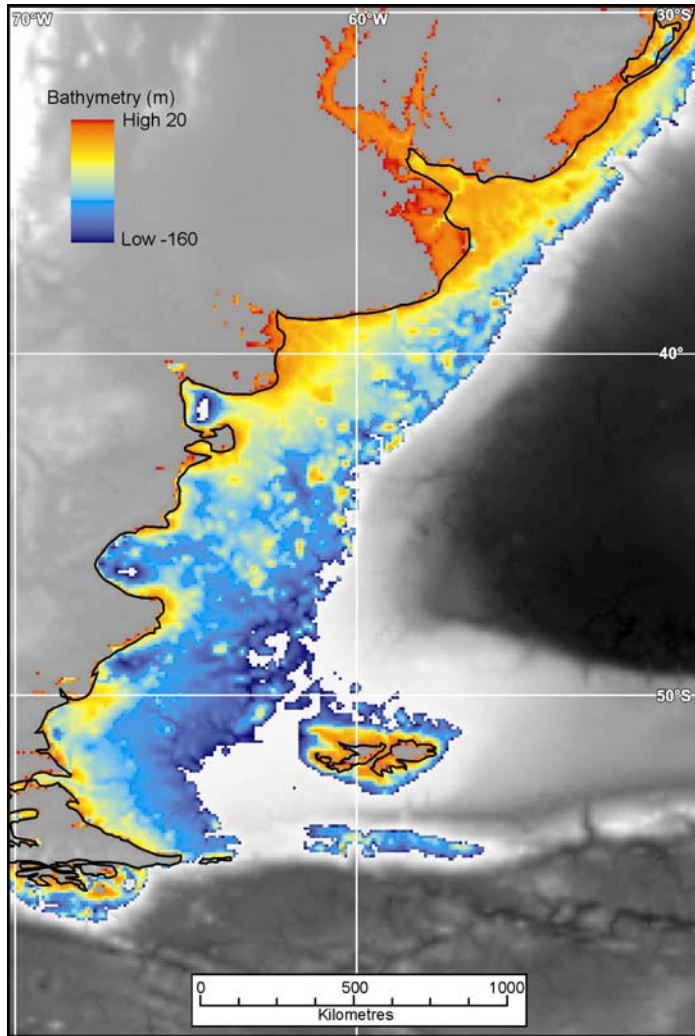
Bathymetric map of southern South America and the adjacent continental shelf.
Coloured contours represent a range of +20 to –160 m compared to present sea level.