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Calibrating Antarctic ice sheet mass loss due to millennial-scale ocean thermal forcing

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Throughout the Late Pleistocene, millennial-scale cycles in the rate of poleward heat transport resulted in repeated heating and cooling of the Southern Ocean¹. Ice sheet models² suggest that this variation in Southern Ocean temperature can force fluctuations in the mass of the Antarctic ice sheet that transiently impact sea level by up to 15 meters. However, current geologic evidence for Antarctic ice response to this ocean thermal forcing is unable to calibrate these models, leaving large uncertainty in how Antarctica contributes to sea level on millennial timescales. Here we present a >100kyr archive of East Antarctic Ice Sheet response to Late Pleistocene millennial-scale climate cycles recorded by transitions from opal to calcite in subglacial precipitates. ²³⁴U-²³⁰Th dates for two precipitates define a time series for 32 mineralogic transitions that match Antarctic climate fluctuations, with precipitation of opal during cold periods and calcite during warm periods. Geochemical evidence indicates opal precipitation via cryoconcentration of silica in subglacial water and calcite precipitation from the admixture of meltwater flushed from the ice sheet interior. These freeze-flush cycles represent changes in subglacial hydrologic-connectivity driven by ice sheet thickness response to Southern Ocean temperature oscillations around the Ross Embayment. Changes in Ross Embayment ice mass require high ocean-ice heat exchange², and would occur only after retreat of the West Antarctic Ice Sheet³ and large portions of the East Antarctic Ice sheet margin⁴. These results point to high Antarctic ice sheet sensitivity to millennial-scale ocean thermal forcing throughout the Late Pleistocene, and when combined with modeling results², predict that an Antarctic ice volume of at least 2–5 meters sea level equivalent is vulnerable to millennial-scale climate forcing.

One of the persistent challenges involved in both reconstructions and projections of future global mean sea level is determining what sectors of the Antarctic Ice Sheet (AIS) are vulnerable to significant retreat, the timescales on which they are vulnerable, and the processes that trigger their retreat⁵. While the AIS has an ice volume equivalent to 58 m of sea level⁶, it remains unclear what fraction of this ice may contribute to sea level rise over the coming decades to millennia. Long-term geologic records of Antarctic ice sheet configuration and ice flux provide evidence for significant AIS mass loss during glacial terminations⁷, but limited spatiotemporal resolution on centennial to millennial timescales restricts their ability to detect AIS response to smaller magnitude, shorter climate cycles. Nonetheless, global sea level

proxy records indicate that variations on the order of 20m occur on millennial timescales⁸, and in some cases these fluctuations match the Antarctic climate rhythm⁹, implying that the AIS may have exerted considerable control on sea level within these timeframes. Modern observations of ice shelf thinning and ice sheet mass loss from the margins of both the West^{10,11} and East^{12,13} Antarctic Ice Sheets (WAIS and EAIS) suggest that the processes leading to rapid AIS sea level input may currently be underway.

Ice sheet simulations² demonstrate the potential for AIS mass fluctuations on short timescales through perturbation of buttressing ice shelves^{3,4} brought on by changing Southern Ocean (SO) temperature¹⁴ (hereafter referred to as ocean thermal forcing). Millennial-scale SO temperature oscillations are driven by the rate of Atlantic Meridional Overturn Circulation (AMOC)¹⁵, which is responsible for cross-equatorial heat transport from the Southern Hemisphere to the Northern Hemisphere (SH and NH). Changes to the intensity of AMOC result in inverse interhemispheric temperature cycles¹⁶ recorded by isotopic climate proxies in polar ice cores, termed Dansgaard-Oeschger cycles in the Greenland and Antarctic Isotope Maxima (AIM) events in Antarctica. For example, during times of decreased AMOC or slow northerly transport of heat — e.g., 48 and 47ka in figure 1a, c — the SH temperature increases at the expense of NH, which is manifested as an increase in the $\delta^{18}\text{O}$ composition in Antarctic ice cores and a decrease in $\delta^{18}\text{O}$ composition in Greenland ice cores. As the AMOC circulation recovers — e.g., at 46.7ka in figure 1a, c — the NH temperature warms rapidly on decadal timescales while the SH gradually cools. This “bipolar seesaw” results in Antarctic atmospheric temperature shifts of only 1-2°C¹⁷, but feedback between AMOC and the strength of the SH westerly winds¹⁸ causes significant fluctuations in the SO temperature structure by modulating the upwelling rate of warm circumpolar deep waters around the AIS¹⁹.

Regional differences in ice bed topography, drainage geometry, and thickness⁶ in peripheral sectors of Antarctica lead to geographic variations in grounding line vulnerability to ocean thermal forcing. For example, numerical experiments indicate that major drainages of ice grounded below sea level in the Weddell Sea and Prydz Bay Embayments respond sensitively to even modest ocean temperature increases, while significant ice loss from the Ross Embayment and the EAIS margins require greater thermal forcing² (Extended Data Fig. 1). In models simulating AIS response to temperature changes in the Southern Ocean, the majority of this sensitivity difference is expressed in the parameter describing heat exchange between the ocean and the ice sheet, which represents one of the largest sources of uncertainty in projections of Antarctic behavior during centennial to millennial-scale climate change². Geologic evidence of millennial-scale AIS evolution could calibrate this heat exchange parameter by describing what regions of the ice sheet lost or gained ice mass following a change in ocean temperature. However, existing records are limited to the highly sensitive Weddell Sea sector^{20,21}, and therefore cannot confirm a change in mass from the less sensitive Antarctic sectors, which make up the majority of the AIS margin. Given this lack of geologic constraint on millennial-scale AIS response to Southern Ocean temperature fluctuations, best estimates for Antarctic contribution on these timescales is between 0 and 15 meters sea level equivalent². Therefore, a long-term, high-resolution record of AIS evolution from a less temperature-sensitive ice sheet sector, as we document here, will improve our ability to constrain the broader Antarctic contribution to sea level on sub-orbital timescales and will help to parameterize projections of future AIS mass loss.

East Antarctic Ice Sheet Subglacial Hydrologic Response to Southern Ocean Temperature

In this study, we present observations from a novel archive of subglacial thermal and hydrologic evolution recorded by chemical precipitates that formed beneath the EAIS. These samples are deposited in aqueous systems beneath the ice sheet on the EAIS side of the Transantarctic mountains (TAM), and are transported to the surface in basal ice, which erodes them from subglacial environments and deposits them in supraglacial moraines. Results are presented here from two samples: PRR50489 formed in the David Glacier catchment and was exhumed at Elephant Moraine, and MA113 formed beneath ice feeding Law Glacier and was exhumed at the Mount Acherar moraine (Fig. 2). These precipitates are 3 and 9cm thick respectively, with alternating layers of calcite and opal indicating cyclic change in the subglacial waters (Extended Data Fig. 2).

We measured ²³⁴U-²³⁰Th ages on eleven opal layers from PRR50489 that constrain the timeframe of precipitation from 230 to 147ka (Fig. 1i), and five opal and calcite layers from MA113 ranging in age

from 55 to 42ka (Fig. 1f). Depth profiles of Si and Ca concentration, collected using Energy Dispersive X-ray Spectroscopy, provide a continuous representation of sample mineralogy: with high Ca areas representative of calcite and low Ca areas representative of opal. We construct depositional age models for each sample by using linear interpolation between dated layers, and pair these age-models with Ca concentration to create timeseries describing the oscillations of precipitate mineralogy. Mineralogic timeseries reveal a temporal cyclicity in opal deposition, with PRR50489 containing opal layers precipitated every 8-10kyr between marine isotope stages (MIS) 7 and 6, and MA113 containing opal layers precipitated every 2-4kyr during MIS 3. To investigate a possible link between cycles of precipitate mineralogy and climate, we compare mineralogic timeseries for each precipitate (Fig. 1f, i) with climate proxies in both Antarctic^{17,22} (Fig. 1a,b) and Greenland²³ (Fig. 1c) ice cores. Comparison between the Ca-spectra and Antarctic temperature proxies shows a strong similarity, with calcite formation (high Ca wt%) during warm AIM peaks, and opal formation (low Ca wt%) during Antarctic cold periods (Fig. 1). These data indicate that thermal and hydrologic conditions beneath the EAIS respond to bipolar-seesaw-driven Antarctic climate cycles on sub-orbital timescales.

To understand the link between ocean-atmosphere-cryosphere teleconnections and the composition of subglacial waters, we first utilize geochemical and isotopic measurements to characterize the waters from which opal and calcite originate. Figure 3 shows the carbon and oxygen isotopic compositions of opal and calcite forming waters for PRR50489 (Fig. 3a) and MA113 (Fig. 3b), which provide evidence that opal and calcite form from two different subglacial fluids. The oxygen isotopic compositions ($\delta^{18}\text{O}_{\text{VSMOW}}$) of opal and calcite forming waters are distinctly different, with calcites forming from waters with extremely depleted $\delta^{18}\text{O}$ (<-50 ‰), and opals forming from waters with $\delta^{18}\text{O}$ values up to 7 ‰ more enriched (Fig. 3). Another distinguishing characteristic of opal and calcite forming waters are their cerium anomalies (Ce^*), a proxy for redox conditions²⁴ (Extended Data Fig. 3c). In both samples, Ce^* correlates with sample mineralogy, with calcite Ce^* values indicating precipitation from oxidizing waters ($\text{Ce}^* < 1$), while the most ^{18}O enriched opals exhibit Ce^* values indicating precipitation from reduced waters ($\text{Ce}^* > 1$) (Fig. 3). In most cases, $\delta^{18}\text{O}$ opal values scale with Ce^* , suggesting that mixing between oxidized and reducing water occurs during the formation of both minerals (Fig. 3). Calcite in both precipitates has $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ compositions that define a trend consistent with formation by mixing between two endmember fluids (Fig. 3). To match the trends in the calcite data for PRR50489 and MA113, one endmember fluid must have ~97% and ~80% of the total carbon in the system, indicating that the calcite forming water is carbon-rich and isotopically light with respect to carbon and oxygen. The depleted $\delta^{18}\text{O}$ compositions of this endmember suggest derivation from meltwaters generated beneath the EAIS interior, as similarly depleted $\delta^{18}\text{O}$ values are found only in ice from the high polar plateau^{25,26}. Depleted $\delta^{13}\text{C}$ compositions (-23 ‰ for PRR50489 and -18 ‰ for MA113) and high carbon concentration of calcite forming subglacial waters suggest that their carbon is sourced from subglacial organic matter that is oxidized during microbial respiration, consistent with observations beneath the EAIS²⁷. Together, redox and isotopic data support the idea that calcite precipitating fluid is a glacial meltwater derived from beneath the EAIS. The heaviest $\delta^{18}\text{O}$ compositions of the opal endmember fluid (-46.15‰ for PRR50489 and -52.10‰ for MA113) suggest that these waters originate closer to the ice sheet margin, and they match the $\delta^{18}\text{O}$ of ice proximal to the region where samples were exhumed^{25,28}. Mixing model results require that the $\delta^{13}\text{C}$ of opal forming waters is heavier (~0 ‰) and the carbon concentration is much lower than in the calcite forming meltwater. Similar mixing relationships between $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{18}\text{O}$ place ~98% - 99% of the total Sr in the opal forming waters, an observation supporting opal formation from a highly concentrated water, and calcite formation from a relatively dilute meltwater (Extended Data Fig. 10). The strontium and calcium concentrations in natural waters scale with one another²⁹ due to their similar geochemical behavior. As such, $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{18}\text{O}$ mixing relationships demonstrate that 98 – 99% of both strontium and calcium are sourced from the opal forming water, while the calcite forming fluid is relatively dilute. Collectively, low carbon and high calcium concentration, heavy $\delta^{13}\text{C}$ composition and reduced Ce^* signature support the idea that opal layers precipitate from a subglacial brine. Candidate compositions for opal forming waters that are observed in the modern ice sheet include CaCl_2 brines that emanate from beneath the EAIS within the McMurdo Dry Valleys (MDV)³⁰. In addition to being reduced³¹, $\delta^{13}\text{C}$ heavy, carbon poor and calcium rich, the bulk REE

and $^{234}\text{U}/^{238}\text{U}$ of MDV brines^{32,33}, match opal compositions from subglacial precipitates (Extended Data Fig. 4) and X-Ray fluorescence microprobe images show high abundance of Cl^- in opal layers (Extended Data Fig. 5). In contrast, the high carbon and low calcium concentrations, extremely depleted $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ compositions, and oxidized Ce^* signature indicate calcite forming are close in composition to glacial meltwaters originating beneath the high domes of East Antarctica. Subglacial water measurements from the EAIS are few, but one candidate water is the high carbon, low salinity jökulhlaup water measured at Casey Station³⁴, which flush from subglacial lakes beneath Law Dome, and, like the precipitates studied here, produced subglacial calcite coincident with a 72 ka AIM warm period³⁵.

We use the water speciation program PHREEQC³⁶ to explore the conditions under which precursory waters precipitate opal during cold periods and calcite during warm periods, while matching geochemical conditions identified in the aforementioned analyses (see Methods for full description of PHREEQC models). Monomineralic opal layers represent periods of amorphous Si saturation, which can occur in subglacial environments due to cryoconcentration^{37,38}. Extended Data figure 6 shows a set of PHREEQC simulations that demonstrate opal saturation during freezing of a CaCl_2 brine, while the deficiency of carbon in the brine precludes calcite precipitation. Since geochemical data suggest calcite precipitation from an oxidized, carbon-rich, and isotopically distinct glacial meltwater, we explore conditions under which calcite saturates upon mixing of opal-forming brine with plausible compositions of EAIS basal meltwater. Mixing the Casey Station meltwater with opal-forming brines, we identify a strong supersaturation in calcite over a broad range of mixing proportions (Extended Data Fig. 7), and a cessation of opal precipitation consistent with discrete calcite pulses during mixing. This model predicts that calcite precipitation occurs immediately upon addition of meltwater to brine, while there could be a significant lag in opal precipitation as the aqueous system transitions to basal freezing and cryoconcentration and in time becomes saturated with opal. Indeed, we may be seeing the effects of this lag in the comparison between climate cycles and precipitate mineralogy, where nearly all warming events have a corresponding calcite layer (e.g., 180 and 190ka), while some particularly short-lived cold events (<4kyr duration) do not have a detectable corresponding opal layer (e.g., 163 and 173 ka).

Collectively, the results presented here indicate that two chemical precipitates, separated by ~900km and deposited tens of thousands of years apart, form as a consequence of subglacial hydrologic cycles that match the patterns of Antarctic temperature changes, implying a link between AIS basal conditions and Antarctic climate. More specifically, the site of precipitate formation oscillates between the freezing of local brines sourced from the proximity of the TAM during cold periods, and the influx of far field EAIS meltwaters during warm periods. Predictions for subglacial thermal conditions³⁹ indicate that large portions of the EAIS are at, or near, the pressure melting point, with widespread meltwaters in the ice sheet interior. In areas on the ice sheet edges, thinner ice permits pervasive basal freezing. Although the exact locations of sample formation are unknown, based on the sample collection sites (Fig. 2) and the short travel distance of most glacial sediment⁴⁰, the most parsimonious explanation is that these chemical precipitates formed close to the boundary between basal melting and freezing regimes which exists where the ice sheet thins as it encroaches on the TAM³⁹ (Extended Data Fig. 8). We thus propose that the cycles of basal melting and freezing interpreted from our opal-calcite precipitates are the result of migrations of this thermal and hydrologic boundary, causing changes in the connectivity between waters from the interior and edge of the ice sheet following millennial-scale climate cycles (Extended Data Fig. 8). Below, we explore a mechanism for these subglacial freeze-flush cycles.

Millennial-Scale Ice Sheet Thickness Changes Driven by Ocean Thermal Forcing

The key finding from our subglacial precipitate archive is that millennial-scale ocean-atmosphere-cryosphere teleconnections cause a hydrologic response beneath the EAIS where AIM warm phases drive increased melting and enhanced hydrologic connectivity between the ice sheet margin and interior. Subsequent AIM cold phases then promote expansion of subglacial freezing beneath the margin causing the subglacial aqueous system at the ice sheet edge to become hydrologically isolated from the ice sheet interior. We investigate how climate cycles may drive subglacial hydrologic change using a reduced complexity model of ice sheet thermodynamics, which simulates basal melting and freezing rates (see

supplementary text for full description). This model assumes that the ice thickness at the foothills of the TAM is a linear function of the isotopic records of climate from either EDC (PRR50489) or WDC (MA113) ice cores (Fig. 1 a, g). This temporal forcing feeds into changes of ice surface slope, basal shear stress, ice velocity, and basal shear heating. The calculated variations in basal freezing/melting rates in the two inferred regions of sample formation provide a satisfactory match to the radiometrically dated records of calcite and opal precipitation from PRR50489 and MA113 (Fig. 1e, h). Our results are consistent with linear sensitivity of ice thickness in the Ross Embayment to the climatic variations reflected in isotopic ice core records from WAIS and EAIS, which are dominated by the variability in ocean conditions with additional impact of atmospheric temperature variability⁴¹. Scaling laws for ice sheet volumes⁴² indicate high sensitivity of ice volume to ice thickness changes, implying that the volume of AIS exhibited non-linear sensitivity to the millennial-scale climate forcing recorded in Antarctic ice cores. Our results show that the AIS experiences significant ice thickness and ice volume fluctuations not only in response to large climate warming events that lead to terminations of major glacial cycles, but also in response to climate fluctuations that are both smaller in amplitude and shorter in duration than major terminations, such as AIM events. This finding has implications for assessment of future mass loss from Antarctica triggered by ongoing anthropogenic warming and for interpretation of distal evidence for sea-level high stands during Quaternary warm climate periods⁸.

The periodic ice thickness change in regions adjacent to our sample locations suggested by our precipitate record corroborate models showing regional-scale ice volume fluctuations during periods of Antarctic millennial-scale climate variability². The driving mechanism for ice mass fluctuation on these timescales is generally regarded to be grounding line migration stemming from subsurface melting of ice shelves⁴³. During AIM cold periods, grounded ice advances towards the continental shelf edge. As the bipolar seesaw takes effect, the ocean-atmosphere teleconnection between slowing AMOC and strengthening SH westerly winds drive upwelling of warm circumpolar intermediate waters⁴¹, which contact the base of the Antarctic ice shelves and accelerate melting. This ocean-driven reduction in ice shelf thickness reduces back stress and enhances grounding line ice discharge generating instability and retreat¹⁴, resulting in enhanced shear stress and consequent melting at the ice sheet base. Comparison between SO sea surface temperature¹ and our subglacial precipitate record shows a similar pattern of millennial-scale variability (Fig.1d), corroborating the idea that bipolar seesaw driven SO temperature changes cause ice sheet thickness variations during AIM cycles². Therefore, we conclude that the freeze-flush cycles that lead to opal-calcite cycles in subglacial precipitates reflect ocean-forced AIS thickness changes (Fig. 2).

Simulations of AIS sea level contribution during millennial-scale climate cycles suggest that SO warming can lead to Antarctic input ranging from 0 to 15 m depending on SO temperature, the duration of warming, and the heat flux between the ocean and ice sheet². Model outputs² predict spatial variability in ice sheet thickness changes and grounding line flux depending on these three variables (Fig. 2). On the basis of the Ross Embayment grounding line retreat implicit in our results, as well as recently published records of SO sea surface temperature during this time¹, we can place bounds on modeled AIS sea level contributions during Late Pleistocene AIM cycles. The widest range of uncertainty for the Antarctic contribution to sea level changes of the three previously mentioned variables results from heat flux between the ocean and ice sheet. However, for thickness change to occur proximal to the sampling locations of our subglacial precipitates, the ice-ocean heat exchange coefficient, used in ref. ² much be between 7 and 15 m a⁻¹ K¹ (Extended Data Figure 1). Within these bounds, millennial-scale climate cycles of a given duration and SO temperature would contribute a sea level equivalent equal to or greater than 2.5 – 5 m during AIM events, which would emanate from significant retreat of the WAIS and thinning over marginal sections of the EAIS (see Methods for full description of ocean-ice heat flux estimates and sea level input; Fig. 2).

Throughout the Pleistocene, global sea level has fluctuated by >100 m⁸ predominantly due to orbital forcing⁵. Within our current interglacial, sea level fluctuations of this magnitude pose no immediate threat on human timescales, but there remains a possibility that the AIS will respond to more abrupt climate events. Here we show that over the past ~230kyr, millennial-scale ocean temperature fluctuations caused periodic widespread Antarctic ice loss and regrowth. Our results reveal millennial-scale ice sheet thinning in the Ross Sea Embayment, which provides constraints on the magnitude of heat-exchange between the

246 Southern Ocean and the AIS. Based on these this new calibration, we estimate an Antarctic sea level input
247 equivalent to 2–5 m during AIM cycles. The >100kyr temporal constraints provided by this novel
248 paleoclimate archive provide the first evidence that the AIS has responded to millennial-scale ocean thermal
249 forcing outside of the last glacial termination, implying that the majority of the Antarctic margins is
250 vulnerable to this forcing during the next millennia.
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Fig. 1 | Comparison of precipitate mineralogy with climate records. Polar temperature records from **a.** West Antarctic Divide Ice Core (WDC)²². Our reduced complexity model of ice thermodynamics for sample MA113 is forced by ice thickness changes calculated as a linear function of the WDC isotopic record, with scale on the right y-axis. **b.** Taylor Dome Ice Core (TDC)^{44,45}. **c.** Northern Greenland Ice Core Project (NGRIP)²³. **d.** Southern Ocean sea surface temperature anomalies from stacked drill core records¹. **e.** Reduced complexity ice sheet model output of basal heat budget over the time frame of sample MA113 in units of mm/year of equivalent basal freezing rate. Negative values indicate freezing. Positive values correspond to basal melt but are truncated at 0 mm/year. **f.** Subglacial precipitate sample MA113 Ca

concentration. Two versions of the record between 46.5ka and 52ka are shown: one based on opal and calcite accumulation rate (orange), and the second based on linear interpolation between ^{234}U - ^{230}Th ages (grey dashed). **g.** δD record from EPICA Dome C Ice Core (EDC)^{17,46}. To highlight bipolar-seesaw-related temperature fluctuations, the EDC record is detrended and converted to a z-score by zero-mean normalization to eliminate orbital trends. Forcing for our reduced complexity model of ice thermodynamics is provided by ice thickness changes calculated as a linear function of the EDC isotopic record, with scale on the right y-axis. **h.** As in **e** over the time frame of sample PRR50489. Reduced complexity model output of basal heat budget over the time frame of sample PRR50489 in units of mm/year of equivalent basal freezing rate. Negative values indicate freezing. Positive values correspond to basal melting but are truncated at 0 mm/yr. **i.** Subglacial precipitate sample PRR50489 Ca concentration. High values in precipitate records represent calcite precipitation; low values represent opal precipitation. Markers above **f** and **i** show locations of ^{234}U - ^{230}Th ages with 2σ uncertainties; square markers represent calcite ages; circles represent opal ages. Records in **c**, **d**, and **g** are synchronized to AICC2012 chronology; the record in **a** is synchronized WD2014 chronology, the record in **b** is visually tuned to match the record in **a**. Isotope ratios are on the VSMOW (Vienna Standard Mean Ocean Water) scale. Marine Isotope substages are marked in grey and labeled. AIM events are marked in yellow and numbered. Yellow areas represent millennial-scale warm periods, white areas represent cold periods.

Fig. 2 | Antarctic Ice Sheet Thickness Change between Cold and Warm Climate Phases. Contour map of the change in ice sheet thickness between millennial-scale cold periods and warm periods² in 100 m intervals. Darker areas are thinner during warm periods and thicker during cold periods. Markers indicate locations of spectra shown in figure 2. Sample locations occur adjacent to areas that experience >100 m thickness change during these timeframes. Yellow line delineates the grounding line during millennial cold period. Ice core locations shown as squares; precipitate locations shown as circles. Ice core abbreviations as in figure 1.

Fig. 3 | Stable isotope mixing models for precipitates PRR50489 and MA113. a. $\delta^{18}\text{O}$ of the precipitating fluid versus $\delta^{13}\text{C}$ composition of the C source, plotted for PRR50489 calcite (markers) and opal (horizontal lines). Endmembers (stars) include an opal precipitating fluid that is a carbon poor, reduced brine; and a calcite precipitating fluid that is a carbon rich, oxidizing meltwater. Solid curved line represents mixing model between the two endmembers⁴⁷. To fit calcite data, mixing model requires a 97:03 ratio of C concentration between the meltwater and brine. **b.** As in **a**, but data are from sample MA113. To fit calcite data, mixing model requires an 80:20 ratio of C concentration between the meltwater and brine. Isotopic compositions corrected to water compositions assuming equilibrium fractionation during calcite formation and a formation temperature corresponding to a datum specific mixing ratio between the -3.5°C brine and the -1.5°C meltwater (full description is provided in Methods). Dashed lines represent mixing models with different C ratios. All data are color coded by Ce^* value, with blue being the lowest, most oxidizing values, and yellow being the highest, most reducing values

Methods

Subglacial precipitate opal-calcite timeseries

Time series describing mineralogic shifts between opal and calcite in two subglacial precipitates are derived from ^{234}U - ^{230}Th ages combined with elemental characterization (see supplementary text for full ^{234}U - ^{230}Th dating methods). Elemental maps showing calcium and silicon concentration (Extended Data Fig. 2) were produced using Energy Dispersive X-ray Spectroscopy (EDS) measured on the Thermo Scientific Apreo Scanning Electron Microscope (SEM) housed at UCSC. EDS data were generated using an Oxford Instruments UltimMax detector and were reduced using AZtecLive software. To quantify the opal-calcite transitions in the samples, Si and Ca concentration data were produced from line scans across precipitate layers (Extended Data Fig. 2). For sample MA113, detritus within two calcite layers results in Si peaks that do not correspond to opal. These areas are identified using Al and are corrected to reflect a calcite composition. An age versus depth model was produced for each precipitate by linear interpolation between each dated layer. In sample MA113, no dates were produced for layers corresponding to the timeframe between 48ka and 52ka, so the primary age versus depth model is derived by applying an accumulation rate for opal and calcite based on the two accumulation rates from the rest of the sample (Fig. 1f, orange curve). A secondary age versus depth model was also produced between 48ka and 52ka using linear interpolation (Fig. 1f, grey, dashed curve), but sparse data coverage during this timeframe likely makes this curve less accurate for this period. Timeseries in figure 1f and 1i were then generated by plotting the age versus depth model, against Si and Ca concentration spectra. 2σ uncertainties on each individual U-series age are between 0.5% and 2% for PRR50489 and between 1% and 5% for MA113; we interpolate across the mean age for each layer. Within these error bounds, we are not able to estimate leads or lags between the subglacial hydrologic system and climate cycles. Nonetheless, stratigraphic consistency between dated layers, the regular frequency of mean ages, and the striking similarity between our mineralogic timeseries and climate proxy records supports our conclusion of a link between climate teleconnections and subglacial hydrology. Furthermore, as was previously mentioned, calcite layers form rapidly upon introduction of carbon-rich, alkaline waters from the EAIS interior to the marginal system, and the system then slowly transitions back to opal precipitation after hydrologic connectivity is shut off and the waters freeze. Therefore, it is possible that there is missing time between calcite layers that is not accounted for by our linear interpolation. However, based on the regularity of opal depositional cycles, and the similarity between precipitate opal-calcite cycles and climate proxies, these unconformities do not represent enough time to disrupt the millennial-scale cyclicity of the precipitate mineralogy.

Geochemical analyses

Stable Isotopic Analyses

Carbonate isotope ratios ($\delta^{13}\text{C}_{\text{CO}_3}$ and $\delta^{18}\text{O}_{\text{CO}_3}$) were measured by UCSC Stable Isotope Laboratory using a Thermo Scientific Kiel IV carbonate device and MAT 253 isotope ratio mass spectrometer. Referencing $\delta^{13}\text{C}_{\text{CO}_3}$ and $\delta^{18}\text{O}_{\text{CO}_3}$ to VPDB is calculated by two-point correction to externally calibrated Carrera Marble 'CM12' and carbonatite NBS-18². Externally calibrated coral 'Atlantis II'³ was measured for independent quality control. Typical reproducibility of replicates was significantly better than 0.05 ‰ for $\delta^{13}\text{C}_{\text{CO}_3}$ and 0.10 ‰ for $\delta^{18}\text{O}_{\text{CO}_3}$.

Opal layers were analyzed at the Stanford University Stable Isotope Biogeochemistry Laboratory for $\delta^{18}\text{O}_{\text{SiO}_2}$ by conventional BrF_5 fluorination (e.g. refs. ^{4,5}) and measured with O_2 gas as the analyte on a Thermo Scientific MAT 253+ dual-inlet isotope ratio mass spectrometer (IRMS)^{6,7}. Briefly, 2-3 mg opal samples were loaded into nickel reaction tubes as described in ref.⁵ and heated for 2 hours at 250 °C at high vacuum. Samples were then repeatedly pre-fluorinated at room temperature with 30 mbar aliquots of BrF_5 until <1 mbar of non-condensable gas was present. A 30x stoichiometric excess of BrF_5 was added to the nickel tubes and sealed. The nickel tubes were then heated at 600 °C for 16 hours to quantitatively produce O_2 . The generated O_2 gas is then sequentially released into the cleanup line, cryogenically cleaned and frozen onto a 5Å mole sieve trap immersed in liquid nitrogen, equilibrated at room temperature with the IRMS dual-inlet sample-side bellows and measured for $\delta^{18}\text{O}$ against a reference tank of known $\delta^{18}\text{O}$.

composition (24.3‰) (for details ref. ⁷). Opal $\delta^{18}\text{O}$ is reported based on daily corrections made to four primary silicate standards (NBS-28, UWG-2, SCO and L1/UNM_Q, which are quartz, garnet, olivine and quartz, respectively), spanning $\sim 13\text{‰}$, and have been recently calibrated to the VSMOW2-SLAP2 scale^{5,8}. Three secondary standards (BX-88 (Stanford Laboratory internal standard), UCD-DFS (obtained from H. Spero, UC Davis; values reported in ref. ⁹) and PS1772-8 (obtained from J. Dodd, Northern Illinois University; measured at U. of New Mexico and reported in ref ¹⁰, which are quartz, opal-CT and opal-A, respectively) were also analyzed over the course of the analyses. Replicate measurements of standards demonstrate reproducibility of $<0.3\text{‰}$ for all secondary and primary standards except the PS1772-8 standard, though heterogeneity in this standard is suspected with laboratory averages reported in the literature¹⁰ ranging from 40.2 to 43.6‰ (average value of 41.5‰ in this study).

Sr Isotopic Analyses

Sr isotopic measurements were made at the UCSC Keck Isotope Laboratory. Sr compositions are measured on a TIMS in a one sequence static measurement: ⁸⁸Sr is measured on the Axial Faraday cup, while ⁸⁷Sr, ⁸⁶Sr, ⁸⁵Rb, and ⁸⁴Sr are measured on the low cups. Accuracy of the ⁸⁷Sr/⁸⁶Sr measurements is evaluated using Sr standard SRM987 compared to a long-term laboratory average value of 0.71024, with a typical reproducibility of ± 0.00004 .

LA ICP-MS Methods

Laser ablation inductively coupled plasma–mass spectrometry (LA ICP-MS) analyses were conducted at the Facility for Isotope Research and Student Training (FIRST) at Stony Brook University. Analyses were made using a 213 UV New Wave laser system coupled to an Agilent 7500cx quadrupole ICP-MS. The National Institute of Standards and Technology (NIST) 612 standard was used for approximate element concentrations using signal intensity ratios. Laser data were reduced in iolite¹¹; element concentrations were processed with the trace-element data reduction schemes (DRS) in semiquantitative mode, which subtracts baselines and corrects for drift in signal.

Geochemical models of mineralogic cyclicity in subglacial precipitates:

To understand the conditions under which discrete pulses of opal and calcite are precipitated following cold and warm Antarctic climate periods respectively, we integrate geochemical and isotopic characterization of the precipitates to inform simulations run using the aqueous geochemical modeling program PHREEQC¹². The high ion concentrations of subglacial fluids necessitates the use of the Pitzer specific ion interaction approach, which allows PHREEQC to model the aqueous speciation and the mineral saturation index of brines, and has been shown to yield results¹³ consistent with the subzero database FREZCHEM¹⁴. Our modeling approach to simulating opal-calcite transitions can be describe in three parts: 1) Identify the water composition and conditions under which opal will precipitate and calcite will not; 2) Identify the composition and volume of water required to mix with opal forming fluids to produce calcite; 3) Utilize the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ isotopic composition of calcite and opal, along with the known or inferred composition of mixing waters (Fig. 3) to constrain the relative volumes of brine and meltwater, thereby testing the validity of the mixing model. While the exact ionic strength of subglacial fluids and temperature of the subglacial aqueous system is unknown, we outline a plausible scenario for discrete layers of opal and calcite the fit modeled conditions at the base of the ice sheet¹⁵, and the geochemical constraints measured in precipitates.

PHREEQC Simulations Part I

Opal precipitation occurs when a solution is saturated with respect to amorphous silica. Opal solubility is both temperature and pH dependent¹⁶, with lower pH favoring precipitation. The silicon concentrations of subglacial waters¹⁷ and mature brines that emanate from ice sheets¹⁸ are typically tens of ppm, —values similar to other surface waters¹⁹— and Si concentration does not scale with total dissolved solids (TDS)²⁰. At these relatively low Si concentrations, saturation of amorphous silica cannot be achieved without a mechanism to concentrate Si in solution. For aqueous systems beneath an ice sheet, this mechanism is very

likely cryoconcentration via subglacial freezing, which extracts water from the cavity at the base of the ice sheet, concentrating solutes and raising mineral saturation^{21–23}. Yet, most surface waters upon reaching saturation of amorphous silica will also be at saturation for calcite^{22,23}, thus not matching the discrete opal layers observed in our precipitates. This suggests that the opals form from a mature brine²⁰ that is relatively free of HCO_3^- . A candidate fluid that fits these compositional criteria are CaCl_2 brines, which occur in the McMurdo Dry Valleys (MDV) as shallow subsurface waters^{24–27}, deep groundwaters^{13,26,28}, and surface waters^{29–31}, most notably feeding Lake Vanda^{18,32} and Don Juan Pond (DJP)^{28,33,34}. Ca-Cl -rich brines also occupy regions that were previously covered by the North American²⁰ and Fennoscandian ice sheet³⁵, implying that they are a natural product of fluid isolation beneath ice sheets. Therefore, CaCl_2 brines are a plausible composition for brine beneath the EAIS. The most well geochemically characterized MDV brines are those that feed DJP, therefore, we explore opal precipitation by equilibrating DJP brine with ice, calcite, and opal at a range of temperatures between -5°C to 5°C . At full concentration, DJP brine causes melting of the overlying ice due to its exceptionally high ionic strength, resulting in significant dilution of the original solution, which inhibits opal precipitation (Extended Data Fig. 5a). Subsequent simulations of 10x and 50x diluted DJP brine over the same range of temperatures result in a gradual increase of opal saturation due to the incremental removal of water via cryoconcentration (Extended Data Fig. 5b, c). In these model runs, opal precipitation is controlled by the amount of water removed from the solution by freezing, which itself is controlled by ionic strength. At 10x concentrated, the solution does not freeze enough to drive opal precipitation, while opal is precipitated from the 50x diluted solution between -3°C and -4°C . A fourth PHREEQC model was run equilibrating DJP brine with ice, calcite, and opal over this temperature range, indicating that opal precipitation is reached once $\sim 75\%$ of the water in the original solution is lost via freezing, which occurs at -3.5°C (Extended Data Fig. 5d).

PHREEQC Simulations Part 2

Simulation of calcite precipitation during interglacial warm periods assumes that ‘meltwaters’ are mixed with the concentrated ‘glacial brines’ from part 1. The decision to model calcite precipitation using the admixture of new waters, rather than to reverse subglacial freezing, is based on the disparity in geochemistry between calcite and opal forming waters. Based on the hypothesis that calcite layers form when waters from the EAIS interior are flushed to the ice sheet edge (Extended Data Fig. 7), meltwaters driving calcite precipitation are likely to have become enriched in alkalinity and dissolved ions through water-rock interaction and chemical weathering of silicate minerals in the substrate during long-term storage beneath the EAIS. Calcite and opal data in $^{87}\text{Sr}/^{86}\text{Sr}$ vs $\delta^{18}\text{O}$ space provide further evidence that the two endmember waters —brine and subglacial meltwater— dissolve silicates with different provenance. Extended Data figure 10 shows $^{87}\text{Sr}/^{86}\text{Sr}$ vs $\delta^{18}\text{O}$ mixing curve between opals and calcite, showing that the brine provides 98% of Sr to the system from a source with an $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.7135, while the meltwater endmember has a far lower concentration of Sr (2 %) derived from a reservoir with an $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.709. These data are consistent with a brine that weathers silicate minerals over long periods, and a meltwater that drives silicate weathering with a very different provenance over a relatively short time duration. The $\delta^{13}\text{C}$ of the calcite (-23‰) (Fig. 3, Extended Data Fig. 2) also provides evidence for the chemical composition of meltwaters, implying that they accumulated carbon through microbial respiration, which does not fractionate during the transition from aqueous CO_2 to HCO_3^- if 100% of the carbon undergoes this conversion. Given, the similarity between $\delta^{13}\text{C}$ composition of calcite and that of respired carbon, it is unlikely that dissolution of sedimentary carbonates took place in the meltwater, which would have added a significantly less depleted source of carbon to the reservoir. This framework suggests that candidate compositions for calcite endmember fluids are waters with a similar history of subglacial exposure to glaciated sediments. The EAIS waters that best fit this description are jökulhlaup waters³⁸ observed near Casey Station, Antarctica. Using PHREEQC, we explore mixing of brine from part 1 with jökulhlaup waters from Casey Station³⁸, by simulating a range of possible mixing ratios between brine and meltwater. We assume, based on the $\text{Ca}:\text{Sr}$ ratios from other surface water systems that contain CaCl_2 brine, that the ratio of Ca concentration between the brine and meltwater matches the ratio of Sr concentration between the two fluids (brine:meltwater = 98:2). Results show that without at least 30% meltwater the mixture too diluted with respect to Ca and

HCO₃⁻ to precipitate calcite. PHREEQC mixing models successfully produced discrete pulses of calcite with mixtures between 30% and 80% meltwater; conditions under which the admixture is undersaturated with respect to opal because the solution is too dilute with respect to Si and is supersaturated with respect to calcite leading to precipitation (Extended Data Fig. 5b). Therefore, the addition of carbon-rich, alkaline meltwaters to opal precipitating, Ca-Cl-rich brines can trigger calcite supersaturation driving rapid calcite growth, consistent with our geochronologic outputs and calcite morphology. Collectively this modeling effort, along with the timescale data presented in figure 1, and the fibrous crystal textures suggests that calcite forms rapidly after meltwaters to the subglacial aqueous system. However, the relative volume of meltwater added is unclear from these results alone and requires further isotopic constraints.

C and O Isotopic Mixing Models Part 3

For both the calcite and opal oxygen isotope data, the formation water $\delta^{18}\text{O}$ (as plotted in our figures and used in mixing model) is calculated using the appropriate equilibrium water-mineral fractionation factors. For the temperature of precipitation, we use the ideal temperature for opal precipitation (-3.5°C shown in Extended Data Fig. 5) as the brine endmember temperature. Based on an addition of 2°C via shear heating to generate melting shown by reduced complexity ice sheet model outputs, we use -1.5°C as the meltwater endmember temperature. We then calculate the temperature of precipitation for each measured opal and calcite based on their relative amounts of brine and meltwater, calculated by their position on the stable isotope mixing model presented in figure 3. For calcite we use the empirical $1000\ln\alpha$ versus $1/T$ relationship of³⁹ and for opal the $1000\ln\alpha$ versus $1/T^2$ relationship of⁴⁰. The $1000\ln\alpha$ values for calcite and opal are 33.6‰ and 44.2‰, respectively, and we calculate the formation waters avoiding the non-linearity associated with delta notation far from the standard of choice (in this case VSMOW). As such, we calculate the formation waters composition as: $\alpha = (1000 + \delta^{18}\text{O}_{\text{mineral}})/(1000 + \delta^{18}\text{O}_{\text{water}})$.

Calcite data, in $\delta^{13}\text{C}$ vs $\delta^{18}\text{O}$ space, define a trend that suggests they form through admixture with an isotopically lighter water with respect to both carbon and oxygen. The carbon concentration dependent mixing curve that best fits that calcite data alone requires that the isotopically light endmember, what we'll refer to here as the "meltwater" endmember carries a higher DIC than the isotopically heavier water, which we'll now refer to as the brine endmember. In figure 3, we assume that isotopically heaviest opals record the $\delta^{18}\text{O}$ composition of the brine endmember and that the $\delta^{13}\text{C}$ composition matches marine carbon derived from the substrate (-0 ‰), the latter of which is recorded by sodic carbonates suspected of forming from brines in the Lewis cliff area⁴¹. Under such assumptions the carbon ratio between meltwater and brine is 97:3 for PRR50489 (Fig. 3a) and 80:20 in MA113 (Fig. 3b), a result that is consistent with the calcite precipitation model presented above, whereby the addition of a carbon rich, oxidized meltwater, to a reduced or intermediate CaCl₂ brine, triggers calcite precipitation. As shown in extended data figure 6, the calcite data imply formation when there is >30% of meltwater in the mixture. The array of calcite data can also be fit by a mixing model that assumes an isotopically lighter carbon composition ($\delta^{13}\text{C} = -15$ ‰). While feasible, this is a less appealing solution as a $\delta^{13}\text{C}$ of -15 ‰ does not match the composition of any specific carbon source and would require a mixture of waters. The data presented here suggests that over the ~100ka of sample precipitation there are two consistent endmember waters: a reduced brine that is locally derived (star in second quadrant, Fig. 3), and an oxidized meltwater that is from the polar plateau (star in third quadrant, Fig. 3).

Ocean-ice heat exchange and sea level input calculations

Our reduced-complexity model of ice sheet thermodynamics requires that ice thickness changes reach an amplitude of a few hundred meters on AIM timescales in the two parts of Ross Embayment proximal to our sample locations. While thickness change adjacent to the David Glacier catchment occurs at moderate levels of ocean-ice heat exchange ($> 5 \text{ m a}^{-1} \text{ K}^{-1}$; Extended Data Fig. 1c), thickness change in the vicinity of Law Glacier, as required by sample MA113, necessitates levels of ocean-ice heat exchange $> 7 \text{ m a}^{-1} \text{ K}^{-1}$ (Extended Data Fig. 1d) and likely closer to $10 \text{ m a}^{-1} \text{ K}^{-1}$ (Fig. 2)⁴². We report AIS sea level contributions based on ice sheet thickness change calculated using the most conservative estimate of ocean-ice heat

exchange that results in substantial thinning of the Ross Sea Ice shelf: $7 \text{ m a}^{-1} \text{ K}^{-1}$. Therefore, both ocean-ice heat exchange and millennial-scale sea level contributions are minimum estimates. We calculate a 2 - 5 m sea level contribution during AIM events using a GRISLI-UCM Ice Sheet Model⁴² with a ocean-ice heat exchange value of $7 \text{ m a}^{-1} \text{ K}^{-1}$ and a range of sea surface temperatures based on ref. ⁴³. To test this calculation for millennial-scale AIS sea level contribution, we model post-LGM Ross Sea ice thickness using the same parameters and compare the results to recent independent model simulations, which describe an AIS contribution of 5 m sea level equivalent following post-LGM collapse⁴⁴. The degree of ice sheet thickness variation we calculate based on precipitate location implies 10-30% ice loss in parts of the Ross Sea following the LGM^{45,46}. Based on simple scaling, a thickness change of this magnitude would result in a WAIS contribution of 0.5-1.5 m on AIM timescales, implying an additional contribution of 3.5 - 4.5 m from East Antarctica. This output is consistent with our estimates of AIS sensitivity to millennial-scale climate forcing that imply major EAIS ice loss on during AIM cycles.

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