Southern Ocean sea-ice extent, productivity and iron flux over the past eight glacial cycles

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Sea ice and dust flux increased greatly in the Southern Ocean during the last glacial period. Palaeorecords provide contradictory evidence about marine productivity in this region, but beyond one glacial cycle, data were sparse. Here we present continuous chemical proxy data spanning the last eight glacial cycles (740,000 years) from the Dome C Antarctic ice core. These data constrain winter sea-ice extent in the Indian Ocean, Southern Ocean biogenic productivity and Patagonian climatic conditions. We found that maximum sea-ice extent is closely tied to Antarctic temperature on multi-millennial timescales, but less so on shorter timescales. Biological dimethylsulphide emissions south of the polar front seem to have changed little with climate, suggesting that sulphur compounds were not active in climate regulation. We observe large glacial–interglacial contrasts in iron deposition, which we infer reflects strongly changing Patagonian conditions. During glacial terminations, changes in Patagonia apparently preceded sea-ice reduction, indicating that multiple mechanisms may be responsible for different phases of CO_2 increase during glacial terminations. We observe no changes in internal climatic feedbacks that could have caused the change in amplitude of Antarctic temperature variations observed 440,000 years ago.

The late Quaternary period is characterized particularly by strong 100,000-year (100 kyr) cycles. Ice cores play a key part in providing an understanding of climate variability during this period because many components of forcing and feedback, including greenhouse gases[1], are represented in a single core. The ionic chemistry in ice cores is mainly representative of aerosol, and has been interpreted as giving information about important environmental features such as sea-ice extent, marine biological productivity of the nearby ocean, aridity of the surrounding continents, and transport strength.

For Antarctica, both dust (representing terrestrial aerosol) and sodium (representing marine aerosol) data have been presented[1] from the Vostok core, extending 420 kyr into the past. The concentrations of both components are significantly increased in glacial periods compared to interglacials. This was attributed to a range of causes, with a particular emphasis on increased meridional transport. A significant increase in methanesulphonic acid concentrations[2] was attributed to increased marine biological productivity in the Southern Ocean. However, more-detailed profiles from other sites, along with a better knowledge of transport, deposition and post-depositional processes[3–5], have called these interpretations into question.

The climate of Antarctica over the longer period of 740,000 yr (740 kyr, to marine isotope stage (MIS)18.4) has recently been

characterized through a new ice-core record[6]. The core, drilled by the European Project for Ice Coring in Antarctica (EPICA) came from Dome C (75° 06′ S, 123° 21′ E, altitude 3,233 m above sea level). The deuterium (temperature proxy) record (Fig. 1) highlighted the change in glacial–interglacial temperature amplitude that occurred around 440 kyr BP (before present); interglacials in the earlier part of the record were much cooler than recent interglacials, despite similar external forcing. Here we present the chemical data only for the main oceanic (sea salt and marine biogenic) and terrestrial (including iron) aerosol components reaching Antarctica. We make new interpretations of the environmental changes during several glacial–interglacial cycles that they represent. We also investigate how the relationship between different variables altered when the climate pattern changed around 440 kyr BP.

Defining the ice-core proxies

All chemical concentrations (see Methods) are higher during glacial periods than during interglacial periods (Fig. 1). However, because of the very low snow accumulation rates at Dome C, the dominant process for aerosol deposition is almost certainly dry deposition[7]. In such a situation, the flux rather than the concentration in ice is expected to be the measure that is indicative of changes in atmospheric concentration. Part of the concentration contrast seen is

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therefore simply due to the fact that the snow accumulation rate is estimated to be more than a factor of two higher in warm interglacials than in the coldest part of each glacial. In Fig. 2, fluxes have been calculated (using the estimated snow accumulation rate[6]) and they are used for the later discussions (see also Supplementary Information).

Iron (Fe) is derived almost entirely from continental terrestrial sources. However, we have more continuous data available for calcium (Ca), which is often used to define terrestrial sources, but which also has a marine source. Sodium (Na) has a mainly marine source, but some continental dust influence. For the remaining figures, we therefore calculated sea-salt Na (ssNa) and non-sea-salt Ca (nssCa) concentrations and fluxes (see Methods). Despite differences in detail, the good general agreement between nssCa and Fe profiles (Fig. 2) suggests that each is suitable as a terrestrial marker element at Dome C, although Fe might be preferred in discussions about iron fertilization of the ocean[8,9].

Methanesulphonate (MS^-) and sulphate (SO_4^{2-}) in Antarctica are both considered to be derived mainly from marine biogenic emission of dimethylsulphide (DMS)[10], followed by oxidation in the atmosphere. MS^- has no other significant source for Antarctica. SO_4^{2-} comes also from sea salt, anthropogenic sources (though these have a very limited influence in Antarctica[11]), terrestrial dust (also limited), and from volcanism—the latter causing intermittent spikes and a continuous background. The sea-salt source of sulphate can be removed using Na data (see Methods) to give non-sea-salt SO_4^{2-} ($nssSO_4^{2-}$). Estimates of the annual downward transport from the stratosphere to the troposphere[11], comparisons of the stratospheric

aerosol burden in non-volcanic and volcanic periods, and modelling studies[10] suggest that the volcanic input during background periods is <10% of the deposition of SO_4^{2-} to the Antarctic ice sheet. Volcanic input during eruptive events[12] can dominate the SO_4^{2-} budget for 1–3 yr, but fills only a small time fraction, representing (for example) only about 6% of the Holocene sulphate budget[13]. In deeper ice, these spikes become diffuse, and eventually cannot be identified against the background: as a result there is no objective way to remove their influence. We have therefore averaged the data without removing the spikes or background, but can assume that the $nssSO_4^{2-}$ flux is strongly dominated by marine biogenic sources throughout the record.

Very large glacial–interglacial contrasts in MS^- (seen also at Dome C) have been widely quoted in the past as evidence[2] of increased glacial-period marine biogenic activity in the Southern Ocean. However, recent evidence[3,4,14] has shown clearly that, under modern conditions at sites with very low snow accumulation rates, MS^- concentration falls rapidly in the upper metres of snow; this is also seen in snowpits at Dome C. This is probably due to a slow evaporative loss of methanesulphonic acid, in a process analogous to that observed for nitrate[15]. In glacial periods, much more terrestrial material is present in the atmosphere and snow. Nitrate and, if
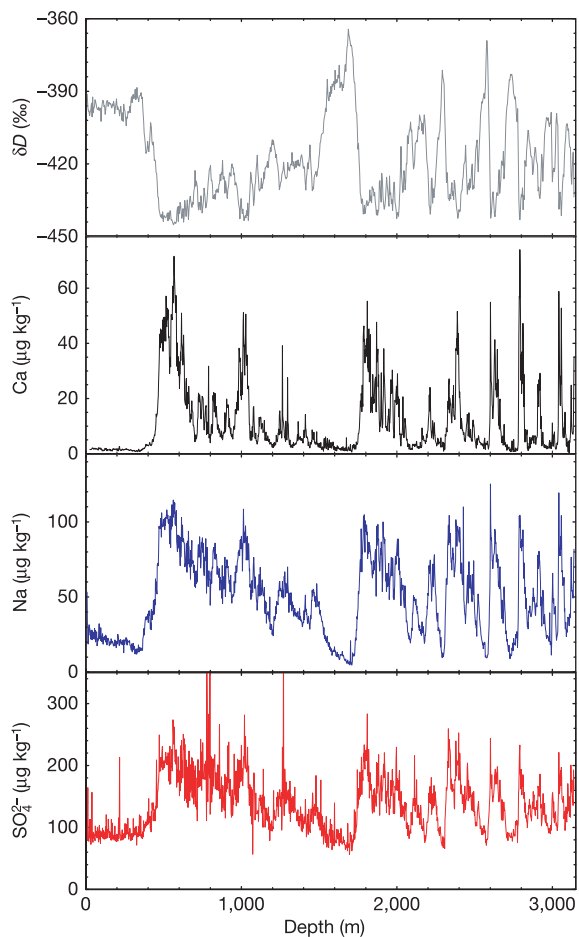

Figure 1 | Measured concentrations from the EPICA Dome C ice core. Data are on an ice depth scale. δD are averaged over 3.85-m sections[6]; chemical concentrations are averaged over 2.2-m sections.
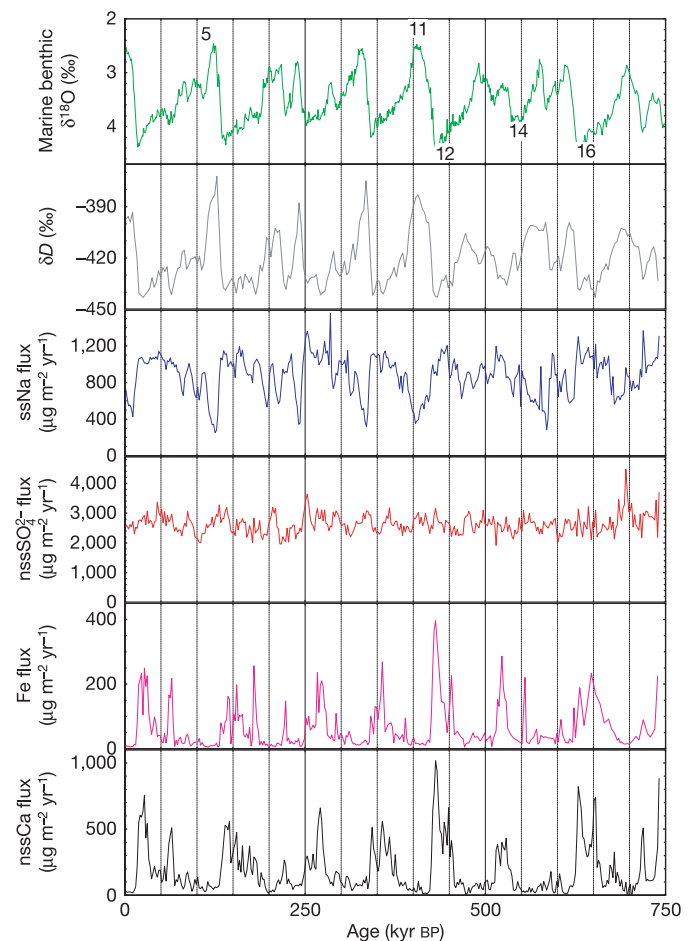

Figure 2 | Chemical measurements from the EPICA Dome C core, on an age scale. Chemical components (2-kyr averages) and δD (3-kyr averages)[6] are from the EDC core; oxygen isotope values (1 kyr averages) from the marine benthic stack (on the LR04 timescale and with selected MIS numbers shown)[39]. While nssCa data represent almost continuous averages within each 2-kyr period, Fe data are averages of a few discrete samples. In the deeper ice, many 2-kyr periods have no Fe data, or are based on a single data point representing only a few decades. The obvious timing mismatch between EDC and the benthic stack around MIS14 is not yet resolved[39].

the analogy holds, MS^-, are no longer mainly present as relatively volatile acids, but are instead preserved as non-volatile neutral salts. Therefore the higher concentrations of both ions in snow from cold periods reflects better fixation (or a different deposition mechanism), and does not indicate the past production of DMS. We therefore use $nssSO_4^{2-}$, which suffers no post-depositional losses, as our marker of marine biogenic emissions.

Sea ice based on sea salt

The ssNa (representing sea salt) flux has minima in interglacials, and maxima in glacial periods. The maximum values are about double the present-day value, while the minimum 2-kyr average observed is about half the present value. There is a very close relationship between Na flux and temperature throughout the 740-kyr period, with cold temperatures leading to higher Na flux (Fig. 3).

Previously, the increased cold period ssNa flux or concentration has been attributed to greater cyclonic activity at the (assumed open-water) source, and to greater meridional transport of sea salt into the continent[1]. Recently, this interpretation has been challenged on several grounds[16]. The chemical signature of both aerosol and snow, showing a characteristic depletion of SO_4^{2-}/Na compared to sea water, suggests that new sea-ice surfaces are the major source of sea salt to coastal Antarctica[17,18]. Sea salt concentrations, even in central Antarctica, peak seasonally when sea ice is at its maximum, and there is no evidence that cyclonic activity has the seasonal contrast needed to overcome the greater travel distance this implies[19]. The modelled flux of sea salt arriving in Antarctica from an open-water source was found to be much lower in the last glacial maximum (LGM) compared to the present, when the data show the opposite[20].

The evidence for a sea-ice source of sea salt to central Antarctica[16] has been circumstantial. Recently, year-round measurements of aerosol concentrations at the high-plateau inland station of Dome Fuji[21] showed SO_4^{2-}/Na ratios that were often below that expected from sea water, with a pattern exactly as found at the coastal sites. A

process of sublimation at the Antarctic snow surface was proposed[21], but this should not lead to fractionation. The most plausible explanation is that the aerosol derives from a source depleted in SO_4^{2-}. We conclude that the sea-ice surface (including frost flowers, brine and brine-soaked snow) is probably the main source of sea salt to central Antarctica for recent winter conditions. This would imply that the sea salt flux at Dome C is related to new sea-ice production in the Indian Ocean sector of Antarctica (see Supplementary Information), at least on longer timescales. Marine diatom evidence suggests that summer sea ice was negligible in this sector even in the LGM[22], which is among the coldest periods in the Dome C deuterium profile. We can conclude that annual production and maximum extent are closely related; with our interpretation, ssNa flux indicates winter sea-ice extent. In the LGM, when ssNa flux is double the present value, winter sea-ice extent is believed to have been about double that of the present[22], providing an approximate calibration of our proxy.

We therefore conclude that, at multimillennial timescales, winter ice extent in this sector is very closely tied to Antarctic temperature (Fig. 3). The relationship is stable throughout the last 740 kyr, implying that the change in climatic pattern at around 440 kyr is not due to any change in the climate–sea-ice feedback. Winter ice extent has probably been considerably below the present value in recent interglacials. Sea-ice extent was intermediate between recent glacial and interglacial values during most of the weak interglacials before 440 kyr BP. The linkage between Antarctic temperature and sea-ice extent is less strong at shorter timescales; changes in sea salt and deuterium are not synchronous during major climate transitions, as discussed later. Although we recognize that our use of sea salt as a sea-ice proxy remains tentative, we suggest that the ssNa flux curve in Fig. 2 may be taken as a first attempt at a quantitative winter ice extent over the last 740 kyr for use in modelling studies. It will also be important for assessing the role of sea-ice mechanisms in CO_2 changes[23].

Marine productivity

High glacial MS^- was used to suggest increased oceanic DMS emissions during the last glacial period[2]. This led to the suggestion that the S cycle has been very sensitive to climate change[2]. Because the products of DMS oxidation, through their role as cloud condensation nuclei, may themselves cause climate feedbacks[24], the Vostok MS^- record is often quoted in discussions about climate self-regulation[25,26]. DMS production is also quoted as one indicator of productivity, relevant to the drawdown of CO_2, although it has to be emphasized that DMS producers may not be representative of total biological production.

In contrast to MS^-, the $nssSO_4^{2-}$ flux is stable, within about 20%, through the entire 740-kyr record (Fig. 2). The single short-lived increase in flux, depending mainly on a single data point at about 700 kyr seems not to be replicated in a parallel analysis by the fast ion chromatography method (see Methods). The low variability in the rest of the record is remarkable, and unique among ice-core chemistry records to date. A similar result (with concentrations approximately doubled in peak glacials compared to interglacials, implying little change in flux) would have been found for Vostok[2] or Dome Fuji[27]. We note that the use of concentrations rather than fluxes would have led to a different conclusion, but our assumptions about aerosol deposition leading to this choice are robust (see Supplementary Information).

The amount of $nssSO_4^{2-}$ reaching Dome C should depend on the production and emission of DMS, on the location of emissions (and hence the transport distance), on transport speed and on transformations en route. The constant $nssSO_4^{2-}$ flux could result from all these factors changing between glacial and interglacial (in which case their effects must fortuitously cancel out), or from the dominant factors remaining constant.

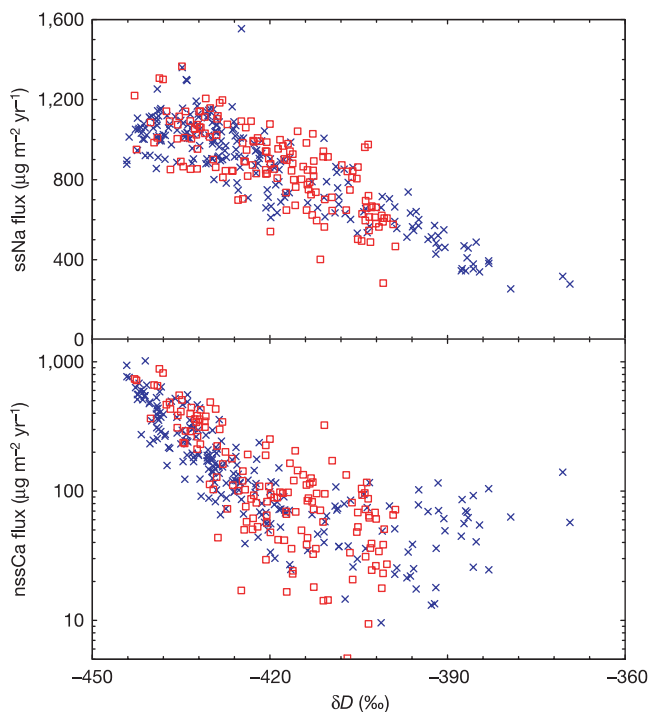The summer sea-ice edge was close to the continent in the sector of

Figure 3 | Relationship between chemistry and climate. ssNa and nssCa fluxes plotted against δD for the entire ice core, using 2-kyr averages. Blue crosses are for the period from 0–440 kyr BP, red squares are for 440–740 kyr BP.

Antarctica nearest to Dome C even in the LGM[22], so that the location of summer DMS emission need not have moved significantly. Model studies of tracer transport, although mainly dealing with transport from further north than the DMS source regions, suggest a rather small change in transport time for the LGM compared to the present[28,29]. The proportion of DMS that is oxidized to SO_4^{2-} or to MS^- might vary with climate, but $nssSO_4^{2-}$ probably remains the dominant product under all conditions[30]. We therefore conclude that these factors are unlikely to have been decisive: allowing for some changes in these factors, and for uncertainty in our assumptions about the dominance of dry deposition and the snow accumulation rate, DMS emissions in the relevant region must have also been constant to within a few tens of per cent. The relevant region (based on model estimates for Vostok) is the Indian Ocean sector, with the largest influence between 55° and 60° S[10].

Marine proxies have suggested that export production south of the present-day Antarctic polar front (APF) was lower in the LGM than in the Holocene[31]. Our result implies that organisms such as *Phaeocystis*, which leave no fossil record, but which are major DMS producers, also had no increased production south of the APF. In fact, production by these organisms remained approximately constant, despite the large changes in Antarctic environmental conditions and the decrease in overall export production. Our measurements are probably less sensitive to changes in DMS production further north. Because DMS emissions south of the APF apparently remained constant to within a few tens of per cent throughout the last 740 kyr, despite very large climate changes, the sulphur cycle does not appear to have responded to climate change with either a positive or negative feedback.

Iron flux and South American climate

The nssCa flux, as also does the Fe flux, shows extreme variations, being about a factor of ten higher in glacial maxima than in interglacial periods (Fig. 2). Both metals are assumed to be representative of terrestrial material, and their concentration profiles look similar to that of insoluble dust mass[6]. The main origin of dust reaching these sites is South America, specifically Patagonia[32]. Model studies[28,29], and previous studies of dust particle size for the more recent part of the record[33], suggest that changes in the transport strength and atmospheric residence time between South America and Dome C were small, despite the changes in precipitation scavenging and atmospheric circulation that must have occurred. Assuming this applies to the whole record then the order of magnitude changes in dust flux seen at Dome C must result primarily from changes in the source region.

Such changes in South America could result from (1) changes in the strength of the Patagonian source due to changes in temperature, moisture and vegetation, (2) changes in uplift of source material due to changes in wind strength, (3) an increased Patagonian source of fine glacial material due to varying glacier coverage, or (4) the addition of new source areas on exposed continental shelf as sea level changed. The latest evidence[34] suggests that geochemical measurements cannot yet distinguish between a Patagonian and continental shelf source.

It is very likely that climate conditions in Patagonia did change during glacial periods. A recent model study suggested that, south of 50° S, the westerlies were intensified at the LGM, and that this was coupled to a reduction in moisture transport to Patagonia from the Atlantic (giving drier conditions)[35]. If the main dust source is well south, then it should be enhanced by such changes. Major glaciations of Patagonia occurred during cold periods in the ice-core record[36], although it is not obvious how this would affect the dust source. Unfortunately, there is no good time-resolved record of any of these factors that we can use to test their influence on the Antarctic dust record.

It has been argued that the detailed timing of sea-level rise is inconsistent with the timing of the main changes in dust flux during

the LGM–Holocene transition[5]. Most of the area of continental shelf south of 45° S that would have been exposed during the LGM would have been re-flooded early in the deglaciation[37] (see Supplementary Information). Nonetheless, the nssCa flux had already halved from its LGM maximum by 17 kyr BP, before any significant change in sea level[38] or exposed area, and the nssCa flux reduction clearly leads the flooding of the shelf. Flooding of the shelf cannot be the main cause of reduced nssCa flux, although the changing exposure of continental shelf could play some part. There is a general correspondence between particularly high marine benthic oxygen isotope values[39], representing—at least in part—changes in sea level, and high nssCa fluxes (Fig. 2); however, there is also a strong correspondence between nssCa flux and other parameters such as Antarctic δD.

We therefore conclude that the nssCa record probably mainly reflects changes in atmospheric circulation influencing Patagonian wind strength and aridity, although changes in glaciation might also have an unspecified role. The increased exposure of continental shelf may amplify the effect when sea level is particularly low. NssCa flux, in some way a record of Patagonian conditions, shows a very close, but nonlinear, link between Patagonian conditions and Antarctic climate throughout the period. NssCa flux (and similarly Fe flux) increases significantly only below a threshold (about −410‰ at Dome C) in Antarctic deuterium (Fig. 3). Fluxes are similar in the first and second halves of the record for a given deuterium value (Fig. 3); slightly higher glacial values earlier in the record rest heavily on a few high flux values in MIS12 and MIS16. There seems to be no significant change in the climate-dust feedback at 440 kyr. Finally, although Australia could also be a significant source of dust, models suggest that Patagonia should also be the main source of atmospheric iron to most of the Southern Ocean[40], and thus our record should
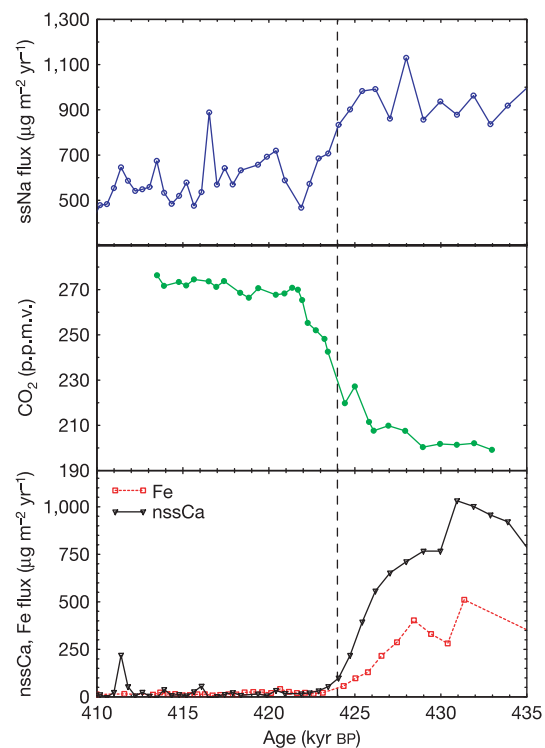

Figure 4 | Chemistry and CO$_2$ across Termination V. Chemical fluxes (averaged over 1.1 m depth increments, equivalent to a few hundred years at this depth, except for Fe, which consists of spot values at irregular intervals), and CO$_2$ concentration[6], across Termination V, between MIS12 and MIS11. Uncertainty in the alignment of the timescales for the CO$_2$ and chemical records is caused by the calculation of the gas-age/ice-age difference[6], and could be several centuries. The vertical dashed line indicates 424 kyr BP (see text).

serve both as a continuous profile of changes in Patagonian climate, and as a suitable input for assessing the influence of Fe fertilization on atmospheric CO_2 concentration.

Phasing of changes at climatic transitions

Although many aspects of climate throughout the 740-kyr record change together at each termination and inception, this is not the case, at least at millennial resolution, for sea salt (representing sea ice) and terrestrial material (representing Patagonian conditions). It was previously noted[5,9,41] that, at Termination I, the main change in nssCa flux occurred in the first half of the transition (18–15 kyr), while the main change in Na flux occurred later (14–12 kyr).

The new record shows that this is a general rule at terminations, as illustrated in detail for Termination V (Fig. 4). In this termination, the main change in terrestrial material flux (at 428–424 kyr) precedes that in sea salt (425–422 kyr), while the CO_2 change occurs mainly between 426 and 422 kyr BP. Deuterium increases between 428 and 422 kyr. The same pattern is seen also at the earlier changes, where there is a lower amplitude in δD (the phasing between CO_2 (ref. 42) and our parameters has yet to be determined at these transitions): at the transition from MIS16 to MIS15, for example, the reduction in nssCa occurs mainly between 629–625 kyr, and the reduction in ssNa occurs mainly between 625–623 kyr BP. This pattern suggests that the main changes in Patagonia generally precede those in sea-ice extent.

It also has strong implications for the possible causes of CO_2 increases during terminations, because mechanisms related to changing Fe fertilization[43] can only be active in the first half of the termination, unless Fe ceases to be the limiting nutrient at deposition rates only just above those seen in the Holocene. In Termination V, at 424 kyr, when the terrestrial dust change is almost complete, CO_2 has increased by <30 p.p.m.v., adding to evidence[9,44] that this is a maximum possible impact of iron fertilization. We note that the increased productivity implied by iron fertilization would have to occur north of the APF. Mechanisms related to changing sea-ice extent[23], at least in the ocean sector represented in our record, should be active in the later stages of each transition only.

Climate and chemistry over eight cycles

Using only Antarctic ice-core chemical data, we describe the dynamics of three external parts of the climate system over a period of 740 kyr, and provide continuous data sets as inputs for climate modelling. According to our interpretation, maximum sea-ice extent in the Indian Ocean sector is tied very closely to Antarctic temperature at multimillennial timescales, but they are not synchronous at short timescales. The part of marine biogenic activity in the Southern Ocean that is related to DMS emission south of the APF seems to have been remarkably constant through the period; atmospheric S compounds had no significant role in climate feedback. Patagonian conditions changed very strongly between glacial and interglacial, leading to a large change in iron input to the Southern Ocean.

The relationship between each chemical component and Antarctic deuterium (temperature) stays remarkably constant through the last 740 kyr, with no significant change at the point where the amplitude of interglacials increases strongly (around 440 kyr). We conclude that change in internal feedbacks represented by these parameters was not responsible for the change in amplitude of interglacial climate.

METHODS

Major ions presented here (Na^+, Ca^{2+}, SO_4^{2-}) were measured using IC (ion chromatography), with an estimated uncertainty on individual measurements of better than 5% (but rather higher at the lowest concentrations seen in interglacial periods)[45]. Samples from 0–580 m depth were cut into discrete samples from a section of the core after removal of the contaminated outer layers, melted and analysed; below 580 m, they were collected into sample vials using a melting device. In the latter case, a 3.4×3.4 cm strip of ice was melted onto a hotplate (either in the field or in a European cold laboratory)[46], and part of the melt from the inner part of the core was led directly to various detection devices (in a

continuous flow analysis (CFA) system), or fed into vials for later IC analysis. Of the components shown here, Na^+ and Ca^{2+} were determined spectrometrically using the CFA system[46] as well as by IC. The results shown here are from IC, but good agreement between methods is generally found[45]. The exception is for Ca^{2+} in the upper 580 m, for which the IC data may be slightly contaminated owing to possible incomplete removal of outer layers. This problem does not affect any other ions, and we found good agreement between IC and CFA Ca^{2+} data, even at the low concentrations found in interglacial periods, beyond 580 m. We have therefore used the CFA Ca^{2+} data for the upper 580 m (27 kyr). SO_4^{2-} was measured by passing some of the CFA water directly into a fast-IC device[47], as well as by conventional IC. A comparison between the two methods shows excellent agreement, but hereafter conventional IC data are used. None of the three methods described here is likely to measure the insoluble fraction of terrestrial dust. For the IC measurements, samples were collected as the cumulative melt or cut from anything between 5 cm to 1.1 m of ice, and in Fig. 1 we present averages of 2.2 m increments.

Fe was measured on 1,038 discrete samples using inductively coupled plasma sector field mass spectrometry (ICP-SFMS). Ice-core sections 5 cm long were decontaminated by three repeat washings in ultrapure water to remove 60% of the material, acidified to pH 1 with ultrapure nitric acid, and then left to stand for at least 24 h before analysis[48]. Precision is around 20% for interglacial and 10% for glacial samples. The discrete samples are rather widely spaced, so that the time averages seen in Fig. 2 often consist of one or more data points representing only a few per cent of the time interval. Some of the detailed differences between nssCa and Fe arise from the fact that the nssCa data are averaged from samples covering most of the averaging interval, in contrast to the Fe data. It is for this reason that we prefer to use nssCa for most of the paper.

The timescale is EDC2 (ref. 6), and the accumulation rates used to calculate flux also derive from EDC2. We calculated ssNa and nssCa assuming a Ca/Na weight ratio of 0.038 for marine aerosols and 1.78 for the average crust[49]. Although the latter figure could be highly variable between different terrestrial sources, leading to a substantial uncertainty in ssNa, previous authors[5,50] have suggested that this is the most suitable ratio to use. If we had used crustal ratios with Fe as the terrestrial marker element, the correction would have been smaller. If the crustal source material is dominated by marine clays or other Na-rich material the correction would be larger. In any case, no reasonable ratios affect the shape of the derived time series, nor the conclusions of this paper. On average we calculate that about 90% of Na is from sea salt, although the proportion occasionally falls below 70% in glacial periods. In glacial periods, about 90% of Ca is from terrestrial sources, but the proportion can be much lower in interglacials.

$nssSO_4^{2-}$ was first derived by subtracting the sea-salt part, traditionally calculated by using ssNa, along with the weight ratio of SO_4^{2-}/Na in sea water (0.25). However, if the main source of sea salt is actually the sea-ice surface, then this source is depleted in sulphate compared to sea water, with a ratio close to 0.1 (refs 17, 18). We present $nssSO_4^{2-}$ fluxes calculated with the latter method—again, our choice does not significantly affect the results of this paper.

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CORRIGENDUM

Southern Ocean sea-ice extent, productivity and iron flux over the past eight glacial cycles

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In calculating the fluxes used in this paper, we made a mistake in the snow accumulation rate used. We calculated fluxes assuming that snow accumulation rates were expressed in metres water equivalent, but they were actually expressed in metres ice equivalent. The result of this error is that the fluxes shown in the original paper are uniformly 8.3% too high. The shape of the affected plots (the lower four panels in Figure 2, both panels in Figure 3, and the top and bottom panels in Figure 4) remains the same if the correct values are plotted, and the affected figures could be corrected by re-scaling the y-axes by 8.3%. Our conclusions are not affected. The flux data in the Supplementary Information of the original paper ('Supplementary Data 2') have now been corrected.