Sunlight-driven nitrate loss records Antarctic surface mass balance

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Standard proxies for reconstructing surface mass balance (SMB) in Antarctic ice cores are often inaccurate or coarsely resolved when applied to more complicated environments away from dome summits. Here, we propose an alternative SMB proxy based on photolytic fractionation of nitrogen isotopes in nitrate observed at 114 sites throughout East Antarctica. Applying this proxy approach to nitrate in a shallow core drilled at a moderate SMB site (Aurora Basin North), we reconstruct 700 years of SMB changes that agree well with changes estimated from ice core density and upstream surface topography. For the undersampled transition zones between dome summits and the coast, we show that this proxy can provide past and present SMB values that reflect the immediate local environment and are derived independently from existing techniques.
Antarctica holds a critical role in the Earth’s hydrosphere, providing long-term storage of 27 million km$^3$ of ice and impacting global ocean and atmosphere circulation through its albedo, topography, export of calved glacial ice, and function as an atmospheric heat sink. Since even small shifts in the surface mass balance (SMB) across Antarctic ice sheets can redistribute huge masses of water between the cryosphere, ocean, and atmosphere, a clear understanding of how its SMB has responded to past climate change is crucial for calibrating forecast models of the global environment and properly interpreting ice cores. Despite this pressing importance, much of Antarctica has insufficient records of both modern and past SMB values, particularly in the transitional zone between the <1000 m elevation wet coastal periphery and the >3000 m elevation ultra-dry dome summits. Although this transitional zone comprises 50% of Antarctica’s surface area, it hosts few long-term scientific stations and is much less targeted for intensive scientific research and deep (>100 m) ice core studies. Because this zone has a highly dynamic SMB system affected by strong wind-driven transport, rugged, small-scale surface features, and infrequent but high-impact precipitation events, our lack of dedicated studies of the transitional zone impedes a comprehensive understanding of past and present SMB changes in Antarctica.

This lack of data is largely a result of logistical challenges with observing the intermediate SMB values in this transitional zone when using existing techniques. Determining modern SMB for new sites typically requires either installing stake transects that need multiple return visits spanning several years or coring several meters of firm to identify the increasingly buried 1992 Pinatubo volcanic horizon with geochemical analysis. However, the limited time and resources during research expeditions to remote areas usually prevents intensive modern SMB surveys with these methods, and, as a result, existing SMB records in the transition zone are largely restricted to a few frequently traveled supply traverse routes. This has left vast regions of Antarctica with no ground-verified SMB data.

Although ice cores have been drilled from a few sites in the transitional zone, extracting SMB histories from these cores is often difficult. At interior dome sites, proxy air temperature from water isotopes ($\delta$PH or $\delta$DO) is used to derive snow accumulation rate through water vapor saturation. However, this approach does not account for wind-driven transport and sublimation of surface snow at warmer and lower elevation sites. Additionally, water isotopes reflect many environmental factors other than temperature, such as atmospheric circulation changes, transport pathways, and moisture sources, which can lead to large uncertainty and/or bias in reconstructed SMB. Changes in ice density along the cores may be converted to SMB provided that they are well-dated, but density-based reconstructions become increasingly uncertain with depth due to thinning and deformation of ice layers and may be impossible in zones with heavy ice deformation. Cores are also commonly damaged during the drilling and transportation process, and this can make accurate physical measurements of mass and volume very difficult, particularly for the shallow firn segments. There is thus a strong need for alternative independent proxies that record local SMB for modern climatology studies, paleoclimate reconstructions, and ice sheet modeling while avoiding the problems inherent in existing methods.

Here, we present one such SMB proxy based on photolysis-induced changes in the $^{15}$N/$^{14}$N ratio ($\delta^{15}$N, defined as $\delta^{15}$N = ($^{15}$N/$^{14}$N)$_{snow}$ / ($^{15}$N/$^{14}$N)$_{air}$ − 1, relative to the N$_2$-air standard) of nitrate (NO$_3^-$) (Fig. 1). Naturally deposited on the Antarctic ice sheet surface as the end product of the atmospheric oxidation of reactive nitrogen, NO$_3^-$ within the Antarctic snowpack can be photolytically converted to gaseous nitrogen oxides (NO$_x$ = NO + NO$_2$) when exposed to ultraviolet light ($\lambda$ = 290–350 nm). Because $^{14}$NO$_3^-$ is more readily photolyzed than $^{15}$NO$_3^-$, the $\delta^{15}$N of NO$_3^-$ ($\delta^{15}$N$_{NO3}$) remaining in the snow will increase from its initial depositional value of $\approx$ +20 to +20 %o to values as high as +400 %o when the isotopically lighter photolytic NO$_x$ product is ventilated and lost to the atmosphere. Although NO$_3^-$ can also be lost through HNO$_3$ volatilization, we interpret $\delta^{15}$N$_{NO3}$ solely through photolysis since volatilization does not strongly fractionate NO$_3^-$ and should be a very minor component of NO$_3^-$ loss outside of the warmest coastal zones. Additionally, while the oxygen in NO$_3^-$ also undergoes isotopic fractionation through photolysis, its interpretation is complicated by isotopic interactions with snow and water vapor and is not further discussed here.

Photolysis is limited to the depth where light penetrates and initiates photochemical reactions, and so the snowpack can be divided into an uppermost photic zone (generally 10–100 cm in East Antarctica) and a deeper archived zone. Photolysis and the resulting isotopic fractionation of NO$_3^-$ cease once snowfall buries NO$_3^-$ beneath the photic zone, and the $\delta^{15}$N$_{NO3}$ value of the NO$_3^-$ buried in the archived zone (($\delta^{15}$N$_{NO3arc}$) is assumed to be preserved indefinitely in glacial ice. The final $\delta^{15}$N$_{NO3arc}$ value reflects the sum total of photolysis inducing radiation experienced by NO$_3^-$ during the burial process, which, assuming stable insolation and photic zone depth, is itself determined by the rate at which the NO$_3^-$ is buried and thus inversely related to SMB. Modeling (Supplementary Discussion 1) and field observations support SMB as the primary driver of spatial variability in $\delta^{15}$N$_{NO3arc}$ values. Based on a new simplified theoretical framework (Methods, Supplementary Discussion 1), this relationship can be expressed as:

$$\ln(\delta^{15}N_{NO3arc} + 1) = \frac{A}{\text{SMB}} + B$$

where the regression coefficients A and B are parameters that subsume constants and linearly co-varying variables associated with photolytic and fractionation processes.
of Eq. (1) can then be used as a transfer function to reconstruct SMB from $\delta^{15}$N$_{NO_3arc}$ values ($SMB_{31SN}$). Calculated and referenced SMB values are given here with units of kg m$^{-2}$ a$^{-1}$, which is equal to mm w.e. a$^{-1}$.

Results and discussion

$SMB_{31SN}$ relationship and spatial applicability. To obtain parameter estimates for Eq. (1), we sampled NO$_3^-$ in snow and

![Map of East Antarctic sites sampled for $\delta^{15}$N$_{NO_3arc}$ and surface mass balance (SMB).](image)

**Fig. 2** The relationship between Antarctic snow $\delta^{15}$N$_{NO_3arc}$ and surface mass balance (SMB). **a** Map of East Antarctic sites sampled for $\delta^{15}$N$_{NO_3arc}$ along different scientific and logistic transect routes. Colored circles indicate the locations and $\delta^{15}$N$_{NO_3arc}$ values of samples included in our field data set, with $\delta^{15}$N$_{NO_3arc}$ data from the EAIIST (pink) and CHICTABA (yellow) transects newly reported here. The base map SMB data were modeled by MAR13 and adjusted for a dry-site bias ($SMB_{adjMAR}$) (Methods, Supplementary Material). The linear regression (gray solid line) is shown with shaded 95% confidence intervals, and regression parameters are displayed at lower left.

The linear regression ($\delta^{15}$N$_{NO_3arc}$ vs. SMB for all sites in the field dataset) is given as

$$\delta^{15}$N$_{NO_3arc} = 6.98 \times \log(SMB) - 0.02$$

with $r^2 = 0.91$ and $n = 135$. This constitutes a database of 135 total $\delta^{15}$N$_{NO_3arc}$ values representing 114 distinct sites across East Antarctica (Fig. 2a). These $\delta^{15}$N$_{NO_3arc}$ data were spatially paired with local SMB measurements either observed directly onsite ($SMB_{ground}$) or as an output from the Modèle Atmosphérique Régional (MAR) forced by ERA-interim reanalysis data13 and adjusted for a dry-site bias ($SMB_{adjMAR}$) (Methods, Supplementary Material).
The sites in our database cover a comprehensive range of East Antarctic SMB, from 20–30 kg m\(^{-2}\) a\(^{-1}\) at dome summits on the high plateau to >300 kg m\(^{-2}\) a\(^{-1}\) for sites on the coastal periphery (Fig. 2b).

The SMB and \(\delta^{15}N_{\text{NO}_3\text{arc}}\) in our field dataset are correlated with a high degree of confidence, producing a linear regression where 
\[
\ln(\delta^{15}N_{\text{NO}_3\text{arc}} + 1) = 6.98 \pm 0.19 \text{ SMB}^{-1} - 0.02 \pm 0.01
\]

Fig. 2c, \(r^2 = 0.91, p < 0.001, n = 135\). Moreover, this relationship is within modeled expectations that use best estimates for photolytic and isotopic fractionation parameters (Supplementary Fig. 1, Supplementary Discussion 1). Although the linear relationship is strong, the spread in regression residuals leads to a relatively large prediction interval of \(\pm 0.0085\) for each reconstructed SMB\(_{\text{MIN}}\) value. This imprecision likely results in part because field sampling techniques varied between studies and best sampling procedures (e.g., well-mixing a >10 cm layer below the photic zone, taking multiple samples per site) may not always have been followed due to logistical challenges and time constraints. Additionally, the resolution of MAR and other regional climate models cannot capture the impact of small surface features on local SMB, and even hyperlocal SMB variability (i.e., the SMB at scales <1 m) caused by sastrugi and drifts might be missed by nearby stakes or other ground observations of SMB. Assuming that these factors are not biased toward over- or underestimating SMB, we can expect the SMB\(_{\text{MIN}}\) regression to provide accurate modeled values despite these prediction intervals. The precision of the regression and its SMB\(_{\text{MIN}}\) modeled outputs should also improve in the future with the addition of data from new sites using best sampling protocols and improved regional climate modeling.

Applying the solved regression to SMB values modeled by MAR across East Antarctica reproduces the spatial variability of \(\delta^{15}N_{\text{NO}_3\text{arc}}\) observed in samples (Fig. 3, Supplementary Table 3). We find that 74% of Antarctica has \(\delta^{15}N_{\text{NO}_3\text{arc}}\) values elevated well above the typical range of atmospheric \(\delta^{15}N_{\text{NO}_3}\) (i.e., >20‰), illustrating the vast spatial impact of photolytic \(\text{NO}_3^-\) loss. The highest modeled values, excluding some small coastal regions with very low or negative modeled SMBs (e.g., the McMurdo Dry Valleys and blue ice zones) where \(\text{NO}_3^-\) archiving is not expected, are found on the interior high plateau of East Antarctica between Dome C and Dome Fuji, in agreement with previous global chemical transport models33. Although millennial-scale changes in global \(\text{NO}_3^-\) dynamics and atmospheric oxidative capacity are not currently well constrained, the factors parameterized in Eq. (1) (Supplementary Discussion 1) have likely been stable enough during the Holocene for the SMB\(_{\text{MIN}}\) proxy’s general use. The large changes in atmospheric chemistry, biogeochemical cycles, and global environment earlier in the Pleistocene possibly changed atmospheric \(\text{NO}_3^-\) isotopic values, snow character, and/or insolation values enough that our SMB\(_{\text{MIN}}\) proxy based on modern observations will not accurately reconstruct past SMB values in glacial times. However, \(\delta^{15}N_{\text{NO}_3\text{arc}}\) changes observed between glacial and interglacial periods in Greenland ice cores have been interpreted to partially record SMB changes38, and thus \(\delta^{15}N_{\text{NO}_3\text{arc}}\) may still offer important insights into relative changes in SMB and into how \(\text{NO}_3^-\) dynamics varied during the Pleistocene.

Since the most advanced established technique for \(\text{NO}_3^-\) isotopic analysis (see Methods) uses \(\approx 5\) nmol of \(\text{NO}_3^-\) for \(\delta^{15}N_{\text{NO}_3}\) analysis and \(\approx 100\) nmol to include oxygen isotope anomaly (\(\Delta^{17}O_{\text{NO}_3}\)) analysis, the potential resolution of the SMB\(_{\text{MIN}}\) proxy depends upon the \(\text{NO}_3^-\) concentration of the snow or ice sample and upon the mass of snow or ice comprising each sample. For the samples included in our field database, \(\text{NO}_3^-\) concentrations ranged between 5 and 131 ng g\(^{-1}\), with lower values at drier sites. To collect 100 nmol of \(\text{NO}_3^-\) for maximum isotopic data, these concentrations require between 0.05 to 1.15 kg of snow or ice, with a median requirement of 0.15 kg. For snow pits, sampling at a 2 cm depth interval requires only 0.01–0.16 m\(^2\) surface area collected per sample, and thus the storage and transport logistics for large numbers of samples are more restrictive for snow pits than physical sampling limitations.

Ice core sampling resolution is dependent upon the core diameter and percent of core available for \(\text{NO}_3^-\) recovery. We find that 2–3 samples per ice core meter are typically achievable even when the ice core is only partly partitioned for \(\text{NO}_3^-\), and higher resolution is possible with cores that are drilled solely or primarily for \(\text{NO}_3^-\) isotopic analysis.

While our field dataset covers sites with a SMB from 22 to 548 kg m\(^{-2}\) a\(^{-1}\), the SMB\(_{\text{MIN}}\) proxy is best suited for sites with SMB values between 40 and 200 kg m\(^{-2}\) a\(^{-1}\). Shallow cores from very dry Dome A and Dome C have lower \(\delta^{15}N_{\text{NO}_3\text{arc}}\) values at 2–6 m below the surface than at the ~1 m base of the photic zone, possibly because photolytic \(\text{NO}_3^-\) can be transported downward through firn air convection and re-oxidized into \(\text{NO}_3^-\) with low \(\delta^{15}N_{\text{NO}_3}\) values (Supplementary Discussion 3). This phenomenon violates the foundational assumption of “locked-in” \(\text{NO}_3^-\) beneath the photic zone, but we observe it only at the ultra-dry interior sites where SMB < 40 kg m\(^{-2}\) a\(^{-1}\). For sites with SMB > 200 kg m\(^{-2}\) a\(^{-1}\), the expected \(\delta^{15}N_{\text{NO}_3\text{arc}}\) value falls within the general range of atmospheric \(\delta^{15}N_{\text{NO}_3}\) (−20 to +20‰) because \(\text{NO}_3^-\) is buried below the photic zone in less than a year. Despite the short photic zone residence time, more than 80% of \(\text{NO}_3^-\) is deposited during summer months outside of winter polar night24,39 and some photolytic loss is still likely. As a result, \(\text{NO}_3^-\) samples that integrate multiple years of accumulation at high SMB sites might still resolve differences in SMB (Supplementary Fig. 3). Additionally, \(\delta^{15}N_{\text{NO}_3\text{arc}}\) values are increasingly less sensitive to SMB changes with higher SMB values due to the asymptotic nature of SMB\(^{-1}\) (i.e., the relationship between \(\delta^{15}N_{\text{NO}_3\text{arc}}\) and SMB is nearly flat where SMB > 200 kg m\(^{-2}\) a\(^{-1}\))
Aurora Basin North SMB reconstruction. As a proof of concept, we applied the SMB$_{\text{B13N}}$ transfer function to $\delta^{15}$N$_{\text{NO3arc}}$ data from the 103 m deep ABN1314-103 ice core. This core was one of three drilled in the Australian Antarctic Program’s 2013–2014 summer campaign at Aurora Basin North (ABN; 71.17 °S 111.37 °E, 2679 m above sea level), a site with moderate modern SMB (≈120 kg m$^{-2}$ a$^{-1}$) located midway between coastal Casey Station and the Dome C summit (Fig. 2a). The SMB$_{\text{B13N}}$ history reconstructed from ABN1314-103 covers the period from −47 to 649 years before present (BP, where present = 1950 CE) and has values ranging from 49 to 208 kg m$^{-2}$ a$^{-1}$ (Fig. 4a). Each SMB$_{\text{B13N}}$ value integrates an average of 2.4 years of accumulation (total range: 0.7–4.5 years), and thus any impacts from individual precipitation events or seasonal extremes are attenuated. Overall, the SMB values at this site show fairly large variability (coefficient of variation = 0.21). The mean SMB$_{\text{B13N}}$ in the 20th century (126 ± 26.5 kg m$^{-2}$ a$^{-1}$) is 34% greater than the mean SMB$_{\text{B13N}}$ before 1900 CE (94 ± 18 kg m$^{-2}$ a$^{-1}$) and nearly 52% greater than the driest century that spans the 1600s CE (83 ± 20 kg m$^{-2}$ a$^{-1}$) (Fig. 4a).

Since $\delta^{15}$N$_{\text{NO3arc}}$ values reflect the snow burial speed of the immediate overlying area, short-term variability in SMB$_{\text{B13N}}$ is likely dominated by small spatial scale factors such as surface roughness (e.g., sastrugi and dune migration) and local weather (e.g., snowfall heterogeneity)40–43. However, the SMB$_{\text{B13N}}$ patterns observed over decadal to centennial scales more likely represent changes to the broader regional environment as the local environmental “noise” has less impact when data is aggregated at longer timescales. Finally, it is important to note that the SMB$_{\text{B13N}}$ values reflect the immediate local snow accumulation, and so some short duration events (e.g., atmospheric rivers) with major region-spanning impacts may not be preserved in an individual ice core due to periods of surface erosion and/or mixing46. This feature should not, however, be viewed as a drawback of the SMB$_{\text{B13N}}$ proxy. Rather, the SMB$_{\text{B13N}}$ record is accurately reflecting the actual SMB experienced at the core site, which is a critical factor to accurately calculating and interpreting other environmental proxies contained in the ice core, such as biogeochemical fluxes.

Validating the SMB$_{\text{B13N}}$ proxy reconstruction. We verified our new proxy’s accuracy by comparing the SMB$_{\text{B13N}}$ values with SMB calculated using the physical density of the ice core and its age-depth relationship (SMB$_{\text{density}}$). Because the measurements for SMB$_{\text{density}}$ are typically performed on each individual ice core segment, it generally has a lower potential resolution than SMB$_{\text{B13N}}$ which, in contrast, can have multiple values per core segment. Still, SMB$_{\text{density}}$ functions well as an established benchmark for validating newer SMB proxies like SMB$_{\text{B13N}}$. For each 1-m core segment of ABN1314-103, we calculated a SMB$_{\text{density}}$ value by dividing the segment’s mass (kg) by both its volume (m$^3$) and the age difference between the top and bottom of the segment (a m$^{-1}$). The SMB$_{\text{B13N}}$ (aggregated to match the 1-m resolution) and SMB$_{\text{density}}$ share very similar mean values (100.8 vs. 98.0 kg m$^{-2}$ a$^{-1}$, respectively) and total SMB ranges (62.0–157.3 vs. 61.7–153.4 kg m$^{-2}$ a$^{-1}$, respectively), and the two SMB reconstructions have a similar pattern of variation with a moderate Pearson correlation ($r = +0.46, p < 0.001, n = 90$) (Fig. 4b). The correlation increases rapidly when a broader running average is applied to the data, reaching +0.72 with 25 year averaging and +0.82 with 50 year averaging. This agreement in mean value, range, and variability validates our SMB$_{\text{B13N}}$ approach and the potential of $\delta^{15}$N$_{\text{NO3arc}}$ as an accurate proxy for paleoenvironmental change.

Interpreting the ABN1314-103 SMB profile is more complicated than for ice cores drilled at dome summits because the ice sheet at the ABN drilling site is flowing horizontally at a rate of 16.2 m a$^{-1}$47. This means that the ice in ABN1314-103 actually accumulated as snow along a continuous 11.5 km transect upstream of the current ABN drilling site, with the oldest and deepest ice originating from the most distant upstream position. Using the horizontal ice flow rate and the ABN1314-103 core’s age-depth model, we can estimate the position along the upstream transect where the snow for each depth in the core originally accumulated48.

Although overall elevation gain is small along the 11.5 km transect (<15 m), the region has abundant 0.5–1 m undulations in surface topography extending over horizontal extents of 3–10 km41 (Fig. 5a). The MAR’s horizontal grid size (35 km) cannot resolve any potential SMB impact from these features, but ground penetrating radar (GPR) data collected along the upstream transect reveals that these surface slope and curvature changes...
correlate with SMB variations of up to 40 kg m\(^{-2}\) a\(^{-1}\) as determined by internal isochronal radar reflection horizons\(^{38}\) (Fig. 5b). These surface features can be identified as buried horizons to depths below the deepest segment of ABN1314-103, which suggests that they have been stable features of the local landscape for at least 700 years.

Because ABN1314-103 is composed of snow that fell along this upstream transect, the ice core SMB record will not only reflect changes due to wetting or drying of the regional climate, but it will also reflect any spatial SMB variability caused by topographic features that existed along the upstream transect. Since the local surface topography has not significantly shifted or changed over the time period covered by ABN1314-103, we take the modern topography-driven SMB changes observed with GPR to be representative of past SMB spatial variability. As each position along the upstream transect is paired to a depth in ABN1314-103, we can transfer the GPR-derived SMB profile along the horizontal transect to ice core depths to produce a SMB reconstruction (SMB\(_{\text{GPR}}\)) that can be directly compared to the SMB\(_{\text{density}}\) and SMB\(_{\text{B15N}}\) reconstructions.

The SMB\(_{\text{GPR}}\) reconstruction for ABN1314-103 (Fig. 4b) represents the component of the SMB record preserved in the ice core that can be explained by upstream surface topography alone. We find that the general pattern of variability in SMB\(_{\text{GPR}}\) correlates very well with the patterns recorded in the SMB\(_{\text{B15N}}\) \((r = +0.74)\) and SMB\(_{\text{density}}\) \((r = +0.63)\) records (Fig. 4b). Thus, it appears that the primary SMB pattern preserved in ABN1314-103 is driven by upstream changes in surface curvature, which is important for properly interpreting other environmental proxies contained in the ice and for understanding the local ice flow history.

Extracting a climate-driven SMB record. To examine whether a secondary signal related to climate change was also preserved by the \(\delta^{15}\text{NNO}_3\) proxy, we removed the spatial impact of upstream topography by subtracting the SMB\(_{\text{GPR}}\) data from the SMB\(_{\text{B15N}}\) record. After this "upstream effect detrending" and accounting for a small consistent offset in mean SMB values (3.7 kg m\(^{-2}\) a\(^{-1}\)) between SMB\(_{\text{GPR}}\) and SMB\(_{\text{B15N}}\), we find that the multi-decadal SMB values have been generally stable over the past 700 years (Fig. 4c), with 50-yr running averages of the SMB always within 15 kg m\(^{-2}\) a\(^{-1}\) from the mean of the detrended data. These running averages suggest that drier conditions existed at ABN between 60 and 350 yr BP (1600 and 1890 CE, partially corresponding to the Little Ice Age) and that precipitation has increased in the most recent 100–150 years. This is generally consistent with what has been observed at other East Antarctic sites\(^{50–53}\) and for Antarctica as a whole\(^{18}\), but we recognize that this pattern is similar to the upstream topographic effect and that it might also arise if the SMB\(_{\text{GPR}}\) Record is excessively smoothed relative to true topographic-driven SMB variability (perhaps by the GPR data processing).

On shorter timescales, SMB values frequently change by \(\approx 50\) kg m\(^{-2}\) a\(^{-1}\) around a common mean within 10–20 year periods. This pattern likely reflects the high interannual snowfall variability expected at sites like ABN\(^{14}\). Located at the transition between the coast and the interior East Antarctic Plateau, annual snow accumulation at ABN is sensitive to frequent intrusions of extreme precipitation events and atmospheric rivers\(^{44,45}\), and the observed sub-decadal SMB\(_{\text{B15N}}\) variability may represent the frequency of their stochastic occurrence at the site. Additionally, small scale surface roughness features like sastrugi may affect hyperlocal SMB through periods of enhanced accumulation and erosion as they migrate and evolve on the snow surface\(^{40–42,54}\). While the temporal evolution and possible life cycle cyclicity of surface roughness features are as yet poorly known, hyperlocal changes in SMB could also explain some of the short-term SMB variability observed in the ABN record if the sampling interval is shorter than the average duration of a surface feature at a given location.

Applied use and potential of the SMB\(_{\text{B15N}}\) proxy. With over 8 million km\(^2\) of Antarctica having a SMB between 40 and 200 kg m\(^{-2}\) a\(^{-1}\) and over 70% of the ice sheet area modeled to have \(\delta^{15}\text{NNO}_3\) values markedly elevated by photolysis, the SMB\(_{\text{B15N}}\) proxy holds great potential for expanding our knowledge of Antarctic SMB variability over time and space and serving as an independent supplemental SMB reconstruction. Currently, regions with moderate SMB have only a handful of sites with SMB records older than 200 years, with the East Antarctic Plateau particularly poorly represented\(^{18}\). For ice coring projects in these regions, the SMB\(_{\text{B15N}}\) proxy can perform better at capturing the local effects of strong winds, irregular surface topography, and high interannual snowfall variability than water isotopic
techniques while avoiding problems with layer thinning, density modeling, and core damage that affect density-based methods. As regional climate models still struggle to accurately simulate drifting snow and sublimation fluxes in the coast-to-plateau transition\(^5\), SMB\(^{15N}\) can provide critical ground-based data for models predicting future contributions to sea level rise. The SMB\(^{15N}\) proxy also holds particular value for helping to constrain and validate models of upstream flow effects in research targeting ice streams and broad-scale glacial flow patterns. The SMB\(^{15N}\) approach may also be useful to estimate relative SMB changes for ice cores that lack robust age-depth models due to severe glacial deformation or discontinuities.

Additionally, sampling for the SMB\(^{15N}\) proxy can save valuable time and cost compared to existing alternatives to expand current records of modern SMB. Obtaining new ground-based SMB measurements using existing techniques for sites without annually resolved layers requires either coring several meters to the increasingly buried Pinatubo volcanic horizon or repeated visits to newly installed stake transects. However, limited time and resources for research expeditions to remote areas precludes intensive SMB surveys with these methods. With the SMB\(^{15N}\) proxy, a mean site SMB could be determined with only a series of shallow snow or firm samples extending deep enough into the archived zone to cover only a few seasonal cycles (much shallower than the Pinatubo horizon). After mixing snow well from multiple samples, only 15–75 g (0.3–1.5 kg if \(^15\delta\)NO\(^3\) results are desired) would need to be kept, transported, and analyzed for each sample, which logistically allows for the rapid collection of robust SMB site means in many locations. On-site melting and NO\(^3\) concentration could further reduce logistical requirements.

The SMB\(^{15N}\) proxy promises to grow and adapt as studies on Antarctic NO\(^3\) dynamics continue. More NO\(^3\) samples coupled with quality environmental context data from East Antarctic will help us better constrain the uncertainty of SMB\(^{15N}\) calculations and allow for more confidence in reconstructions. As additional ice cores are analyzed for \(^15\delta\)NO\(^3\)\(_{arc}\) we can better understand under which exact conditions \(^15\delta\)NO\(^3\)\(_{arc}\) most accurately records SMB variability and if we can improve our reconstructions with a more complex model. Differences between calculated SMB\(^{15N}\) values and well-constrained SMB density values may also prove useful in identifying periods of unusual environmental conditions that alter typical photolytic reactivity.

Because the resolution of \(^15\delta\)NO\(^3\)\(_{arc}\) sampling is limited only by the minimum amount of NO\(^3\) needed for analysis, very finely-resolved \(^15\delta\)NO\(^3\)\(_{arc}\) records can be obtained by increasing the mass of ice collected per depth unit (e.g., by specifically drilling whole cores or replicate cores for NO\(^3\) isotopes) and with advances in NO\(^3\) isotopic analysis expected in the near future\(^35\). This may allow for more precise multi-annual aggregations for SMB\(^{15N}\) reconstructions and permit a deeper examination of subannual NO\(^3\) dynamics that can improve the proxy. Given the potential of the SMB\(^{15N}\) proxy to advance our understanding of the Antarctic environment and its sensitivity to climate change, we strongly recommend that potential ice coring projects incorporate NO\(^3\) analyses into their planning and urge continued studies on Antarctic NO\(^3\) dynamics.

**Methods**

**Mathematical framework for \(^15\delta\)NO\(^3\)\(_{arc}\) and SMB relationships.** A linear relationship between \(^15\delta\)NO\(^3\)\(_{arc}\) and the reciprocal of surface mass balance (SMB\(^{-1}\)) has been previously observed and reported in Antarctica\(^19,28,36\). Here, we mathematically illustrate how this relationship between \(^15\delta\)NO\(^3\)\(_{arc}\) and SMB arises through photolysis of NO\(^3\). We focus solely on the characteristics of NO\(^3\) contained within a given horizontal plane of snow that is located at the snowpack surface at \(t = 0\). We assume simplified conditions with a constant surface mass balance (SMB), clear sky conditions, no surface roughness, and no significant compaction with burial in the photonic zone. Any NO\(^3\) that is photolyzed is immediately and permanently removed from the plane of snow, and NO\(^3\) recycling\(^23,36\) is assumed not to affect NO\(^3\) in the plane of snow during the burial process modeled here (i.e., after \(t = 0\)).

Defining the relationship between \(^15\delta\)NO\(^3\)\(_{arc}\) and SMB. The time that it takes for a given horizontal plane of snow to be buried from the surface to a particular depth \(z\) is determined by the SMB (kg m\(^{-2}\) a\(^{-1}\), converted to an equivalent vertical velocity in cm s\(^{-1}\)):

\[
\begin{align*}
\frac{dc}{dt} & = \frac{x}{\text{SMB}} \\
\end{align*}
\]

The concentration of NO\(^3\) within a plane of snow decays through time according to:

\[
\begin{align*}
\frac{d[\text{NO}_3^-]}{dt} & = -I_{\phi}(\text{NO}_3^-) \gamma(t) \\
\end{align*}
\]

where \(I_{\phi}\) is the photolytic rate constant at a given depth defined as:

\[
I_{\phi} = \phi(\text{NO}_3^-) \\
\]

where \(\phi\) is the absorption cross section for NO\(^3\) photolysis (cm\(^2\)), \(\phi\) is the quantum yield for NO\(^3\) photolysis (molec photon\(^{-1}\)), and \(I_{\phi}\) is the actinic flux of ultraviolet irradiance (photon cm\(^{-2}\) s\(^{-1}\) nm\(^{-1}\)) integrated over wavelengths that can induce photolysis of NO\(^3\). However, this photolytic rate “constant” changes with depth because actinic flux exponentially decays with depth as:

\[
I_{\phi} = I_{\phi} e^{-\gamma z} \\
\]

where \(I_{\phi}\) is the initial actinic flux that strikes the snow surface and \(z\) is the e-folding depth (cm) of the snowpack. Note that non-exponential decay of \(I_{\phi}\) in the top ~2 cm of snowpack\(^32\) is simplified here by assuming the decay to be exponential from the snow surface. Equation (3) can then be expressed as:

\[
\frac{d[\text{NO}_3^-]}{dt} = -\phi(\text{NO}_3^-) e^{-\gamma z} (\text{SMB}) \\
\]

And integrate to produce:

\[
\ln[\text{NO}_3^-]_{\gamma(t)} = \phi(\text{NO}_3^-) e^{-\gamma z} \text{SMB} + C \\
\]

Which simplifies to:

\[
[\text{NO}_3^-]_{\gamma(t)} = e^{-\gamma z} \text{SMB} + \text{C} \\
\]

At \(t = 0\), [NO\(^3\)]\(_{\gamma(0)}\) = [NO\(^3\)]\(_{\gamma(t)}\) and therefore:

\[
[\text{NO}_3^-]_{\gamma(t)} = e^{-\gamma z} \text{SMB} \\
\]

And thus combining Eqs. (10) and (11):

\[
[\text{NO}_3^-]_{\gamma(t)} = [\text{NO}_3^-]_{\gamma(0)} e^{-\gamma z} \frac{\text{SMB}}{[\text{NO}_3^-]_{\gamma(t)}} = [\text{NO}_3^-]_{\gamma(0)} e^{-\gamma z} \frac{\text{SMB}}{[\text{NO}_3^-]_{\gamma(t)}} \\
\]

According to Eq. (12), as time (i.e., burial depth) increases, the NO\(^3\) concentration will decrease. However, the rate of decrease will lessen over time as the value of SMB \(\times t\) approaches 3\(\gamma\) and 95% of the initial irradiance is gone. Here, below the photic zone (i.e., \(z > 3\gamma\)), the NO\(^3\) concentration is largely stable and equal to \(e^\gamma\).

Therefore, we can calculate the fraction of NO\(^3\) archived below the photic zone (\(\beta_{\text{arc}}\)) as:

\[
f_{\text{arc}} = \frac{e^\gamma}{[\text{NO}_3^-]_{\gamma(0)}} = \frac{\text{[NO}_3]_{\gamma(0)} e^{-\gamma z} \text{SMB}}{[\text{NO}_3^-]_{\gamma(t)}} \\
\]

To determine the \(^15\delta\)NO\(^3\)\(_{arc}\) of this NO\(^3\), Rayleigh fractionation states that \(^15\delta\)NO\(^3\) can be calculated with the fractionation factor \(a\) by:

\[
\ln[\delta_{15}\text{NO}_3]_{\gamma(t)} + 1 = (a - 1) \ln(f_{\text{arc}}) + \ln[\delta_{15}\text{NO}_3]_{\gamma(0)} + 1 \\
\]

Through our prior calculation of \(f_{\text{arc}}\) in Eq. (13), we thus produce:

\[
\ln[\delta_{15}\text{NO}_3]_{\gamma(t)} + 1 = (a - 1) \frac{\phi(\text{NO}_3^-) e^{-\gamma z}}{\text{SMB}} + \ln[\delta_{15}\text{NO}_3]_{\gamma(0)} + 1 \\
\]

Because \((a - 1)\) is negative for nitrogen during photolysis of NO\(^3\)\(^-23,34,35,56-58\) and the other parameters are positive, this means that \(^15\delta\)NO\(^3\)\(_{arc}\) will vary linearly and positively with SMB\(^{-1}\) when other parameters are held constant or scale linearly with SMB\(^{-1}\). We examine the potential impacts of variability in these other parameters more thoroughly in Supplementary Discussion 1.
Based on modeling and field observations, SMB is the primary driver of change in $\delta^{15}$NNO3arc values. Thus, the non-SMB variables can be subsumed into two parameters $A$ and $B$ to function as linear regression coefficients, producing Eq. (16) of the main text:

$$
\ln \left( \delta^{15}N_{\text{NO3}} + 1 \right) = \frac{A}{\text{SMB}} + B
$$

The inverse function of Eq. (16) can be used as a transfer function to calculate SMB based on a $\delta^{15}$NNO3arc value:

$$
\delta^{15}N_{\text{NO3}} = (a - 1) - \frac{\text{SMB}}{A} + \delta^{15}N_{\text{NO3}}
$$

Finally, since $\ln(x + 1) = x$ when $x = 0$, a simpler relationship of Eq. (15) can be observed in a form that was previously reported from field observations.

**Snow sampling techniques.** The $\delta^{15}$NNO3arc values in our database are taken from a mix of previously reported values from Antarctic research traverses and values newly reported here (Fig. 2). For all values, snow and ice containing NO3– was sampled in the field in one of three techniques: 1) 1–2 m deep snow pit with continuous sampling at regular intervals from top to bottom, 2) single sample taken of a well-mixed 5–10 cm layer around the 1 m-depth layer, and 3) drilled core later cut at desired intervals. For isotopic measurement of NO3– that included $\delta^{15}$O2O3 analysis, 0.3–1.5 kg of snow or ice per sample were gathered to ensure a sufficient mass of NO3–. Generally, the multiple samples produced by the snow pit technique offered the best and most flexible results, but the 1-m depth layer technique was valuable for quick sampling during limited stops, and cores are necessary to collect samples deeper than 5 m.

**Laboratory analyses.** For $\delta^{15}$NNO3 results included in our database that have previously been reported, readers are directed to the original papers for specific analytical and sampling techniques. For the $\delta^{15}$NNO3arc data newly reported here, snow and ice samples were collected into clean sealed plastic bags or tubs and stored frozen until melted at room temperature for analysis. The NO3– mass fraction ($\omega(\text{NO3}–)$) was determined on aliquots by either a colorimetric method or ion chromatography with detection limits <0.5 mg L$^{-1}$ and precision of <3%.

The remaining melted samples were passed through an anion exchange column (Bio-Rad™ AG 1-X8, chloride form), and the resulting trapped NO3– was eluted with 10 mL of NaCl 1 M solution.

Isotopic analysis occurred at IGE-CNRS, Grenoble, France, where NO3– in these samples was converted to N2O with the denitrifying bacteria Pseudomonas aureofaciens (lacking nitrate reductase), then thermally decomposed, to $\delta^{15}$NNO3 values for 16 pits along the JARE transect upstream of the coring site as part of the 2013 campaign. Radar was triggered every 2 s (i.e., every 6.7 m along the transect) with a recording time window of 3000 nanoseconds that captured returns down to 300 m depth. After postprocessing, isochronal internal reflecting horizons were identified to 220 m depth, digitized with ReflexW software, and dated by connecting to the 2011–2018 age model. Using a density profile taken from a longer ice core simultaneously drilled at ABN, 2D fields (depth by transect distance) were calculated for age, mean accumulation rate, and local accumulation rate. The mean accumulation rate to the most shallow reflecting horizon was taken as the upstream topographical effect on SMB (i.e., SMBarc).

For the laboratory analyses, regression to the transfer function, and SMB reconstruction, we modeled linear relationships between $\ln(\delta^{15}N_{\text{NO3arc}} + 1)$ and SMB (1) using the previously reported parameter values to compare our theoretical framework to field results and to help us understand the relationship to other climatic and fractionation factors (Supplementary Discussion 1). To determine the coefficients in Eq. (1) from our field data, we performed linear regressions using all database $\delta^{15}$NNO3arc samples and the primary SMB dataset of best available SMB. Additional regressions (Supplementary Discussion 2) were performed for subsets of the data based on SMB type (SMBarc vs. SMBground), geographic location, core age, or other climate factors. We therefore calculated the regression coefficients for determined Eq. (1), we modeled the spatial distribution of $\delta^{15}$NNO3arc values across Antarctica using gridded mean SMB (MAR-Era-interim, 1979–2015) at a 35 km resolution that were converted to SMBadjMAR as previously described. For reconstructing the ABN SMB500 history, the ABN313-104 ice core was cut into 0.33 m samples from 5 to 103 m, and these were processed for NO3– isotopes in 2016 as previously described. We applied an annually resolved age model (ALCO1112018) based on seasonal ion and water isotope cycles and constrained by volcanic horizons that was originally developed for a longer core on site. Each 1-m depth layer was sampled for NO3–, and the mass and volume were used to calculate a SMB profile based on dated ice density changes (SMBground).

To determine past topographical effects on SMB, a MALA GRP device towing a RTA antenna on the surface (50 MHz out, 100 MHz in) was operated for a 65 km transect upstream of the coring site as part of the 2013–2014 campaign. Radar was triggered every 2 s (i.e., every 6.7 m along the transect) with a recording time window of 3000 nanoseconds that captured returns down to 300 m depth. After postprocessing, isochronal internal reflecting horizons were identified to 220 m depth, digitized with ReflexW software, and dated by connecting to the 2011–2018 age model. Using a density profile taken from a longer ice core simultaneously drilled at ABN, 2D fields (depth by transect distance) were calculated for age, mean accumulation rate, and local accumulation rate. The mean accumulation rate to the most shallow reflecting horizon was taken as the upstream topographical effect on SMB (i.e., SMBarc). Regional climate models can be used to estimate modern SMB rates for sites lacking ground observations, and photic zone corrections were thus not warranted.
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