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 40Ar 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 CO2 and CH4 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 CO2 values in the 1-Ma ice fall within the range of interglacial values of the last 450 ka and 800 ka. The lowest CO2 values are 30 ppm higher than during any glacial period and represent most of the amplitude of contemporaneous climate cycles and atmospheric CO2 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 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. 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 40Ar/39Ar with the stratigraphy of both 6D of the ice [isotopic temperature (11)] and δ18O of paleoatmospheric O2 [δ18O atm (12)]. Measurements of CO2 and CH4 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 CO2 concentrations decreased by 800 ka. They also show that the link between CO2 and Antarctic temperature extended into the warmer world of the mid-Pleistocene.


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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 (δ18O/2N2 and air content) (SI Text).

Measured 40Ar 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 40Ar 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 40Ar 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 δ18O of paleoatmospheric O2 (Fig. 2 and Table S2). Two independent lines of evidence support an 40Ar atm age >800 ky for the ice below 117.4 m at Site BIT-58. First, 3 of 15 CO2 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. 3B and Table S3). Second, a subset of the paired measurements of CO2 and CH4 shows no overlap with known atmospheric values between 450 and 800 ky (Fig. 3B).

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
above and below 113-m depth (Fig. S3 and Table S4). Measured δ 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., δ ∼ +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 δ18Oatm 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 δ18Oatm suggest that the ice within the 320-ka unit at Site BIT-58 is stratigraphically disturbed. δD and δ18O vary 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
snaps 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 CO₂, CH₄, δ¹⁸O of O₂, and Antarctic δDIC 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 Allain 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 δ¹⁸O stack (4) and Mg/Ca records (18); Fig. 1] over the same time periods.

Considering only the benthic δ¹⁸O 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 δ¹⁸O 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 δ¹⁸O 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 CO₂ and CH₄ concentrations in the 1-Ma ice are also reduced compared with glacial cycles over the last 800 ky (Fig. 1). Measured CO₂ concentrations range from 221 to 277 ppm or ~45–50% of the average glacial cycle since ~800 ka (1, 19, 20). Measured CH₄ 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 CO₂ concentrations in the 1-Ma ice is comparable with that observed for 6DICE between the 1-Ma ice and MIS 5/6 at Site 27, whereas the reduction in the range of measured CH₄ concentrations in the 1-Ma ice is slightly larger. Three of twelve measured CO₂ concentrations in the 1-Ma ice are higher than any CO₂ concentrations between 450 and 800 ka (Fig. 3B). Minimum CO₂ concentrations are also ~30 ppm higher than any glacial maxima values since ~800 ka. Cross-plots of CO₂ and δDIC for the 1-Ma ice indicate a relationship between East Antarctic temperature change and CO₂ that is similar to that for MIS 5/6 at Site 27 and other Antarctic sites (Fig. 3A). Cross-plots of CH₄ and CO₂ show that 1-Ma samples fall within the envelope of glacial–interglacial variability over the last 800 ky. However, for a given CO₂ concentration, CH₄ concentrations in the 1-Ma ice populate the lower end of the range (Fig. 3B).

**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 CO₂ levels from measurements of B isotopes in planktic foraminifera have shown that interglacial CO₂ was similar to present values and that glacial CO₂ 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 CO₂ concentrations were slightly higher than interglacial values between ~450 and 800 ka and comparable with values between 0 and 450 ka. Our record is also consistent with higher CO₂ 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—CO₂, CH₄, and 6DICE—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 6DICE and CO₂ concentrations in the 1-Ma ice are also shifted toward higher (warmer) values, consistent with warmer climates during the MPT.

Third, measured CH₄ concentrations in the 1-Ma ice are low relative to coeval CO₂ concentrations in the context of the ~800-ka ice core record (Fig. 1). The CH₄ 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 CH₄ 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 CH₄ concentrations would not be expected to co-occur with cooler Antarctic temperatures and lower CO₂ concentrations.

**Conclusions**

Ice cores containing archives of 1-Ma yr have been recovered from shallow depths in Antarctic BIsA, 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 diminished during this time, climates were warmer, interglacial CO₂ concentrations were greater than between ~450 and 800 ka, and glacial CO₂ concentrations, at most, were ~30 ppm higher than between 0 and 800 ka. Our record also provides reconstructions of atmospheric CH₄ >800 ka and shows that CH₄ 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**

40Ar/38Ar Geochronometer. In the solid earth, 40K decays to stable 40Ar. Because 40Ar slowly leaks into the atmosphere, its concentration increases with time. In contrast, because 39Ar and 36Ar are stable, primordial, and nonradiogenic, their atmospheric concentrations are constant. Thus, the 40Ar/39Ar ratio of the atmospheric 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 40Ar/39Ar ratio, which is defined as 40Ar/39Ar = 40Ar/39Ar – 1.002(40Ar/39Ar) – 1.002(39Ar/36Ar).

The latter term corrects for gravitational fractionation, so that 40Ar/39Ar, is a measure of the paleoatmospheric 40Ar/39Ar ratio. Studies of 40Ar/39Ar 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 51). Reported errors (1σ) for each sample reflect both analytical errors and uncertainties in the calibration slope of the 40Ar/39Ar geochronometer.

Procedures for Ar analysis 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 99.999% of N₂, O₂, and other nonnoble gases. Samples were then admitted to a Finnigan
MAT 252 Mass Spectrometer, which simultaneously measures $^{40}\text{Ar}/^{36}\text{Ar}$ and $^{38}\text{Ar}/^{36}\text{Ar}$. The SD of a single measurement of $^{40}\text{Ar}/^{36}\text{Ar}$ in a sample of local air (Princeton Air) is $\pm 0.0140\%$ or $\pm 213$ 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 $\pm 0.005 \pm 0.0100\%$ ($n = 16$), corresponding to an age uncertainty of $\pm 149$ 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 $\pm 213$ ka; $n = 16$) for this study. When possible, samples were measured in replicate from the same depth. Each 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 $\sim 3$ h on the mass spectrometer. This long analysis period permits the precise measurement of $^{40}\text{Ar}/^{36}\text{Ar}$, despite the very low natural abundance of $^{38}\text{Ar}$. Measured $^{40}\text{Ar}/^{36}\text{Ar}$ ratios in the ice samples deviate from the air standard because of gravitational fractionation in the firm, with the magnitude of the gravitational fractionation in $^{40}\text{Ar}/^{36}\text{Ar}$ being roughly two times that expected for $^{15}\text{N}/^{14}\text{N}$.

$^{40}\text{Ar}/^{36}\text{Ar}$ and $^{38}\text{Ar}/^{36}\text{Ar}$. Analyses for the $^{36}\text{Ar}/^{36}\text{Ar}$ ratio, $^{40}\text{Ar}/^{36}\text{Ar}$, and $^{40}\text{Ar}/^{36}\text{Ar}$ of $^{36}\text{Ar}$ 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 temperature, and the samples were admitted to the mass spectrometer (Thermo Finnigan Delta Plus XP) for elemental and isotope ratio analyses. External reproducibility is typically about $\pm 0.02\%$ for $^{40}\text{Ar}/^{36}\text{Ar}$ and $\pm 0.03\%$ for $^{38}\text{Ar}/^{36}\text{Ar}$. Samples with poor reproducibility in $^{38}\text{Ar}/^{36}\text{Ar}$ ($\sim 0.1\%$) 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 in vacuum, then, refrozen at about $\sim 70$ °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 NOAA40 scale. Precision was generally better than $\pm 4$ 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 $^{38}\text{Ar}$ at Site BIT-58. Individual sample uncertainties are reported in Table 53. This 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 53.

$\delta$D$_{\text{snow}}$ and $\delta^{18}O_{\text{snow}}$. When possible, samples for Site BIT-58 were subsampled from cut slabs at 15-cm resolution in a $\sim 20$ °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 $\delta$D$_{\text{snow}}$ and $\delta^{18}O_{\text{snow}}$ measurements, ice samples were melted to liquid H$_2$O 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 2120i Ultra High-Precision Isotopic Water Analyzer coupled with a High-Precision Vaporizer and liquid autosampler module. $\delta^{18}O_{\text{snow}}$ and $\delta$D$_{\text{snow}}$ were measured simultaneously with an internal precision at $2\sigma = 0.05\%$ for $\delta^{18}O_{\text{snow}}$ and $0.10\%$ for $\delta$D$_{\text{snow}}$.

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**Table 53.**