Supplementary Information for:

Gas isotope thermometry in the South Pole Ice Core provides evidence for a seasonal rectifier in ice core gas records

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# Supplementary Text

# Modifications to the Analytical Method

## Hydrogen Chemical Slope Correction to δ15N

During the gas extraction, hot copper turnings are used to remove oxygen from the sample gas by reaction to copper oxide. After each extraction, we flow pure hydrogen (H2) over the turnings to reduce the copper oxide back to copper and water vapour. Because the turbomolecular pumps used to evacuate the vacuum line do not pump H2 effectively, there is the potential for residual H2 to be present in the vacuum line after copper regeneration. This H2 may then be incorporated in the sample gas during the following extraction. In the mass spectrometer source, the H2 is ionised and bonds with 28N2+ producing H28N2+, which adds an isobaric interference to the beam of 29N2+ ions. Higher concentrations of H2 in the sample therefore cause an artefactual enrichment of δ15N (Figure S1a). We correct for this by measuring the amount of H2 in each sample and removing its effect using the empirically determined chemical slope:

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|  |  | (1) |

where δ15NCS Corr is the chemical-slope-corrected delta value, δ15Nmeas is the measured delta value, kCS is the chemical slope (units of ‰/mV H2), and ΔH2 is the sample–reference difference in the H2 beam intensity. To find the value of the chemical slope, we add increasing amounts of pure H2 to aliquots of a reference gas with a well-known isotopic composition and measuring the resulting mass 29 enrichment.

We also found that we could fully regenerate the copper with approximately one tenth of the H2 recommended by Orsi (2013). This is advantageous not only for the savings in time and materials, but also because it means samples contain less H2 and the magnitude of this correction is smaller.

## Thermal Fractionation Artefact

During routine testing we found a transient, artefactual isotopic enrichment of the sample δ15N value by 0.01–0.015‰ at the start of the analysis, which decayed to zero over the course of approximately 30 minutes. This problem is also described by Orsi (2013, p.4.3.4.5), and we confirmed it had unknowingly affected previous, unpublished data. Using data from our new tests, we infer that this enrichment is caused by the large expansion of reference gas from the low-volume, high-pressure (~1.4 cc at 5 atm) working cylinder pipette volume, relative to the small expansion of the sample gas from the high-volume, low-pressure (~13 cc at 0.6 atm) dip tube. The expansion of the reference gas cools the metal of the bellows and/or the upstream end of the capillary that carries gas to the mass spectrometer. These components are enclosed in a large metal housing and are not exposed to circulating room air. In contrast, the downstream end of the capillary is located far from the expansion and is exposed to circulating room air so remains at ambient temperature. This gradient from cold to warm, from the reservoir of reference gas in the bellows to the point where it enters the mass spectrometer, also sets up an isotopic gradient according to thermal fractionation. That is, the reference gas in the bellows is isotopically heavy relative to the gas entering the mass spectrometer. Because isotopically lighter reference gas is entering the mass spectrometer the sample appears isotopically heavier at the start of the analysis (Figure S1b). The magnitude of the artefactual enrichment diminishes over time as the metal components gradually warm back up to ambient temperature and the isotopic depletion of the reference gas entering the mass spectrometer diminishes accordingly. We circumvent the problem by incorporating a 30-minute delay between the admission and isolation of the sample and reference gas in the bellows and the beginning of the measurement sequence. These modifications granted us the two-fold improvement in measurement reproducibility that is necessary to resolve the signals we expect to find in Antarctic ice cores.

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| **Figure S1.** **(a)** Results of a H2 chemical slope experiment showing the increase in δ15N associated with an imbalance in the H2 concentration in the sample and reference aliquots. The slope and squared correlation coefficient of a least squares linear fit is also indicated. **(b)** Measurements of δ15N from single sample-reference integration cycles (red and blue points), plus a 16-cycle running mean, showing the heavy bias immediately after expansion of the reference aliquot into the dual inlet bellows. Data from two replicate aliquots are shown, together with the average (horizontal black line) and standard deviation (grey shading) of all data later than 30 minutes after expansion (vertical dotted line). |

# Gas Loss Correction

Argon isotopes are known to be enriched due to preferential leakage of the light isotope from the recovered ice core during storage (Severinghaus et al., 2003). Previous authors have corrected for this bias using δAr/N2 as an indicator of the amount of gas lost (Severinghaus et al., 2003; Kobashi et al., 2008). However, δAr/N2 is known to be fractionated by multiple processes including bubble close off, clathrate formation, and escape from the ice post-coring by diffusion through the ice lattice and along cracks. These processes likely affect Ar isotopes differently, making a one-size-fits-all correction inappropriate. This is particularly true for our dataset, which spans the BCTZ. Instead, we use a novel approach to make a gas loss correction, which takes advantage of the fact that δ15N is not fractionated by gas loss (Grachev, 2004; Severinghaus et al., 2009).

To isolate the gas loss fractionation signal in our time-series, we attempt to empirically capture and remove the shared climate variability of δ15N and δ40Ar by spline fitting. The smoothness of each fitted spline is set by a smoothing parameter, *S*, with 0 ≤ *S* ≤ 1 and we fit splines for a range of values. We fit analogous splines to δAr/N2 grav to capture the effect of fractionation during bubble close off and in the BCTZ. The smoothing parameter for the δAr/N2 grav spline is set to be exactly two orders of magnitude smaller than for the isotope splines due to smoother variations in δAr/N2 grav than the isotopes. Next, we calculate the residuals from each spline (denoted by Δ) and examine the correlation of the δ15N and δ40Ar residuals with the δAr/N2 grav residuals. For values of *S* close to 1, the splines approach an interpolant passing exactly through all points. Therefore, there are no residuals and no significant correlation for either isotope ratio. For values of *S* close to 0, the splines approach a linear fit and the spline residuals do not reflect solely gas loss processes. However, we find that there is a range of intermediate values of *S* for which Δδ40Ar is significantly negatively correlated with ΔδAr/N2 grav (minimum r = ‑0.33), while Δδ15N is not. We attribute this correlation to fractionation due to post-coring gas loss. We rule out changes in gravitational or thermal fractionation as these processes would affect both Δδ15N and Δδ40Ar and would result in a positive, not negative, correlation with ΔδAr/N2 grav. We choose a smoothing parameter of 2.78×10‑8, close to the steepest slope and maximum r2 for Δδ40Ar and indicated by the grey vertical line in Figure S2b, and correct δ40Ar by subtracting the gas loss component from the measured value:

where k has a value of -5.80 per meg/per mil, i.e., the slope of the linear regression between Δδ40Ar and ΔδAr/N2 grav for our chosen smoothing parameter.

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| **Figure S2. (a)** From top to bottom: **(I)** measurements of SPICEcore δ15N and **(II)** δ40Ar with fitted splines. Both splines have a smoothing parameter of 2.78×10‑8, which is the value used to make the gas loss correction. **(III)** Residuals of δ15N (Δδ15N) and **(IV)** residuals of δ40Ar (Δδ40Ar) from their respective splines. **(V)** Measurements of SPICEcore δAr/N2 grav and a fitted spline with a smoothing parameter of 2.78×10‑6. **(VI)** Residuals of δAr/N2 grav (ΔδAr/N2 grav) from the fitted spline.  **(b)** From top to bottom: the slope **(I)**, r2 **(II)**, and p-value **(III)** of linear fits to Δδ15N versus ΔδAr/N2 grav (blue lines), or Δδ40Ar versus δAr/N2 grav (orange lines), plotted as a function of the smoothing parameter of the δ15N and δ40Ar splines. The vertical grey line indicates the smoothing parameter used to make the gas loss correction.  **(c)** Cross plots of Δδ15N and Δδ40Ar **(d)** vs ΔδAr/N2 grav for the smoothing parameter used to make the gas loss correction. |

# Present-Day Δ*T*z

We estimate the present-day temperature difference (Δ*T*z) in the firn column at South Pole, Dome C, and Dome F for comparison to our record of past Δ*T*zfrom SPICEcore. Because diffusion in the firn smooths out high frequency oscillations, ice core gas records reflect some multidecadal average of firn conditions (Schwander et al., 1993; Epifanio et al., 2020; Fourteau et al., 2020). Therefore, for our present-day estimates of Δ*T*z to be comparable to our gas-isotope-derived record, we ought to determine the temperature difference recorded by the gases at the close-off depth or in recently occluded bubbles at each site. This will differ from any observed, in situ temperature profile, which will be affected by seasonal and multiannual variability near the surface.

The Δ*T*z recorded by the gases in the deep firn can either be directly observed by measuring δ15N and δ40Ar in the deep firn and calculating Δ*T*z, or estimated from observations of the temperature profile in the firn. The former is preferable as it takes advantage of the natural averaging that happens in the firn (assuming no rectification of seasonal signals in the modern). In the latter approach, the shallower parts of the temperature profiles will contain information about temperature oscillations on seasonal or annual timescales, so will not reflect the multidecadal average Δ*T*z recorded in the deep firn. Additionally, borehole temperatures will likely contain artefactual temperature biases related to thermal disturbance during drilling unless the borehole is allowed several years to come to thermal equilibrium with the ice before the temperature is measured (Dahl-Jensen et al., 1998). In the case of significant anthropogenic warming over the past few decades, neither approach will capture the pre-industrial Δ*T*zthat we might prefer to compare to our Holocene ice core data. Below, we compare estimates made using both methods from South Pole, Dome F, and Dome C and find the results to be comparable, within quoted uncertainties.

## South Pole

Severinghaus and Battle (2006) made measurements of δ15N and δ40Ar in the deep firn at South Pole (Figure S3a). This allows us to calculate δ15Nexcess, as we do with our SPICEcore measurements. The average δ15Nexcess in the deep firn (>60 m depth) is 0.001 ± 0.002‰ (Figure S3b). This corresponds to a Δ*T*z indistinguishable from 0°C, implying no detectable firn temperature difference over the past few decades. The authors find some artefactual sampling bias in the data from the lock-in zone (>116 m), which may have affected δ15Nexcess (Severinghaus and Battle, 2006). Excluding this data gives a Δ*T*zof 0.6°C, consistent with a small amount of recent warming.

As well as the gas isotope data, the following observations of South Pole firn temperature are available: (1) a summer and winter temperature profile of the upper 15 m from 1998 (Severinghaus et al., 2001); (2) repeated observations of snow temperature in the upper 12 m of the firn made over an 10 month period in 1958 (Giovinetto, 1960); (3) time-series of snow temperature in a firn core borehole between the surface and 40 m depth at a site 50 km upstream of South Pole between January and December 2017 (Stevens et al., 2022); and (4) observations of the temperature in the SPICEcore borehole deeper than 120 m made in December 2016 (Hawley, R. L., personal communication, 2021). From these datasets, we can make another estimate of the present-day Δ*T*zat South Pole. Uncertainty comes from several sources. First, we are comparing temperatures measured using different thermistors, at different times (up to 60 yr apart), and in different locations (up to 50 km apart, in the case of the Stevens et al. dataset). Second, although the deep borehole temperatures represent an average of the past several decades, as mentioned above, the shallower temperatures are affected by seasonal and multiannual temperature variability.

We circumvent the problems of the seasonal cycle in the Giovinetto dataset by fitting a regularly spaced spline to the data and computing the annual average. We apply the same approach to the Stevens dataset. In contrast, the Severinghaus dataset consists of only a single snapshot for summer and winter so the best we can do is average the two profiles. The resulting averages are shown in Figure S3c. There is almost no change in temperature below 10 m depth, but, between 0 and 10 m, the temperature increases by ~2°C. This may be due to our relatively crude attempts at annual averaging, which are unlikely to reflect a realistic annual mean at shallow depths where the seasonal cycle is larger and contains more high frequency variability. Alternatively, the increase in temperature shallower than 10 m may be due to recent warming at South Pole in the case of the Stevens dataset (Clem et al., 2020).

We compute an estimate of Δ*T*z by subtracting the mean of data between 6 and 20 m from the mean of the shallowest 5 m of borehole temperatures (118–123 m depth) from the Hawley dataset and find Δ*T*zequal to 0.4°C. Despite the considerable uncertainty, the temperature data give a Δ*T*z within 0.5°C of the gas isotope estimate.

Both estimates of Δ*T*z also agree well with three published model estimates of the ice sheet temperature profile at South Pole, constrained by temperatures measured deeper in the ice sheet as part of the AMANDA neutrino observatory (Price et al., 2002; Beem et al., 2018; Buizert et al., 2021). Altogether, multiple lines of evidence support the conclusion that the magnitude of the present-day Δ*T*z recorded by gases in the deep firn is smaller than ±1°C. This is in good agreement with our Holocene data and is much smaller than the -4°C minimum in Δ*T*z that we observe at 20 kyr BP.

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| **Figure S3. (a)** South Pole firn air δ15N (blue) and δ40Ar (orange) measurements from Severinghaus and Battle (2006). Black dotted lines indicate the lock-in depth. **(b)** Firn air δ15Nexcess calculated from the Severinghaus and Battle data. Error bars represent their stated analytical precision. **(c)** Temperature observations in the upper 200 m of the firn column at South Pole. Legend indicates the first author of each dataset, see text for details. |

## Dome Fuji

At Dome F, similar firn air data exist. Gas isotope measurements, including δ15N and δ40Ar, were made in 2008 on samples collected in 1998 and described in Kawamura et al. (2006). We calculate the average of δ15Nexcess in the deep firn, excluding one outlier at 100 m depth that is anomalously low in δ15N. The average is ‑0.006 ± 0.002‰, which corresponds to an implied Δ*T*z of ‑1.2°C (Figure S4). Including the outlier gives a Δ*T*z of ‑1.8°C instead. At Dome F, Δ*T*z is negative due to the influence of geothermal heat on the base of the firn column due to the low accumulation rate.

In addition to the gas isotope measurements, Buizert et al. (2021) made a model estimate of the present day ice sheet temperature profile, constrained by observed borehole temperatures. Their temperature profile gives an estimate of Δ*T*z equal to ‑1.0°C.

Both lines of evidence imply a present-day Δ*T*z at Dome F that is more negative than the present-day Δ*T*z at South Pole, in line with expectations given the lower accumulation rate. The Dome F value is more positive than both the glacial values we reconstruct at South Pole and the Holocene values from Dome F we present in Sect. 5.2.

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| **Figure S4. (a)** Dome F firn air δ15N (blue) and δ40Ar/4 (orange) (Kawamura et al., 2006, remeasured in 2008). **(b)** Firn air δ15Nexcess calculated from the Dome F firn air data. Error bars represent estimated 0.002‰ analytical precision. Black dotted lines indicate the lock-in depth. |

## Dome C

At Dome C, no gas isotope data were available for estimating Δ*T*z. Instead we use an estimate of the ice sheet temperature profile, constrained by borehole temperature measurements from the same work referenced above (Buizert et al., 2021). The authors find Δ*T*z is equal to ‑0.95°C. This is in good agreement with a similar model estimate from Haeberli (2019), who reported Δ*T*z equal to ‑0.6°C. Haeberli also used isotope measurements in shallow ice samples from the Dome C ice core to estimate Δ*T*z, which they find are within 0.2°C of their observations and the model estimate we describe here (Haeberli et al., 2021).

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