Atmospheric composition 1 million years ago from blue ice in the Allan Hills, Antarctica

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Here, we present direct measurements of atmospheric composition and Antarctic climate from the mid-Pleistocene (~1 Ma) from ice cores drilled in the Allan Hills blue ice area, Antarctica. The 1-Ma ice is dated from the deficit in ^{40}Ar relative to the modern atmosphere and is present as a stratigraphically disturbed 12-m section at the base of a 126-m ice core. The 1-Ma ice appears to represent most of the amplitude of contemporaneous climate cycles and CO_2 and CH_4 concentrations in the ice range from 221 to 277 ppm and 411 to 569 parts per billion (ppb), respectively. These concentrations, together with measured δD of the ice, are at the warm end of the field for glacial–interglacial cycles of the last 800 ky and span only about one-half of the range. The highest CO_2 values in the 1-Ma ice fall within the range of interglacial values of the last 400 ka but are up to 7 ppm higher than any interglacial values between 450 and 800 ka. The lowest CO_2 values are 30 ppm higher than during any glacial period between 450 and 800 ka. This study shows that the coupling of Antarctic temperature and atmospheric CO_2 extended into the mid-Pleistocene and demonstrates the feasibility of discontinuously extending the current ice core record beyond 800 ka by shallow coring in Antarctic blue ice areas.

climate change | glacial cycles | atmospheric CO_2 | ice cores | greenhouse gases

Ice cores serve as a critical archive of past environmental conditions, providing constraints on global atmospheric composition and the climate of polar regions (1). Reconstructions of atmospheric CO_2 and CH_4 from air trapped in ice cores dating as far back as 800 ka indicate a link between greenhouse gases and global climate in the form of 100-ky glacial cycles (Fig. 1). These climate cycles are recorded in proxy records from deep sea sediments reflecting variations in ocean temperature and continental ice volume (2). Deep sea records indicate that the 100-ky glacial cycle developed only ~900,000 y ago [the mid-Pleistocene transition (MPT)] (3). Before this time and going back to 2.8 Ma, glacial cycles lasted, on average, 40 ky (4). The origins of both the 100- and 40-ky glacial cycles, their links to orbital forcing, and changes in atmospheric greenhouse gases are debated. Extending ice core records to earlier times would advance our understanding of links between greenhouse gases, climate, and causes of the MPT.

One archive for extending ice core records beyond 800 ky is blue ice areas (BIAs), outcrops of glacial ice brought to the surface by ice flow guided by bedrock topography (5). These records are likely to be stratigraphically complex because of deformation associated with ice transport but may also contain the oldest easily accessible ice on the planet. In the Allan Hills, Antarctica, the antiquity of shallow ice is documented by terrestrial ages of englacial meteorites exposed on the surface by ablation (6). These ages cluster between 100 and 400 ky, with a small number that extend to 1 Ma and a single meteorite yielding an age of 2.2 Ma (7).

Here, we present the first, to our knowledge, direct snapshots of atmospheric composition during the MPT from an ice core drilled at Site BIT-58 (8) in the Allan Hills BIA (Fig. S1). We date ice and trapped gases directly, taking advantage of the slow leak of ^{40}Ar into the atmosphere from the decay of ^{40}K in Earth's interior (the $^{40}Ar_{atm}$ geochronometer). The observed increase in the $^{40}Ar/^{38}Ar$ ratio of the atmosphere is small, resulting in uncertainties for a single sample of ±213 ky (9). Measurements of Ar isotope ratios date a 12-m section at the base of Site BIT-58 to ~1 Ma (Fig. 2). We report on measurements of CO_2 and CH_4 concentrations, the $\delta^{18}O$ of paleoatmospheric O_2, δD, and deuterium excess (d) in the 1-Ma ice from Site BIT-58. This work provides a direct window into atmospheric composition and Antarctic climate during the mid-Pleistocene.

Climate Records from Ice Cores in the Allan Hills BIA

Previous research using surface samples and vertical ice cores from the Allan Hills Main Ice Field (MIF) has shown that shallow coring (<200 m) can yield high-quality records of Antarctic climate and atmospheric composition that are continuous over long time intervals (10). In particular, results from surface samples and cores drilled along the MIF flow line reveal a continuous climate record spanning marine isotope stage (MIS) 5/6 (Fig. 1). It is exposed both at the surface along a 5-km transect and in the long core (225 m) at Site 27 (10). The ice was dated to 85–250 ka by combining $^{40}Ar_{atm}$ with the stratigraphy of both δD of the ice [isotopic temperature (11)] and $\delta^{18}O$ of paleoatmospheric O_2 [$\delta^{18}O_{atm}$ (12)]. Measurements of CO_2 and CH_4 at Site 27 are also consistent with records from other Antarctic ice cores for this time period (Fig. S2). The climate record from Site 27 across MIS 5/6 provides an important reference frame for comparison with ice of greater antiquity found in the Allan Hills BIA, because environmental conditions in the source regions are expected to be similar.

Significance

Bubbles of ancient air trapped in ice cores permit the direct reconstruction of atmospheric composition and allow us to link greenhouse gases and global climate over the last 800 ky. Here, we present new ice core records of atmospheric composition roughly 1 Ma from a shallow ice core drilled in the Allan Hills blue ice area, Antarctica. These records confirm that interglacial CO_2 concentrations decreased by 800 ka. They also show that the link between CO_2 and Antarctic temperature extended into the warmer world of the mid-Pleistocene.

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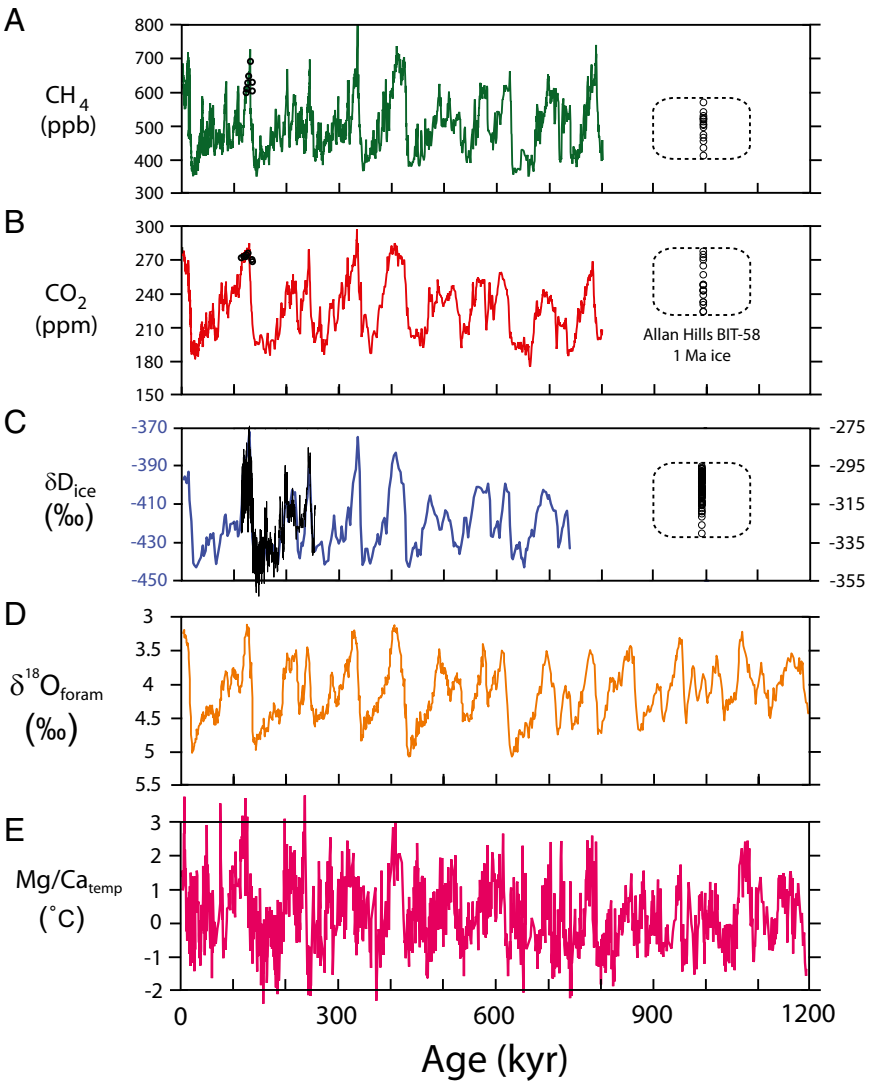

Fig. 1. Records of (*A*) CH_4, (*B*) CO_2, and (*C*) δD from the Allan Hills BIA (Site 27; black line and black symbols between 115 and 250 ka) compared with records from Vostok/EPICA Dome C (green, red, and blue lines) (11, 18–20). The range of gas and ice properties in the 1-Ma ice from Site BIT-58 is shown to the right (Tables S1–S4). Boxes around the 1-Ma data indicate an age uncertainty of ±89 ky (SE) for $n = 6$ measurements of ice below 117 m assuming an external reproducibility (1σ) of ±213 ky (*Materials and Methods* has additional details). *D* shows the stacked benthic foraminiferal $\delta^{18}O$ record (4), and *E* shows a record of deep ocean temperature based on foraminiferal Mg/Ca (17). ppb, parts per billion.

Site BIT-58 sits near the crest of the northwest to southeast trending ice ridge off the MIF in an area of Allan Hills where terrestrial meteorite ages suggest ice older than 1 Ma (6, 7). Although directions and magnitudes of ice flow at Site BIT-58 are not known, measurements from the nearby MIF are consistent with flow to the east or northeast. Bedrock topography, determined using ground penetrating radar, indicates that Site BIT-58 sits on a local bedrock high with a total ice thickness of ∼130 m. Although drilling came to within 5 m of bedrock, recovered ice was clean, and there was no evidence for contamination from bedrock from visual inspection or the chemistry of trapped gases ($\delta O_2/N_2$ and air content) (*SI Text*).

Measured $^{40}Ar_{atm}$ ages from the 126-m core at Site BIT-58 are shown in Fig. 2. The core can be separated into two distinct sections. An upper unit extends from 25 to 113 m, with a weighted mean $^{40}Ar_{atm}$ age of 320 ± 160 ky (1σ; $n = 19$) (Table S1). Below is a basal unit from 113 m to at least 126 m (the bottom of the core), with an average $^{40}Ar_{atm}$ age of 990 ± 110 ky (1σ; $n = 6$). The transition between 320-ka and 1-Ma ice occurs between Ar-dated samples at 112.8 and 117.4 m. The shift in age occurs across an interval from 113- to 115-m depth that is also associated with relatively large changes in the δD of the ice and $\delta^{18}O$ of paleoatmospheric O_2 (Fig. 2 and Table S2). Within the 1-Ma ice, the $^{40}Ar_{atm}$ ages from different depths are indistinguishable. As a result, although the ice below 117 m at Site BIT-58 likely reflects a range of ages around 1 Ma, the range is less than our analytical uncertainty (±213 ky; 1σ).

Two independent lines of evidence support an $^{40}Ar_{atm}$ age >800 ky for the ice below 117.4 m at Site BIT-58. First, 3 of 15 CO_2 measurements yield concentrations that are higher than any measured from European Project for Ice Coring in Antarctica (EPICA) Dome C between 450 and 800 ky (Fig. 3*B* and Table S3). Second, a subset of the paired measurements of CO_2 and CH_4 shows no overlap with known atmospheric values between 450 and 800 ky (Fig. 3*B*).

In addition, water isotopes show that there is an abrupt transition in ice age at ∼113 m. Records of deuterium excess (d) in the Site BIT-58 ice—a measure of temperature, relative humidity, seasonality of precipitation, and wind speed in the precipitation source region (13)—indicate two distinct populations

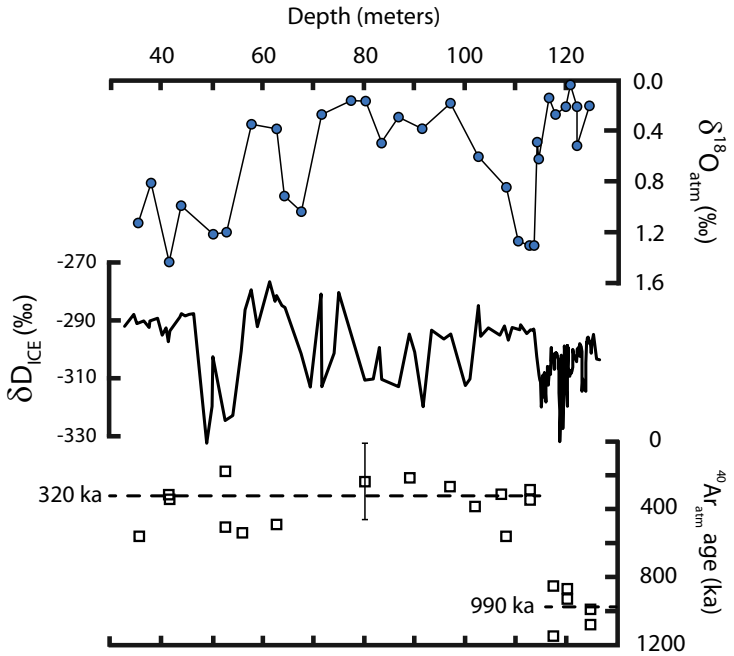

Fig. 2. Measured $\delta^{18}O_{atm}$, δD_{ice}, $^{40}Ar_{atm}$ ages, CO_2, and CH_4 concentrations of the 126-m ice core from Site BIT-58. Error bars on $^{40}Ar_{atm}$ ages of ±213 ky represent 1σ uncertainties associated with repeat measurements of Princeton Air (n = 67).

above and below 113-m depth (Fig. S3 and Table S4). Measured d values for both populations range from +0.9‰ to −10.7‰. Parenthetically, these values are extremely depleted relative to those observed in the Antarctic interior [e.g., d ∼ +4‰ to +12‰ at EPICA Dome C (14)], consistent with a local source of precipitation for the 320-ka and 1-Ma ice in the Allan Hills BIA (13).

The variability in δD and $\delta^{18}O_{atm}$ observed in the 320-ka unit at Site BIT-58 is comparable in magnitude with the variability associated with MIS 5/6 at nearby Site 27 (10). However, the abrupt transitions in δD and $\delta^{18}O_{atm}$ suggest that the ice within the 320-ka unit at Site BIT-58 is stratigraphically disturbed. δD_{ice} varies on submeter scales within the 1-Ma ice (i.e., between 118 and 120 m) (Fig. 2), indicating that this unit is stratigraphically complex as well (Fig. 2 and Fig. S4). Stratigraphic disturbance associated with ice transport is not surprising in the Allan Hills BIA given the subglacial topography of the region, which includes large and abrupt changes in ice thickness [from >1 km to <200 m over a few kilometers (15)], and the distance over which the ice has been transported from its source region [∼20 km at present (16)]. As a result, the Allan Hills BIA is unlikely to preserve long (>100 ky) continuous records of ice >800 ky in age. Records may also be difficult to interpret, because layers can be overturned or oriented parallel to the drilling direction. However, deformation and folding also confer a benefit by increasing the likelihood that a given volume of ice samples a wider range of time periods and climate states. In addition, the shallow burial depths and cold temperatures that characterize ice core records from the Allan Hills BIA should minimize diffusive exchange of gases and the loss of paleoclimatic information in ice older than 1 My (17).

Given the evidence for stratigraphic disturbance, records of ice and gas chemistry in the 1-Ma unit at Site BIT-58 represent

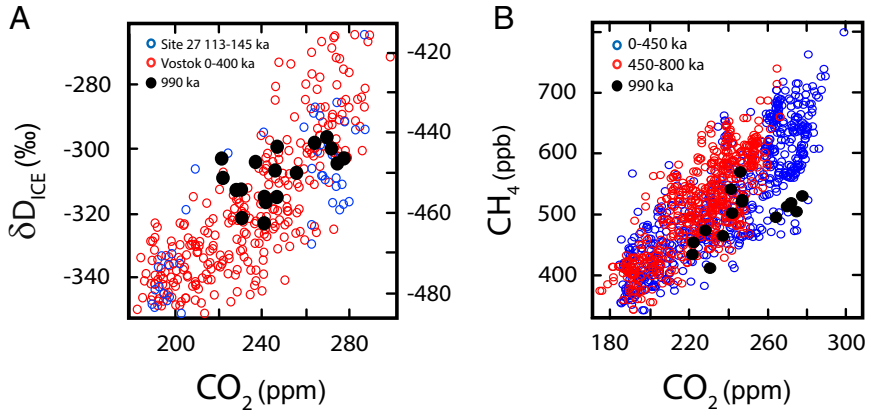

Fig. 3. (*A*) Cross-plot of δD_{ice} and CO_2 from Allan Hills Site 27 (114–155 ka; open blue circles), 1-Ma ice from Site BIT-58 (filled black circles), and Vostok (0–400 ka; open red circles) (1) assuming a zero gas age/ice age difference. CO_2 concentrations are taken from the Vostok record (1) and paired with δD from Site 27 using the $\delta^{18}O_{atm}$ chronology from ref. 12. (*B*) Cross-plot of CO_2 and CH_4 concentrations for Site BIT-58 (filled black circles) compared with Vostok/EPICA Dome C (18–20) for 0–800 ka [0–450 ka (open blue circles) and 450–800 ka (open red circles)]. ppb, parts per billion.

snapshots or short intervals of mid-Pleistocene climate that span some fraction of the full range of glacial–interglacial variability. Despite these limitations, our data represent the oldest direct measurements of atmospheric CO_2, CH_4, $\delta^{18}O$ of O_2, and Antarctic δD_{ice} and permit important preliminary conclusions to be drawn about atmospheric composition, Antarctic climate, and glacial cycles during the mid-Pleistocene.

Snapshots of Atmospheric Composition and Antarctic Climate at 1 Ma

Given the disturbed nature of the 1-Ma ice from Site BIT-58, we treat each of our data points as a snapshot of mid-Pleistocene climate. We then compare the field of values in the 1-Ma ice with those of younger ice in stratigraphically continuous cores at Allan Hills Site 27, Vostok, and EPICA Dome C. Exactly how many unique views exist in the 1-Ma ice is uncertain. Cross-plots of the data do not show correlations that would reflect simple mixing of two end members. To estimate the fraction of glacial–interglacial variability captured in our 1-Ma ice, we compare the range of variability in the 1-Ma ice and the MIS 5/6 ice from Site 27 with the range of variability in marine climate proxies [benthic foraminifera $\delta^{18}O$ stack (4) and Mg/Ca records (18); Fig. 1] over the same time periods.

Considering only the benthic $\delta^{18}O$ stack, the amplitudes of glacial cycles between MISs 19 and 38 average ~1.1‰ or ~60% of the amplitude of MIS 5/6 (1.9‰). In comparison, the range in δD values that we observe in the 1-Ma ice is 46–51% of the range for MIS 5/6 at Site 27, suggesting that we have recovered 80–88% of the full mid-Pleistocene glacial–interglacial variability. Taking into account the effects of changes in the partitioning of the $\delta^{18}O$ signal between deep ocean temperature and ice volume using Mg/Ca-based temperature reconstructions (18) lowers this estimate to ~75% of the full glacial–interglacial range. Therefore, the 1-Ma ice at Site BIT-58 represents most (75–88%) but probably not all of the glacial–interglacial climate range during the MPT. The missing ice most likely comes from glacial maxima, because these intervals are generally underrepresented in ice cores due to lower accumulation rates.

The ranges of measured CO_2 and CH_4 concentrations in the 1-Ma ice are also reduced compared with glacial cycles over the last 800 ky (Fig. 1). Measured CO_2 concentrations range from 221 to 277 ppm or 45–50% of the average glacial cycle since 800 ka (1, 19, 20). Measured CH_4 concentrations range from 411 to 569 parts per billion or 35–40% of the average glacial cycle since 800 ka (21). The reduction in the range of measured CO_2 concentrations in the 1-Ma ice is comparable with that observed for δD_{ice} between the 1-Ma ice and MIS 5/6 at Site 27, whereas the reduction in the range of measured CH_4 concentrations in the 1-Ma ice is slightly larger. Three of twelve measured CO_2 concentrations in the 1-Ma ice are higher than any CO_2 concentrations between 450 and 800 ka (Fig. 3*B*). Minimum CO_2 concentrations are also ~30 ppm higher than any glacial maxima values since 800 ka. Cross-plots of CO_2 and δD for the 1-Ma ice indicate a relationship between East Antarctic temperature change and CO_2 that is similar to that for MIS 5/6 at Site 27 and other Antarctic sites (Fig. 3*A*). Cross-plots of CH_4 and CO_2 show that 1-Ma samples fall within the envelope of glacial–interglacial variability over the last 800 ky. However, for a given CO_2 concentration, CH_4 concentrations in the 1-Ma ice populate the lower end of the range (Fig. 3*B*).

Implications for Glacial Cycles During the MPT

Our results support and reveal a number of features of mid-Pleistocene atmospheric composition and Antarctic climate. First, previous reconstructions of MPT CO_2 levels from measurements of B isotopes in planktic foraminifera have shown that interglacial CO_2 was similar to present values and that glacial CO_2 was 30 ppm higher than 0- to 800-ka glacial values during the MPT (22). In agreement with these reconstructions, Site BIT-58 values indicate that maximum CO_2 concentrations were slightly higher than interglacial values between 450 and 800 ka and comparable with values between 0 and 450 ka. Our records are also consistent with higher CO_2 concentrations at glacial maxima during the MPT. However, the Site BIT-58 record is probably incomplete, and our minimum measured value of 221 ppm is an upper bound.

Second, all of the climate indicators—CO_2, CH_4, and δD_{ice}—exhibit smaller amplitude variability in the 1-Ma ice than in glacial cycles from 0 to 800 ka. Nevertheless, the relationships between climate properties are indistinguishable from those observed for glacial cycles over the last 800 ky. Some of the reduced variability in the 1-Ma ice may come from the fact that the record likely captures most but not all of the glacial–interglacial range during the MPT. Mean δD_{ice} and CO_2 concentrations in the 1-Ma ice are also shifted toward higher (warmer) values, consistent with warmer climates during the MPT.

Third, measured CH_4 concentrations in the 1-Ma ice are low relative to coeval CO_2 concentrations in the context of the 800-ka ice core record (Fig. 1). The CH_4 concentration range in the 1-Ma ice also accounts for a smaller fraction of the 0- to 800-ka range than any other climate property. One possible explanation is that variations in atmospheric CH_4 during the MPT lacked the overshoots associated with rapid Northern Hemisphere warming events (23). Although ice rafting in the North Atlantic predated the MPT (24), millennial-scale climate variability was much stronger after the MPT (25). In the absence of these millennial events during the MPT, high CH_4 concentrations would not be expected to co-occur with cooler Antarctic temperatures and lower CO_2 concentrations.

Conclusions

Ice cores containing archives of 1-My air have been recovered from shallow depths in Antarctic BIAs, providing the first, to our knowledge, direct measurements of atmospheric composition during glacial cycles of the mid-Pleistocene. Although these records are stratigraphically complex and likely incomplete, our results are consistent with the prevailing views (4, 22) that the amplitude of glacial cycles was diminished during this time, climates were warmer, interglacial CO_2 concentrations were greater than between 450 and 800 ka, and glacial CO_2 concentrations, at most, were ~30 ppm higher than between 0 and 800 ka. Our record also provides reconstructions of atmospheric CH_4 >800 ka and shows that CH_4 concentrations are both surprisingly low and exhibit less variability than the other climate indicators compared with glacial cycles over the last 800 ky.

Materials and Methods

$^{40}Ar_{atm}$ Geochronometer. In the solid earth, ^{40}K decays to stable ^{40}Ar. Because ^{40}Ar slowly leaks into the atmosphere, its concentration increases with time. In contrast, because ^{38}Ar and ^{36}Ar are stable, primordial, and nonradiogenic, their atmospheric concentrations are constant. Thus, the $^{40}Ar/^{38}Ar$ ratio of the atmosphere rises with time (toward the future) and decreases with age (toward the past), providing a tool for dating. The term of merit is the paleoatmospheric $^{40}Ar/^{38}Ar$ ratio, which is defined as $^{40}Ar_{atm} = \delta^{40}Ar/^{38}Ar - 1.002\delta^{38}Ar/^{36}Ar$.

The latter term corrects for gravitational fractionation, so that $\delta^{40}Ar_{atm}$ is a measure of the paleoatmospheric $^{40}Ar/^{38}Ar$ ratio. Studies of $^{40}Ar_{atm}$ as a function of age in the Dome C and Vostok cores characterize its rate of change over the last 800 ka, enabling its use for dating ice (9). We linearly extrapolate the rate of change over the last 800 ka to older periods (i.e., 1–2 Ma), although even for ice of this age, the signal is small and uncertainties are large for a single measurement at 213–246 ky (Table S1). Reported errors (1σ) for each sample reflect both analytical errors and uncertainties in the calibration slope of the $^{40}Ar_{atm}$ geochronometer.

Procedures for Ar analyses are a modification of the methods used in ref. 9. Trapped air was wet-extracted from an ~500-g ice core sample. Two getters were used to sequentially purify the Ar by removing more than 99.9999% of N_2, O_2, and other nonnoble gases. Samples were then admitted to a Finnigan

MAT 252 Mass Spectrometer, which simultaneously measures $\delta^{40}Ar/^{38}Ar$ and $\delta^{38}Ar/^{36}Ar$. The SD of a single measurement of $\delta^{40}Ar_{atm}$ in a sample of local air (Princeton Air) is ±0.0143‰ or ±213 ka. Reproducibility of natural ice core samples from repeated measurements of Holocene age ice from Antarctica from this study and the study in ref. 9 is −0.005 ± 0.0100‰ (n = 16), corresponding to an age uncertainty of ±149 ka. The reason for the difference is unclear at present, and as a result, we adopt the more conservative estimate of uncertainty (replicate measurements of Princeton Air or ±213 ka; 1σ) for this study. When possible, samples were measured in replicate from the same depth. Each ice sample was measured in conjunction with an aliquot of an in-house Ar standard and Princeton Air that had been processed through the same procedures as the ice core samples, with the exception of wet extraction. Each sample was analyzed for ∼3 h on the mass spectrometer. This long analysis period permits the precise measurement of $\delta^{40}Ar_{atm}$, despite the very low natural abundance of ^{38}Ar. Measured $^{38/36}Ar$ ratios in the ice samples deviate from the air standard because of gravitational fractionation in the firn, with the magnitude of the gravitational fractionation in $^{38/36}Ar$ being roughly two times that expected for $^{15/14}N$.

$\delta^{18}O_{atm}$ and $\delta^{15}N$. Analyses for the $O_2/N_2/Ar$ ratio, $\delta^{18}O$ of O_2, and $\delta^{15}N$ of N_2 were carried out as described in ref. 26. Briefly, ice was melted in vacuum, the dried headspace gases were collected by condensation at liquid helium temperatures, and the samples were admitted to the mass spectrometer (Thermo Finnegan Delta Plus XP) for elemental and isotope ratio analyses. External reproducibility is typically about ±0.02‰ for $\delta^{15}N$ and ±0.03 ‰ for $\delta^{18}O_{atm}$. Samples with poor reproducibility in $\delta^{15}N$ (>0.1‰) were omitted (n = 2).

CH_4, Air Content, and CO_2. CH_4 was analyzed using a melt–refreeze technique most recently described in ref. 27. Samples (∼60–70 g ice) were trimmed, melted under vacuum, and then, refrozen at about −70 °C. Methane concentrations in released air were measured using a gas chromatograph and referenced to air standards calibrated by National Oceanic and Atmospheric Administration (NOAA) Global Monitoring Division (GMD) on the NOAA04 scale. Precision was generally better than ±4 parts per billion. Measured CH_4 concentrations were not corrected for gravitational fractionation, which had an effect that is minor given the small gravitational fractionation observed in $\delta^{15}N$ at Site BIT-58. Individual sample uncertainties are reported in Table S3. The measurement also quantifies the total air content of the sample, an important parameter for evaluating sample quality and possibly, elevation of the deposition site.

CO_2 concentrations were measured using the dry extraction (crushing) method described in ref. 28; 8- to 15-g samples were crushed under vacuum, and the sample air was condensed in steel tubes at 11 K. CO_2 concentrations were measured after equilibration to room temperature using gas chromatography and referenced to air standards calibrated by NOAA GMD on the World Meteorological Organization (WMO) scale. Generally, several replicate ice samples were analyzed for each depth, and results were averaged to obtain final CO_2 concentration. Typical SEMs are <1 ppm for four to six replicates. Measured CO_2 concentrations were also not corrected for gravitational fractionation. Individual sample uncertainties are reported in Table S3.

δD_{ice} and $\delta^{18}O_{ice}$. When possible, samples for Site BIT-58 were subsampled from cut slabs at 15-cm resolution in a −20 °C working freezer at the Climate Change Institute, University of Maine. Because some portions of the core were heavily fractured, continuous sections were not available at all depths. For δD_{ice} and $\delta^{18}O_{ice}$ measurements, ice samples were melted to liquid H_2O at room temperature, and 1.6-mL aliquots were transferred to glass vials for analysis. Samples and laboratory standards, which span a wide range of naturally occurring isotopic values previously calibrated against standard mean ocean water, standard light Antarctic precipitation, and Greenland ice sheet precipitation, were measured by cavity ring-down spectroscopy using a Picarro Model L2130-i Ultra High-Precision Isotopic Water Analyzer coupled with a High-Precision Vaporizer and liquid autosampler module; $\delta^{18}O_{ice}$ and δD_{ice} were measured simultaneously with an internal precision at 2σ = ±0.05‰ for $\delta^{18}O$ and ±0.10‰ for δD_{ice}.

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