Constraints on soluble aerosol iron flux to the Southern Ocean at the Last Glacial Maximum

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Relief of iron (Fe) limitation in the Southern Ocean during ice ages, with potentially increased carbon storage in the ocean, has been invoked as one driver of glacial-interglacial atmospheric CO₂ cycles. Ice and marine sediment records demonstrate that atmospheric dust supply to the oceans increased by up to an order of magnitude during glacial intervals. However, poor constraints on soluble atmospheric Fe fluxes to the oceans limit assessment of the role of Fe in glacial-interglacial change. Here, using novel techniques, we present estimates of water- and seawater-soluble Fe solubility in Last Glacial Maximum (LGM) atmospheric dust from the European Project for Ice Coring in Antarctica (EPICA) Dome C and Berkner Island ice cores. Fe solubility was very variable (1–42%) during the interval, and frequently higher than typically assumed by models. Soluble aerosol Fe fluxes to Dome C at the LGM (0.01–0.84 mg m⁻² per year) suggest that soluble Fe deposition to the Southern Ocean would have been ≥10 × modern deposition, rivalling upwelling supply.
Changes in atmospheric iron (Fe) supply to the oceans (described here as aerosol Fe) during glacial intervals have been suggested as one of a number of possible drivers for changes observed in atmospheric CO₂ between glacial and interglacial climate states (The Iron Hypothesis)3–5. Fe fertilization of the presently Fe-limited Southern Ocean during glacial times could be responsible for up to 40 p.p.m.v. of the regular 80–120 p.p.m.v. cycles in atmospheric CO₂ that coincide with glacial–interglacial cycles over at least the last 800,000 years. Increased atmospheric Fe supply to the glacial Southern Ocean, where today low dissolved Fe concentrations limit phytoplankton growth6,7, may have enhanced the efficiency of the 'biological pump', retaining more carbon in the deep ocean and driving a reduction in pCO₂ (refs 1,2). While changes to ocean circulation and deep ocean carbon storage may play a dominant role in glacial–interglacial cycling8–10, atmospheric Fe may also strongly influence the efficiency of the biological pump on both glacial and millennial timescales11,12, with potentially large effects on the carbon cycle. Indeed, a recent study showed that enhanced nutrient utilization and greater productivity in the Sub-Antarctic are linked to periods of increased dust (and Fe) supply over the past 160,000 years,13, highlighting atmospheric Fe fertilization in the Sub-Antarctic surface ocean as a candidate for explaining millennial-scale fluctuations in atmospheric CO₂.

Through this mechanism, Fe fertilization may play an important role in glacial–interglacial cycling, in combination with other processes9,13,14. Evidence for higher dust fluxes comes from Antarctic ice cores, which record marked increases in atmospheric dust deposition to Antarctica during colder intervals over the past 800,000 years15, most likely due to expanded dust source areas in South America and enhanced atmospheric lifetime and transport16. Sedimentary records also show that the temporal pattern of Antarctic ice-core dust fluxes is representative of dust reaching the Southern Ocean, with the dust–climate coupling extending back at least 4 million years. However, modelling efforts to understand the sensitivity of the oceans and climate to Fe (for example, ref. 17) are still limited by poor constraints on aerosol Fe solubility and the fluxes of 'bioavailable' (the Fe that can be taken up for growth by phytoplankton) aerosol Fe to oceans during glacial times.

Converting ice and sedimentary dust records to bioavailable aerosol Fe fluxes is not straightforward. Previous studies have used dust flux records with fixed composition and Fe solubility18, or non-seasalt Ca (nss-Ca) as proxies for dissolved Fe (ref. 11). Recently, measurements of Fe concentration and fluxes in ice cores have become available19–23; however, these were made under acidic conditions (pH 1–2), and are thus far removed from dissolution in seawater (pH ~ 8) where Fe solubility can be <1% (ref. 18). Fe solubility is strongly pH dependent (Supplementary Discussion), and acid leaches may access a variable fraction of the total Fe present22,24. Equally, dissolved Fe concentrations within melted Antarctic ice of glacial age (for example, 1–70 ng g⁻¹ in this study) are typically well above the low-equilibrium saturation concentration of Fe(III) (~0.1 ng g⁻¹; Supplementary Fig. 1), meaning that Fe loss due to precipitation/adsorption of Fe hydroxides is likely under weakly acidic pH conditions (Supplementary Discussion). While Fe(II) is more soluble than Fe(III) under these conditions25, a recent study suggests that a large proportion of Fe within ice-core material is present as Fe(III) (ref. 26). Any loss of Fe(III) via precipitation or adsorption to plastic equipment during processing that is not recovered during acidification will lead to underestimation of soluble Fe, which might affect studies analysing Fe after melting using discrete bottled samples or flow-through systems (for example, refs 19,20,23,26). Thus, while previous ice-core records provide valuable information about broad-scale changes in aerosol Fe fluxes, they provide incomplete information about soluble or bioavailable aerosol Fe supplied to the oceans. We were therefore motivated to seek techniques for more representative estimates of soluble Fe flux to the Southern Ocean during glacial intervals to allow models to more accurately assess the effect of changing atmospheric Fe supply on the carbon cycle.

Here we present high-resolution fluxes of total and soluble atmospheric Fe, as well as calculated aerosol Fe solubility, from the Last Glacial Maximum (LGM; 21–26 ky before present (BP)) of the EPICA Dome C ice core15,20 from East Antarctica (EDC; 75° 06’ S 123° 21’ E, 3,233 m.a.s.l.; Fig. 1) and from Marine Isotope Stage (MIS) 2-3 (22–52 ky BP) from an ice core from Berkner Island (79° 32.9’ S 45° 32.9’ E; Fig. 1). Soluble Fe was determined using a novel rapid-filtration technique, in meltwater at pH ~5.3 (the natural pH of the melted ice) or following leaching of sublimated dry dust with natural seawater, analogous to instantaneous techniques used with modern aerosols27. Our data are much more representative of dissolution of atmospheric dust in the ocean than previous ice-core studies, avoiding both unrealistically high Fe solubilities and soluble aerosol Fe fluxes higher than those at Dome C during the LGM. While these calculated soluble Fe fluxes are not fully representative of bioavailable Fe fluxes to the Southern Ocean, they enable an improved estimate of the atmospheric Fe that would have been deposited and dissolved in seawater at the LGM compared with previous studies. Our measured aerosol Fe solubilities and soluble aerosol Fe fluxes are higher than typically used in models of ocean biogeochemistry, and thus we suggest that models should consider higher and more spatially and temporally variable soluble atmospheric Fe fluxes to the Southern Ocean during glacial intervals.

Figure 1 | The locations of EPICA Dome C and Berkner Island coring locations on Antarctica.
Results

Figure summary. Aerosol Fe solubility and calculated total and soluble Fe fluxes from EDC and Berkner ice cores are shown compared with other ice-core parameters in Figs 2–4, with a comparison of Fe solubility in EDC ice of LGM age at pH ~ 5.3 and in seawater shown in Fig. 2b. The data are also available in Supplementary Data.

Aerosol Fe solubility in EDC and Berkner ice cores. Fe solubility in atmospheric dust deposited at Dome C across the LGM had a mean of 10% (n = 23) and 17% (n = 11) at pH ~ 5.3 and in seawater, respectively, and a median of 6% at pH ~ 5.3 (Fig. 2 and Supplementary Data). These aerosol Fe solubilities are higher than solubility of loess and desert dust (< 0.5%; refs. 18, 28) or glacial flour (2–3%; ref. 28), but consistent with higher than solubility of loess and desert dust (Fig. 2 and Supplementary Data). These aerosol Fe solubilities are the result of changing contributions from different types of dust dry-deposited at Dome C during the LGM (Fig. 2a) and assumed atmospheric transport pathways 16, with transport-induced size/compositional fractionation and chemistry enhancing Fe solubility away from source regions 29,30. Indeed, dust dry-deposited at Dome C during the LGM represents the distal fine fraction of dust leaving the source regions on Patagonia 1. EDC dust is enriched in both Al and Fe compared with both the crust and Patagonian topsoil (Supplementary Data), suggesting that high Fe solubility at Dome C could be driven by a compositional bias towards smaller clay particles containing more readily soluble Fe 32 during atmospheric transport 30,33. By contrast, mean Fe solubility at Berkner Island, closer to South American dust sources 18, was only 3% during 23–50 kyr BP (Fig. 2c) and 1–5% at the LGM.

Fe solubility in EDC samples was very variable across the interval (Fig. 2a; 1–42%). At several points within the LGM, we measured samples of very similar ages (Fig. 3), showing that variability sometimes also occurs at annual–decadal scales (Figs 2a and 3); for example, Fe solubility in samples at 23,350 and 23,352 kyr BP were 4 and 14%, and samples at 23,391 and 23,396 kyr BP were 17 and 6%, respectively (Supplementary Data and Fig. 3). Variability in Fe solubility through the LGM could be driven 34,29 by seasonal changes in dust supply or discrete dust events, but is notable in ice samples, which by their nature represent combined dust deposition over several years. The observed variability in Fe solubility has no clear relationship with total Fe, dust loading or particle size (Fig. 4), suggesting that, if real, it is driven either by particle composition or transport-induced changes in Fe speciation. Similar EDC temperature (Fig. 2a) and assumed atmospheric transport pathways 16, combined with a homogenous grain-size distribution through the interval (Fig. 4), suggest that variability is more likely the result of compositional and Fe-speciation changes than transport-induced changes in Fe chemistry. Mineralogy exerts a strong control on Fe solubility, with Fe in clay and silicate minerals much more soluble than Fe hydroxides 32, and glacial flour enriched in both Fe(II) and clays compared with loess 28. While higher solubility may be driven by relative enrichment of clay minerals with transport 30,33, variable solubility could be the result of changing contributions from different types of South American dust (for example, loess or glacial material 34). Contributions from local dust sources is unlikely at Dome C,
where most glacial-age dust is considered to be from Patagonia\textsuperscript{31}, but they could play a role at Berkner Island.

Comparison of solubility at pH $\sim$ 5.3 and in seawater (Fig. 2b) also shows scatter about a 1:1 line, similar to that observed in modern studies comparing ultrapure water and seawater rapid-leaching techniques\textsuperscript{27}. This scatter may reflect heterogeneous particle distribution and chemistry or could partly be the result of differences between the two methods, such as temperature, number of leaches, or solution chemistry enhancing dissolution in seawater. Similarly, while comparison of pH $\sim$ 5.3 leaching between three samples of identical age showed broadly similar solubility, there was also some variability (6 and 6%, 2 and 5% and 3 and 7%; Fig. 3). It is therefore possible that the full observed variability between samples in this study is not real; however, if anything, we would expect methodological concerns to result in underestimation of Fe solubility due to incomplete leaching or precipitation, which does not change our primary observation of high aerosol Fe solubility at times within LGM ice.

**LGM aerosol Fe fluxes at Dome C and Berkner Island.** Decadal to centennial variability in both Fe solubility and total Fe fluxes throughout the LGM at Dome C (Fig. 2a; 0.3–2 mg m$^{-2}$ per year; mean 0.76 ± 0.4 mg m$^{-2}$ per year) combines to mean that soluble Fe fluxes show great variability (Fig. 2a; 0.01–0.84 mg m$^{3}$ per year), with mean values of 0.09 ± 0.17 mg m$^{-2}$ per year (1 s.d.) for pH $\sim$ 5.3 soluble Fe and 0.15 ± 0.13 mg m$^{-2}$ per year (1 s.d.) for seawater-soluble Fe. Despite the lower Fe solubility at Berkner Island compared with Dome C, higher atmospheric Fe fluxes at the LGM (0.95 ± 0.07 mg m$^{-2}$ per year), probably attributable to greater dust deposition owing to closer proximity to South American dust sources\textsuperscript{18}, result in similar mean soluble Fe fluxes (0.03 ± 0.02 mg m$^{-2}$ per year) compared with those at Dome C. Total Fe fluxes at Berkner Island were almost an order of magnitude lower during Antarctic Warm Events A1 and A2 than during colder periods (Fig. 2c), reflecting lower regional dust fluxes during warmer intervals\textsuperscript{13}.

**Discussion**

The aerosol Fe flux data presented here can be compared with previous ice-core estimates of Fe fluxes to Antarctica and the nearby Southern Ocean, during the LGM. We find that our total EDC aerosol Fe fluxes ($5.3–36 \mu$mol m$^{-2}$ per year; mean $13.7 \mu$mol m$^{-2}$ per year) are considerably higher than previous estimates based on acidic (pH $\sim$ 1–2) leaching or mineral dust proxies at several Antarctic locations (4.3–8 $\mu$mol m$^{-2}$ per year; refs 22,23), including those based on acidic leaches at EDC with a conversion to total Fe (refs 19,22; 6.6 $\mu$mol m$^{-2}$ per year). The difference may partially reflect the high-resolution variability in Fe flux at EDC, but also the fact that, similar to modern dust\textsuperscript{24}, an acidic leach represents a variable portion of the total Fe, dependent on dust composition and leaching timescale. While pH $\sim$ 1 EDC Fe fluxes are generally higher than estimates at pH 5–8 (Fig. 2a), the two ranges overlap, meaning that acidic leaches of ice core do not represent either total or soluble aerosol Fe, although they may capture broad-scale trends. This offset between acidic leaches and total digested Fe may be partially to do with methodology; the pH 1 EDC Fe records were measured in samples that were melted, acidified and only left to dissolve for $>$ 24 h (refs 19,20), while other studies have shown that Fe continues to dissolve at pH 1–2 for up to 3 months\textsuperscript{22,35}. As a result, these short timescale acidic leaches in EDC ice samples may not have fully captured the pH 1 leachable fraction that is present. Previous comparison of pH 1 leached methods with digestion procedures on EDC ice suggested that 30–65% of total Fe was recovered by pH 1 leaching methods\textsuperscript{19,21}, but it seems likely that the proportion accessed by these short-term acidic leaches would vary with dust composition and mineralogy. Also, even with 1–3 month leaching times, acidic leaches are unlikely to fully dissolve dust particles.

Our data also allow evaluation of the use of other proxies for ice core Fe (Fig. 5). We find that both nss-Ca\textsuperscript{11} (Ca with Na-calculated seashell component removed) and total Al are good proxies for the flux of total Fe (Fig. 5). However, taking the EDC dust flux and calculating total Fe concentrations, assuming a constant crustal Fe percentage of $\sim$ 4% in dust\textsuperscript{19} underestimates total Fe for EDC samples, which are enriched in Fe (mean 8 wt%; Supplementary Data) compared with crustal values of 2–3% (ref. 36) or Patagonian topsoil (2–6%; ref. 37). EDC samples are similarly enriched for Al (mean 15 wt%; Supplementary Data), compared with crustal values of 8% (ref. 36) and Patagonian topsoil of 6–10% (ref. 37). This difference in the dust composition presumably relates to compositional-fractionation processes during transport, such as relative enrichment in silicate minerals, such as clays and feldspars\textsuperscript{33}. As such, changes in composition and mineralogy may be spatially variable and site specific for ice-coring locations, complicating efforts to use dust, Ca or Al fluxes as proxies for total Fe. In addition, despite the possible usefulness of these proxies for providing information about timing and magnitude of changes in atmospheric Fe\textsuperscript{11}, the lack of relationship between total and soluble Fe (Fig. 5c) means that they do not approximate soluble or bioavailable Fe. Instead, direct measurements of soluble Fe, together with biological experiments, are needed for constraining changes in soluble and bioavailable Fe supply to the oceans during climatic change and especially within stable climate intervals. However, we do note the strong covariance between ice-core dust and Fe fluxes and both Sub-Antarctic productivity and heavier Sub-Antarctic surface nitrogen isotope ratios (indicative of increased nutrient utilization) during the last 160 kyr (ref. 13), as well as a similar covariance between ice-core dust and (pH 1) Fe fluxes, sediment Fe mass accumulation rates and Sub-Antarctic export productivity over the last eight glacial cycles\textsuperscript{5,38}; these relationships suggest that both dust or (pH 1) EDC
ice-core Fe fluxes do capture the order of magnitude changes in Fe supply to the Southern Ocean that are important for understanding millennial-scale climate and pCO2 variability. By comparison with estimates of Holocene Fe fluxes to Antarctica22, our mean total Fe flux estimates (13.7 m mol m$^{-2}$ per year) represent a $\sim$30–50$\times$ increase over EDC (0.3–0.4 m mol m$^{-2}$ per year), and a $\sim$10–20$\times$ increase over coastal sites such as Law Dome (ref. 22; 0.8–1.1 m mol m$^{-2}$ per year). The modern gradient in dust deposition between coastal sites and EDC is thought to be largely influenced by wet deposition, which dominates at coastal sites and is a minor factor inland, and thus might be somewhat smoothed out during drier glacial intervals22. In terms of soluble Fe, the mean EDC seawater-soluble Fe flux of 2.7 m mol m$^{-2}$ per year represents a $\sim$10-fold increase over modern soluble Fe fluxes (even assuming a similar high solubility in modern dust), and is $\sim$10$\times$ higher than modern calculated Southern Ocean atmospheric Fe fluxes (0.2 $\mu$mol m$^{-2}$ per year; ref. 4). This suggests that the soluble atmospheric Fe flux to the Southern Ocean increased by at least a factor of 10 at the LGM. Such an Fe flux would be broadly equivalent to the expected upwelling supply of deep Fe, which would be reduced from calculated modern values of 8–16 $\mu$mol m$^{-2}$ per year due to decreased circulation and stratification due to increased sea ice2,4. The range in soluble Fe fluxes observed in this study (0.2–15 m mol m$^{-2}$ per year) is also similar to modelled modern upwelling Fe flux values for entrainment (deep winter mixing: 9.1–33 $\mu$mol m$^{-2}$ per year) and vertical diffusion (1.2–3.6 $\mu$mol m$^{-2}$ per year), which have been suggested to sustain surface water Fe concentrations in the modern Southern Ocean39.

Figure 4 | Variability in EPICA Dome C over the LGM. (a) pH $\sim$5.3 dissolved Fe concentration, (b) pH $\sim$5.3 Fe solubility and (c) pH $\sim$5.3 Fe solubility shown with grain size (fine particle, FPP; coarse particle, CPP) from coulter-counter analysis5,70. The relationship between pH $\sim$5.3 Fe solubility and (d) dust concentration15, (e) Total Fe concentration (this study), (f) Dome CA air temperature68. Data points represent two measurements of a single sample, and errors are smaller than the size of points.
Although a recent ocean Fe biogeochemical modelling study\(^1\) observed that Fe concentration in EDC ice of LGM age (left panel) and Berkner Island (BI) ice from MIS 2–3 (right panel), is shown to affect aerosol Fe in ice cores. Regression lines with especially in the Sub-Antarctic zone of the Southern Ocean\(^9,13\). Bioavailable Fe to fully utilize all the upwelled nutrients, surface carbon, and it is the proportion of this carbon that is utilized by carbon cycling of the past thus requires not only knowledge of double export production\(^40\), meaning that the LGM EDC soluble Fe solubility is likely higher than previously considered. Both Fe content (8 wt%) and mean Fe solubility (pH = 5.3 10\(^{-7}\)) in EDC dust are greater than typically assumed by models (~1–10%; refs 17,18,41–44), suggesting that models may underestimate solubility (and therefore bioavailable) Fe fluxes to the Southern Ocean at the LGM. This might especially be the case in modelling studies where 0.5–2% Fe solubility is used\(^17,41–43\). To address this, the median LGM pH ~ 5.3 Fe solubility from this study (6%) is simplest for consideration in models, but the rapid variability in Fe fluxes on short timescales and higher solubilities should also be considered. We attribute variability in aerosol Fe solubility to changes in the composition and fluxes of atmospheric dust arriving at EDC, even on decadal timescales. Therefore, to fully capture the influence of atmospheric Fe on glacial–interglacial cycling, models must take into account both temporal and spatial variability in dust composition and Fe solubility. Closer to source regions, higher dust fluxes may offset lower Fe solubility, and short-term changes in the contribution of different dust types could have important effects on surface ocean biogeochemistry. We anticipate that these better general constraints on the soluble Fe flux to the Southern Ocean will be useful for modellers determining Fe’s role in marine biogeochemical cycles over glacial–interglacial changes, as well as providing insight into the response of the oceans to anthropogenic CO\(_2\) release.

**Methods**

**General laboratory procedures and equipment cleaning.** All ice-preparation was carried out in a cold room (~20 C) at a British Antarctic Survey, Cambridge, and all sample processing and analysis were carried out in clean laboratories at the University of Cambridge. Seawater analysis was carried out at Old Dominion University, USA. All clean work was carried out within a Class 1,000 HEPA-filtered clean laboratory and/or under Class 100 laminar flow air. All glassware used was ultrapure (18.2 M\(\Omega\) cm) and acids were either quartz-distilled (QD) to high purity from reagent grade or purchased as ultrapure (Fisher Scientific). Strict trace metal protocols were used, including wearing polyethylene (PE) gloves to minimize metal contamination during cleaning, processing and sampling. All plastic equipment was rigorously acid-cleaned following the procedures outlined below, which were based on previously published work\(^45\) or adapted from routine cleaning procedures in the Department of Earth Sciences at Cambridge.

New perfluoroalkoxy (PFA) or fluorinated ethylene propylene (FEP) Teflon filter rig, vials, jars, and micro centrifuge tubes were cleaned by sequential immersion in weak (~5%) Decon detergent (24h), warm 50% (v/v) reagent-grade HNO\(_3\) (24–48 h) and 6 M reagent-grade HCl (48 h) and ~1% (v/v) QD-HCl (>3 months), with extensive rinsing with ultrapure water between steps. Bottles were conditioned to neutral pH by filling with ultrapure water for 1 week before use. Whatman Nucleopore PC membranes for filtration (0.2 \(\mu\)m) were cleaned by immersion in 6 M QD-HCl (48 h) and then rinsed extensively with ultrapure water. Membranes were always handled with clean PFA tweezers to minimize contamination. Membranes were stored in and flushed with ultrapure water before use to condition the plastic to near-neutral pH for contact with ice samples. Pipette tips were either acid-cleaned\(^46\) with 50% (v/v) reagent-grade HCl (24 h) and rinsed with ultrapure water (seawater samples), or rinsed twice with 10% (v/v) QD-HNO\(_3\), and twice with ultrapure water before use (non-seawater samples).

For handling and decontamination of ice samples, Kyocera ceramic knives and polytetrafluoroethylene (PTFE) Teflon boards were used. Knives were cleaned by...
Sequential immersion in 6 M reagent-grade HCl (24 h) and 1 M reagent-grade HCl (24 h), followed by extensive rinsing with ultrapure water. PTFE boards were cleaned by immersion in 6 M reagent-grade HCl and then rinsed extensively with ultrapure water. Arm-length PE gloves for handling ice were cleaned by immersion in weak (~0.01% v/v) QD-HCl (24 h) and rinsed thoroughly with ultrapure water to ensure no transfer of acid to samples.

**Ice samples and cutting and decontamination.** Detailed information about the age of ice sampled in this study is shown in Supplementary Data. EDC samples from 23 October 2014 were chosen to cover the LGM (~0.6–1.2 mg kg⁻¹ dust; ref. 15) based on previous work15,46. ‘A cuts’ (or ~1/2 of the core) from 15 separate ‘bags’ of ice (55 cm vertical section; ~50 years) from the EDC ice core were supplied by EPICA (see EPICA cutting plan in Supplementary Fig. 2a). For EDC sampling, ~3 cm pieces were typically cut from either the bottom or top of the bags using a steel bandsaw within the cold room (~20 °C) at the British Antarctic Survey. Two vertical cuts were then made to create three subsamples of identical age (Supplementary Fig. 2b), which were then taken for decontamination and processing to generate subsamples of identical age for total or soluble analysis. The sampling resolution was therefore typically 50 years, although each sample was chosen to cover >3 years. For Rigs, ~959, 1984, and 987 cm samples were also selected at higher resolution (two to four 3 cm subsamples per 50 years) to investigate higher-resolution variability as well as reproducibility between ice subsamples of identical age. Precise age for each 3 cm sample was calculated from depth within each bag and the EDC age scale53. Berkner samples were chosen to cover 25 October 1975 at 26 kyr BP and 25 October 1976 at 26 kyr BP. Samples across the ‘A’ events48 of MIS 3 (36–50 kyr BP) based on the Berkner δ6 record (Mulvaney, unpublished data). Ice was supplied as 3 cm pieces of Berkner core (diameter 50 mm), with 3 cm vertical pieces cut and subsampled analogous to EDC samples.

The outside of ice core material is typically unavoidably contaminated with trace metals from drilling, cutting with bandsaws and handling with gloves49. Thus, the outside of the ice must be decontaminated to remove outer layers where contamination overwhelms the natural signal. Previously, this has been carried out using a melt-head50, polyethylene lathe51, stainless steel blade52, ceramic blade or chisels53. Decontamination may require removal of several cm of core22,51,52,54 during low-dust or less-compacted intervals, or when elements of interest are only present in weak concentrations. Ice samples for rapid filtration during low-dust or less-compacted intervals, or when elements of interest are only weakly cleaned by immersion in 6 M reagent-grade HCl and then rinsed extensively with ultrapure water. PTFE boards were covered to prevent contamination. Liquid that formed was quickly sublimated in several hours, but were typically left overnight to ensure all ice was gone.

Once all ice had sublimed, the desiccator was sealed, disconnected and returned to the laminar flow bench to slowly allow clean air to enter the chamber; this prevented both dust being blown into the air and an increase in pressure and the entry of dirty air from the pump. The bottles containing the dry dust samples were then carefully bagged and taken for ‘seawater-leaching’ procedures (see next section). Blank contamination for the whole procedure over 24 hours was found to be negligible (<2.5 pg or 0 mg Fe per ice sample).

**Seawater-leaching procedures and Fe analysis.** Ice samples for seawater-soluble Fe analysis ('seawater-leaching') were placed on a membrane on a PFA rig within a 1 PFA jar within a glass desiccator at ~20 °C, and quickly placed under water to prevent evaporation. Water was sublimed from the vacuum until all the ice had sublimed, leaving dry dust on the membrane (see ‘Sublimation’ section). The dust on the membrane was then leached with four 60-ml aliquots of low-Fe Ross Sea seawater at 2 °C. The Ross Sea seawater used in leaching was previously collected53 from 10 m depth in the Southern Ross Sea (76°62’S, 169°38’E) using a 25-litre PolyCline tube sampler. The samples were filtered through 0.2 μm polypropylene cartridges and stored in 1251 polyethylene barrels, before being subsampled for this work using clean procedures61. We determined the

**Fe analysis.** Samples from total digestion or rapid filtration were analysed for dissolved Al, Ca, Fe and other cations using a Varian Vista ICP-OES at the University of Cambridge. Each sample was analysed six times and a mean concentration was determined by reference to a quadratic calibration curve generated using standards. Solutions prepared from internal multi-element reference standard for Al, Ca and Fe was >99.6% with precision of 0.41% (1 s.d.; n = 10). Long-term reproducibility of the standard was 100 ± 1% for all elements (n = 60). Detection limits for Fe were 0.1–0.4 ng g⁻¹. We assign 5% uncertainty on data to account for weighing, pipetting and %RSD of six ICP-OES analyses (typically <5%).
background dissolved Fe concentration in this seawater is 4.7 pg g\(^{-1}\) (0.11 ± 0.02 nmol l\(^{-1}\), 2 s.d.; n = 4), consistent with previous determination\(^{6\text{a},6\text{b}}\) of 0.07 ± 0.02 nmol l\(^{-1}\). Each aliquot of seawater was allowed to leach the dust momentarily, vacuum was applied and then the liquid was pulled through and acidified to pH 1.6 with 120 µl of conc. ultrapure HCl. Samples were left acidified for >2 weeks before being analysed for dissolved Fe by FA-81HQ, following published techniques\(^{45}\). This method has low detection limits (< 5 pg g\(^{-1}\)) and analytical precision is typically 5-10% during routine analysis; we therefore applied 10% uncertainty on seawater Fe concentration. Fe concentrations from four leaches were combined in final calculations.

**Berkner Deuterm and parameters and age scales.** The ice core at Berkner Island was drilled to bedrock, and completed in 2005 (ref. 65 and Fig. 2). Deuterm (δD) ratios (expressed relative to the international standard Vienna Standard Mean Ocean Water) were measured at the NERC Isotope Geosciences Laboratory using standard methods\(^{66}\) and have a typical precision of 1.0‰. In Fig. 2b, the Berkner δD record across A events A1 and A2 is shown overlain on the EPICA Dronning Maud Land (EDML) δD\(^{18}O\) record\(^{57}\), which is shown on the EDML age model that has been synchronized to EDC3\(^{57,67}\). In the absence of an official age model for this part of the Berkner Island ice core, Berkner δD is approximately visually tuned to the EDML δD\(^{18}O\) record so that EDML δD\(^{18}O\) Berkner δD and Berkner Fe data are all shown on approximately the EDC3 age scale. Dust and temperature in Fig. 2a are from the EDC core\(^{56,68}\), while atmospheric CO\(_2\) concentration (pCO\(_2\)) in both Fig. 2a is taken from the composite CO\(_2\) record of Schilt et al.\(^{46}\).

**Fe solubility and flux calculation.** Elemental fluxes were calculated:
\[
\text{Fe flux (mg m}^{-2} \text{per year)} = \left[\text{Fe}\right] \times A_k
\]
(1)
where [Fe] is the concentration of Fe (mg kg\(^{-1}\)) in the ice, \(A_k\) is the calculated ice-accumulation rate (kg m\(^{-2}\) per year; ref. 47, Mulvaney, unpublished data). Fe solubility was defined:
\[
\text{Fe solubility (‰)} = 100 \times \left[\frac{\left[pH \approx 5.3 \text{ or seawater soluble Fe}\right]}{\left[\text{total Fe}\right]}\right]
\]
(2)
where \([pH \approx 5.3 \text{ or seawater-soluble Fe}]\) and \([\text{total Fe}]\) are the concentration in ice meltwater (ng g\(^{-1}\)) combined from multiple leaches.

**Calculating nss-Ca.** nss-Ca in each ice-core sample was calculated in this study from measured dissolved Ca and Na concentration data using paired simultaneous equations\(^{46}\):
\[
[\text{ss-Na}^{+}] = [\text{dNa}] - \left[\text{Ca}^{2+} + \left[\text{Na}^{+}\right]\right] / \left[R_\text{m}\right]
\]
(3)
\[
[\text{ss-Ca}^{2+}] = [\text{dCa}] - \left[\text{Na}^{+}\right] / \left[R_\text{m}\right][\text{ss-Na}^{+}]
\]
(4)
where \(ss\) denotes from seashell, nss from non-seasalt sources, \([\text{dNa}]\) dissolved Na concentration at pH ≈ 5.3, \([\text{dCa}]\) dissolved Ca concentration at pH = 5.3, \(R_M\) and \(R_m\) are the Ca/Na ratios in crustal material (1.78) and seashell (0.038), respectively\(^{49}\).

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Author contributions

All authors devised the study. T.M.C performed sample processing and analysis, R.M. supplied samples and data, and the paper was written by T.M.C. and E.W.W. with contributions from other authors.

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