Photolytic modification of seasonal nitrate isotope cycles in East Antarctica

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Abstract. Nitrate in Antarctic snow has seasonal cycles in ~~its~~ nitrogen and oxygen isotopic ratios that reflect its sources and atmospheric formation processes, and as a result, nitrate archived in Antarctic ice should have great potential to record atmospheric chemistry changes over thousands of years. However, sunlight that strikes the snow surface results in photolytic nitrate loss and isotopic fractionation that can completely obscure the nitrate's original isotopic values. To gain insight into how photolysis overwrites the seasonal atmospheric cycles, we collected 244 snow samples along an 850 km transect of East Antarctica during the 2013–2014 CHICTABA traverse. The CHICTABA route's limited elevation change, consistent distance between the coast and the high interior plateau, and intermediate accumulation rates offered a gentle environmental gradient ideal for studying the competing pre- and post-depositional influences on archived nitrate isotopes. We find that nitrate isotopes in snow along the transect are indeed notably modified by photolysis after deposition, and drier sites have more intense photolytic impacts. Still, an imprint of the original seasonal cycles of atmospheric nitrate isotopes is ~~still~~ present in the top 1–2 m of the snowpack and likely preserved through archiving in glacial ice at these sites. Despite this preservation, reconstructing past atmospheric values from archived nitrate ~~along CHICTABA and~~ in similar transitional regions ~~remains~~ will remain a difficult challenge without having an independent proxy for photolytic loss to correct for post-depositional isotopic changes. Nevertheless, nitrate isotopes should function as a proxy for snow accumulation rate in such regions if multiple years of deposition are aggregated to remove the seasonal cycles, and this application can prove highly valuable in its own right.

1. Introduction

Nitrate (NO_3^-) is one of the most prevalent ions in Antarctic snow and ice, arriving as an end product of the atmospheric oxidation of nitrogen oxides ($NO_x = NO + NO_2$) in wet or dry deposition of nitric acid (HNO_3) or particulate nitrate (p-NO_3^-) (Neubauer and Heumann, 1988; Wolff, 1995; Röthlisberger et al., 2000; Savarino et al., 2007; Frey et al., 2009; Shi et al., 2018b). Because the isotopic ratios of nitrogen and oxygen in atmospheric NO_3^- reflect differences in the original sourcing of the NO_3^- and its atmospheric reaction history, a long-term NO_3^- archive could reveal how the atmosphere's oxidative capacity and chemical reaction pathways have changed over time (Legrand et al., 1999; Michalski et al., 2005; Wolff et al., 2007; Alexander et al., 2009; Kamezaki et al., 2019). Despite its paleoenvironmental potential, NO_3^- has been difficult to interpret in ice cores because post-depositional processes in the uppermost snowpack often result in substantial mass loss and isotopic changes (Wolff et al., 2002; Grannas et al., 2007; Frey et al., 2009; Erbland et al., 2013; Meusinger et al., 2014; Traversi et al., 2014; Geng et al., 2015). Before the paleoenvironmental potential of NO_3^- can be fully realized, we require an improved understanding on how the isotopic values in NO_3^- are altered during the archiving process ~~from~~ in the snowpack from the ~~atmosphere~~ atmospheric source ~~to the snowpack and finally to~~into eventual glacial ice.

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Atmospheric NO_3^- sampled 1–10 m above the snow surface in Antarctica has clear annual cycles in concentration and isotopic values related to seasonal changes in NO_3^- source and formation reaction pathways (Wagenbach et al., 1998; Savarino et al., 2007, 2016; Frey et al., 2009; Erbland et al., 2013; Ishino et al., 2017; Winton et al., 2020). Through wet or dry NO_3^- deposition, these annual cycles are transferred ~~to~~ with the NO_3^- ~~present onto~~to the snow surface. After deposition, NO_3^- photolysis, HNO_3 volatilization, and physical snow mixing can alter and obscure these cycles, but post-depositional NO_3^- processes are largely restricted to a shallow (i.e., 0.1–1.0 m) surface layer of the snowpack where light can penetrate, interstitial air can exchange with the atmosphere, and snow can be eroded and mixed by wind (e.g., Grannas et al., 2007; Wolff et al., 2002; Röthlisberger et al., 2002; Frezzotti et al., 2002; Libois et al., 2014; Scarchilli et al., 2010; Picard et al., 2019). After NO_3^- in a snow layer is buried beneath this "active zone" by additional snow accumulation, it is believed to be generally nonreactive and stable.

As a result, the magnitude of post-depositional ~~mass loss and~~ isotopic changes relative to the initial depositional values is heavily controlled by the speed at which NO_3^- is buried, i.e., the local surface mass balance (SMB, equivalent here to "net accumulation rate"). At very high SMB sites near the Antarctic coast, NO_3^- is rapidly buried, and the original chemical nature of the atmospheric NO_3^- is largely preserved through the burial process. At very low SMB sites, in contrast, it may take several years for NO_3^- to be buried below the zone of active post-depositional processes, and NO_3^- observed in ice cores and snow pits at dry interior Antarctic stations has such substantial isotopic changes and extreme mass loss that the original depositional values of NO_3^- are completely obscured (Freyer et al., 1996; Frey et al., 2009; Erbland et al., 2013; Shi et al., 2015). Most of Antarctica, however, falls between these two SMB extremes ~~environments~~ (Agosta et al., 2019), and archived NO_3^- concentration and isotopic profiles throughout Antarctica likely exhibit a gradient between full preservation of the atmospheric NO_3^- characteristics and the complete post-depositional loss of these characteristics ~~due to overwhelming post-depositional changes~~. Snow and ice from intermediate SMB sites can thus offer valuable insight into exactly how post-depositional processes interact with and change the initial isotopic chemistry of NO_3^- that is deposited in Antarctica.

We present here NO_3^- data of snow samples taken during the CHICTABA ("Chemical-physical analyses of snow and firn for determining accumulation in Terre Adélie and Aurora Basin North") traverse across a ~~relatively wetter and~~ lower elevation region of the East Antarctic Plateau in austral summer 2013–2014. The NO_3^- data include NO_3^- mass fractions ($\omega(NO_3^-)$), isotopic ratios ($\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$, where $\delta = \frac{R_{sample}}{R_{reference}} - 1$, with R denoting the $^{15}N/^{14}N$ or $^{18}O/^{16}O$ isotopic ratios of NO_3^-, reported relative to the standards N_2-Air (Mariotti, 1983) and Vienna Standard Mean Ocean Water (VSMOW) (Baertschi, 1976), respectively), and the oxygen isotope anomaly ($\Delta^{17}O_{NO3}$, where $\Delta^{17}O_{NO3} = \delta^{17}O_{NO3} - 0.52 \times \delta^{18}O_{NO3}$) (Thiemens and Heidenreich, 1983). The sites sampled along this traverse have climatology and SMB intermediate to the coast and interior plateau, and thus the NO_3^- offers an important link between existing studies focused on ~~these~~ those two environments. With our new data, we confirm the partial preservation of seasonal isotopic cycles, quantify isotopic fractionation due to post-depositional effects, and consider how these dual effects interact to produce the NO_3^- values that will be archived into deeper ice.

2. Processes affecting NO_3^- isotopic variability in Antarctica

2.1. Annual cycles in atmospheric NO_3^- chemistry and sourcing

Seasonal changes of near surface atmospheric NO_3^- concentration and isotopic ratios (Figure 1) are well-documented at multiple sites across East Antarctica (Wagenbach et al., 1998; Savarino et al., 2007; Frey et al., 2009; Erbland et al., 2013; Ishino et al., 2017; Xu et al., 2019; Winton et al., 2020; Shi et al., 2022a). Atmospheric NO_3^- concentrations peak in late spring and early summer (Nov–Jan) and are 5–10 times lower in autumn and winter (Mar–Jul). Values of $\delta^{18}O_{NO3}$ and $\Delta^{17}O_{NO3}$ both peak in late winter (Jul–Sep) and are lowest in summer (Dec–Feb), resulting in a seasonal cycle that is offset four months earlier from the NO_3^- concentration cycle. The $\delta^{15}N_{NO3}$ values also vary seasonally, but with a less clear cycle.

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While the highest $\delta^{15}N_{NO3}$ values coincide with the late winter peak in $\delta^{18}O_{NO3}$ and $\Delta^{17}O_{NO3}$ values, the lowest $\delta^{15}N_{NO3}$ values occur in spring (Oct–Nov), 1–2 months before the minima in $\delta^{18}O_{NO3}$ and $\Delta^{17}O_{NO3}$. Additionally, a minor secondary peak in atmospheric $\delta^{15}N_{NO3}$ has also been observed at Dome C in January (Figure 1b) (Frey et al., 2009; Erbland et al., 2013; Winton et al., 2020).

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These annual cycles have been attributed to changes in NO_3^- sourcing and reaction pathways related to the distinctly different extreme environments of polar summer and winter. During daytime, photolysis can be a significant local source of NO_3^- when ultraviolet solar radiation converts NO_3^- in the snowpack into NO_x gases that then ventilate upward into the atmosphere and oxidize back into HNO_3 (Frey et al., 2009; Erbland et al., 2015; Winton et al., 2020). In polar winter, however, the limited or complete lack of sunlight largely prevents photolysis from occurring, and atmospheric NO_3^- over Antarctica in winter is thought to be largely supplied through long-distance transport from lower latitudes (Savarino et al., 2007; Lee et al., 2014; Shi et al., 2018b; Walters et al., 2019). Substantial influx of this low latitude NO_3^- is limited ~~in winter~~ by the intense Antarctic polar vortex, and~~,~~ NO_3^- concentrations in winter are very low as a result. During the coldest conditions in late winter and early spring, stratospheric denitrification through polar stratospheric cloud sedimentation supplies a small amount of NO_3^- with relatively high $\delta^{15}N_{NO3}$, $\delta^{18}O_{NO3}$, and $\Delta^{17}O_{NO3}$ values to the troposphere above Antarctica (Fahey et al., 1990; Van Allen et al., 1995; Santee et al., 2004; Savarino et al., 2007; Ishino et al., 2017; Shi et al., 2022a). This stratospheric supply produces a small observed increase in NO_3^- concentration and contributes to the annual peaks in isotopic values (Figure 1). Additionally, because ozone (O_3) transfers its anomalously high $\Delta^{17}O$ value to NO_3^- when it is involved in NO_x cycling, the higher $\Delta^{17}O_{NO3}$ values observed in Antarctic winter are attributed to this NO_3^- being sourced from lower latitudes and the stratosphere where O_3 oxidation is more important (Alexander et al., 2009; Savarino et al., 2016; Ishino et al., 2017).~~Additionally, as ozone (O_3) transfers its anomalously high $\Delta^{17}O$ value to NO_3^- when NO_x is oxidized through O_3 pathways, higher $\Delta^{17}O_{NO3}$ values are favored in the dark polar winter when O_3 oxidation does not compete with alternative photochemical oxidation pathways (Alexander et al., 2009; Savarino et al., 2016; Ishino et al., 2017).~~

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With the return of intense sunlight in spring, photolysis will convert much of the NO_3^- that has accumulated in the near surface snowpack through winter into NO_x which is rapidly re-oxidized into HNO_3 upon reaching the atmosphere (Wolff et al., 2002; Davis et al., 2004, 2008; Grannas et al., 2007; Jacobi and Hilker, 2007; Erbland et al., 2015; Winton et al., 2020; Barbero et al., 2021). This new source of "recycled" NO_3^- produces a rapid rise in atmospheric NO_3^- concentration in November, with some NO_3^- possibly supplied by additional recycled HNO_3 transported from upwind regions of Antarctica (Savarino et al., 2007; Shi et al., 2018a). The recycled NO_3^- has isotopic values lower than the mean atmospheric NO_3^- values due to strongly negative isotopic fractionation factors during NO_3^- photolysis (Frey et al., 2009; Erbland et al., 2013; Berhanu et al., 2014, 2015; Shi et al., 2015) and incorporation of oxygen atoms from local water sources (snow and water vapor $\delta^{18}O = -20$–-80 ‰, $\Delta^{17}O \approx 0$ ‰) during re-oxidation (McCabe et al., 2005; Erbland et al., 2013; Winton et al., 2020). Sunlight also triggers additional oxidation pathways for NO_3^- formation through HO_x, RO_x, and H_2O_2 that lack the anomalous $\Delta^{17}O$ value of O_3 (i.e., their NO_3^- product has $\Delta^{17}O = 0$), and $\Delta^{17}O_{NO3}$ values are expected to decline in summer as these pathways compete with the O_3 pathway (Alexander et al., 2009; Savarino et al., 2016; Ishino et al., 2017). Several unknowns still exist ~~regarding the atmospheric NO_3^- budget for Antarctica, however,~~based on disagreements between field observations and model predictions for isotopic values and photolytic constants, and ~~this~~ the atmospheric NO_3^- budget for Antarctica remains an active field of research (e.g., Savarino et al., 2016; Walters et al., 2019; Barbero et al., 2021).

2.2. Snow skin layer NO_3^- chemistry

The seasonal variability of NO_3^- in the snowpack's "skin layer" (i.e., the uppermost 2–6 mm layer of loose snow grains) generally follows that of the local atmospheric NO_3^- (Figure 1~~Figure 1~~e-h). This similarity is because skin layer NO_3^- is in a close exchange with atmospheric NO_3^-, being sourced from recently deposited atmospheric NO_3^- and also supplying NO_3^- to the atmosphere through photolysis during sunlit times. Spatially across Antarctica, skin layer $\omega(NO_3^-)$ is generally higher at drier and more inland regions (Frey et al., 2009; Erbland et al., 2013; Shi et al., 2015, 2018b)~~.Although~~ despite atmospheric NO_3^- concentrations showing far less spatial variability (Savarino et al., 2007; Frey et al., 2009; Shi et al., 2022a). The higher $\omega(NO_3^-)$ observed in the skin layer at drier sites is attributed to increased local NO_3^- deposition from photolytic recycling as well as the fact that drier sites will dilute the NO_3^- less when NO_3^- deposition rates are similar across Antarctica (Erbland et al., 2013; Shi et al., 2018b; Winton et al., 2020)~~.observations are uncommon outside of a few scientific stations, higher skin layer $\omega(NO_3^-)$ values have been observed at drier and more inland regions (Frey et al., 2009; Erbland et al., 2013; Shi et al., 2015, 2018b).~~

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Some differences between atmospheric and skin layer values do exist, however. Notably, $\delta^{15}N_{NO3}$ values in the skin layer are 5–15 ‰ higher than the atmosphere, possibly due to isotopic fractionation as atmospheric HNO_3 gas adsorbs onto the snow surface (Erbland et al., 2013; Winton et al., 2020). Additionally, the NO_3^- oxygen isotopes in the skin layer are consistently higher than those observed in atmospheric NO_3^- (Erbland et al., 2013; Winton et al., 2020), and this unexpected discrepancy is ~~unexpected and~~ currently unexplained and puzzling. This difference is greatest in the early winter, when $\delta^{18}O_{NO3}$ and $\Delta^{17}O_{NO3}$ values can be up to 20 ‰ and 10 ‰ higher, respectively, in the skin layer than the atmosphere. Full annual skin layer observations of $\omega(NO_3^-)$ and NO_3^- isotopes ~~are only available to date~~have until recently been only available from Dome C (Figure 1~~Figure 1~~e–h) (Frey et al., 2009; Erbland et al., 2013; Winton et al., 2020), but a recent record from Zhongshan station suggests that oxygen isotopic values at coastal sites may match more closely between the atmosphere and snow surface (Shi et al., 2022a). Additional data from Zhongshan station and other sites will allow us to better judge the representativeness of the Dome C data with regards to the broader Antarctic environment.

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~~and it is thus unfortunately not known if the patterns observed at Dome C are representative for other Antarctic sites with higher SMB (Frey et al., 2009; Erbland et al., 2013; Winton et al., 2020).~~

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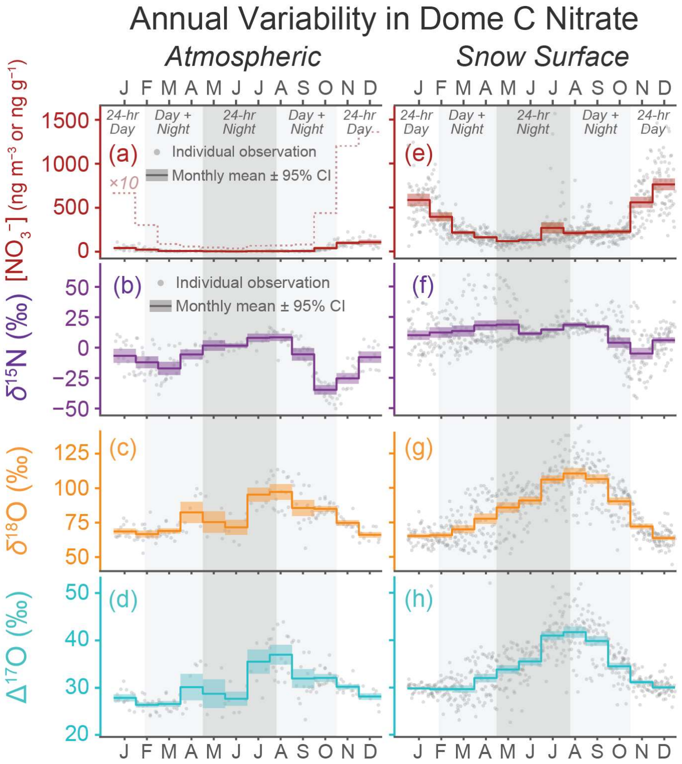

Figure 1. **Annual patterns of NO_3^- variability in the atmospheric and snow surface at Concordia station, Dome C, Antarctica. Data shown covers previously reported samples taken in 2009–2014 (Erbland et al., 2013; Winton et al., 2020). Atmospheric NO_3^- (a~~–~~–d) was collected over week-long periods with a high-volume air filter located 5 m above the snow surface, and snow surface samples (e–h) were taken every 1–7 days from the 2–6 mm thick skin layer in the clean sector outside Concordia ~~Station~~station. Individual points represent individual samples, and the thick colored lines represent the monthly mean values with the 95 % confidence interval of the mean shown as colored shading. Note that the units for NO_3^- concentration is ng m^{-3} for atmospheric NO_3^- (a) and ng g^{-1} for the snow surface NO_3^- (e). A dashed line representing the atmospheric NO_3^- concentration multiplied by 10 is included in (a) for better observation of the annual variation pattern.**

2.3 Post-depositional processes affecting NO_3^-

During burial, several post-depositional processes can alter the values of skin layer NO_3^-. Past studies of buried NO_3^- on the interior East Antarctic Plateau have highlighted photolysis as the primary post-depositional process that affects NO_3^- in East Antarctic snow, resulting in substantial NO_3^- mass loss that can reach > 90 % reduction at dome summits. The NO_3^- remaining in snow ~~at depth~~after mass loss shows marked increases in $\delta^{15}N_{NO3}$ values due to a negative photolytic isotopic fractionation factor for nitrogen. ~~Although f~~Fractionation factors for $\delta^{18}O_{NO3}$ and $\Delta^{17}O_{NO3}$ are theoretically predicted to be negative, and therefore oxygen isotopic values of remaining NO_3^- should increase ~~in a similar fashion to~~like $\delta^{15}N_{NO3}$ after photolysis (Frey et al., 2009). ~~, actual observations of NO_3^- in Antarctic snow conditions revealed that~~However, NO_3^- at sites with clear photolytic mass loss ~~produces~~ typically has ~~lower~~ $\delta^{18}O_{NO3}$ and $\Delta^{17}O_{NO3}$ values lower than atmospheric values (Frey et al., 2009). This discrepancy has been explained as the NO_3^- incorporating and exchanging isotopically lighter oxygen from local water reservoirs (e.g., snow and ~~interstitial~~ water vapor) through a cage effect during re-oxidation ~~after~~ of photolytic ~~conversion to NO_x~~products (McCabe et al., 2005; Erbland et al., 2015). There is no significant similar reservoir of

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exchange for nitrogen, and as a result, the net effect of photolysis and re-oxidation produces so-called "apparent" fractionation constants that are negative for $\delta^{15}N_{NO3}$ and positive for $\delta^{18}O_{NO3}$ and $\Delta^{17}O_{NO3}$ (Röthlisberger et al., 2002; Wolff et al., 2002; Blunier et al., 2005; Grannas et al., 2007; McCabe et al., 2007; e.g., Frey et al., 2009; Winton et al., 2020). As sunlight is rapidly attenuated beneath the snow surface, photolytic loss is restricted to the photic zone (i.e., the 0.1–1.0 m deep zone that light can penetrate and sustain photochemical reactions) and is most pronounced in the uppermost few centimeters of the snowpack (Frey et al., 2009; Zatko et al., 2013; Erbland et al., 2015; Winton et al., 2020).

Although photolysis dominates post-depositional changes to NO_3^-, other factors can also play minor roles. Wind can physically mix snow bearing NO_3^- from different seasons or years ~~which may~~and blur pre-existing NO_3^- cycles. Additionally, the development and migration of surface features like dunes and sastrugi can result in wildly variable hyperlocal accumulation rates on short timescales (0.5–5 yr) and across very short distances (< 5 m), even if the mean SMB for the broader region stays constant. These phases of erosion and deposition can result in NO_3^- cycles that appear stretched or compressed relative to expectations from regional SMB or even create stratigraphic unconformities with missing periods of deposition (Frezzotti et al., 2002; Scarchilli et al., 2010; Gautier et al., 2016; Picard et al., 2019). NO_3^- volatilization can also be a source of NO_3^- mass loss in Antarctic snow, but it is largely restricted to the warmest coastal regions of Antarctica and is believed to have little isotopic fractionation impact (Erbland et al., 2013; Shi et al., 2019). Finally, downward ~~NO_x~~ transport and ~~reoxidation~~re-oxidation of photolytic NO_x within the firn may also occur, but as of yet this process is poorly attested and significant impacts appear to be largely restricted to very dry interior sites (SMB < 40 kg m^{-2} a^{-1}) (Akers et al., 2022). Once ~~snow is~~ buried beneath the depth where post-depositional processes are active, NO_3^- ~~it~~ is assumed to be practically chemically inert ~~(especially for $\omega(NO_3^-)$ and $\delta^{15}N_{NO3}$)~~ and physically immobile (Frey et al., 2009; Erbland et al., 2013; Shi et al., 2015; Noro et al., 2018), aside from volcanic H_2SO_4-driven NO_3^- displacement with no changes to isotopic compositions (Wolff, 1995; Röthlisberger et al., 2002; Jiang et al., 2019).

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Winton et al., 2020; Akers et al., 2022; Cao et al., 2022; Shi et al., 2022b). Still, these other photolytic factors remain enticing targets for paleoenvironmental reconstruction. ~~(Zatko et al., 2016; Winton et al., 2020; Akers et al., 2022; Cao et al., 2022; Shi et al., 2022b)~~

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3. Methods

We sampled snow for NO_3^- analysis in Nov–Dec 2013 at 23 sites along the CHICTABA traverse (Table 1~~Table 1~~) from the D85 skiway (70.425° S, 134.146° E, 2848 m a.s.l.) to the Aurora Basin North (ABN) ice core drilling site (71.167° S, 111.367° E, 2689 m a.s.l.) (Figure 2~~Figure 2~~). For each snow sample, 100–600 g of snow were collected into clean sealed plastic bags~~,~~ and stored frozen in clean conditions until the return to Concordia station. All samples were taken upwind of the traverse route to avoid possible contamination. Total snow sampling consisted of 23 “skin layer” samples that collected the top 2–6 mm of loose surface snow, nine “1 m depth layer” samples taken by mixing a 5–10 cm thick layer of snow from 1 m below the surface, and five snow pits sampled in 3 cm increments to depths of 99 cm (P1), 102 cm (P2, P3, P4), or 201 cm (P5) for 202 total pit samples. Due to the absence of ground-observed SMB values, we used the 35 km grid output from the Modèle Atmosphérique Régional (MAR) version 3.12.1 ~~driven~~ forced by ERA5 data for the period 1979–2021 (Agosta et al., 2019; Amory et al., 2021). Site-specific SMB values were extracted from the MAR output through bilinear interpolation of the four nearest grid cells, and SMB uncertainties were estimated by comparing model output to known in situ observations (Supplementary Text S1). As the entire transect is located south of the Antarctic Circle, each site experiences extreme seasonal changes in daylength with a period of 24 hr night in the winter and a period of 24 hr daylight in the summer.

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Each snow sample was melted at room temperature ~~at~~ in Concordia s~~S~~tation, Dome C, Antarctica~~,~~ and NO_3^- concentrations of the melted samples were determined on aliquots by a colorimetric method with a detection limit of 0.5 ng g^{-1} and precision < 3 % (Frey et al., 2009; Erbland et al., 2013). Melted samples were immediately passed through an anionic exchange resin (Bio-Rad™ AG 1-X8, chloride form), and the resulting trapped NO_3^- eluted with 2 x 5~~10~~ ml of NaCl 1 M solution. These concentrated samples were then frozen and shipped to the Institut des Géosciences de l’Environnement (IGE), Grenoble, France, for isotopic analysis. Once re-melted, NO_3^- in these samples was converted to N_2O with a strain of the denitrifying bacteria *Pseudomonas aureofaciens* that lacks the ability to reduce N_2O into N_2. The N_2O was thermally decomposed into O_2 and N_2 on a 900° C gold surface, separated by gas chromatography with a GasBench II™, and oxygen and nitrogen isotopic ratios measured on a Thermo Finnigan™ MAT 253 mass spectrometer (Sigman et al., 2001; Casciotti et al., 2002; Kaiser et al., 2007; Morin et al., 2009). Isotopic effects from this analysis were corrected using ~~the~~ calibration regressions based on standards of international reference materials USGS 32, USGS 34, and USGS 35 processed and analyzed along with each set of samples ~~(Frey et al., 2009; Morin et al., 2009),~~ (Frey et al., 2009; Morin et al., 2009). Standards and samples strictly follow an identical treatment, having the same liquid volume, bacterial culture, and water isotope composition. Isotopic values~~and~~ are reported relative to the N_2-Air and VSMOW standard references (Baertschi, 1976; Mariotti, 1983)~~. T~~, and the root mean square errors of ~~of calibration regressions~~standards run alongside our ~~for these~~ samples over four analytical runs were ±0.7–1.1 ‰ for $\delta^{15}N_{NO3}$, ±0.8–2.3 ‰ for $\delta^{18}O_{NO3}$, and ±0.2–0.4 ‰ for $\Delta^{17}O_{NO3}$. For statistical results reported throughout this paper, uncertainties are given as 95 % confidence intervals unless otherwise stated, and statistical significance is identified as p-values < 0.05.

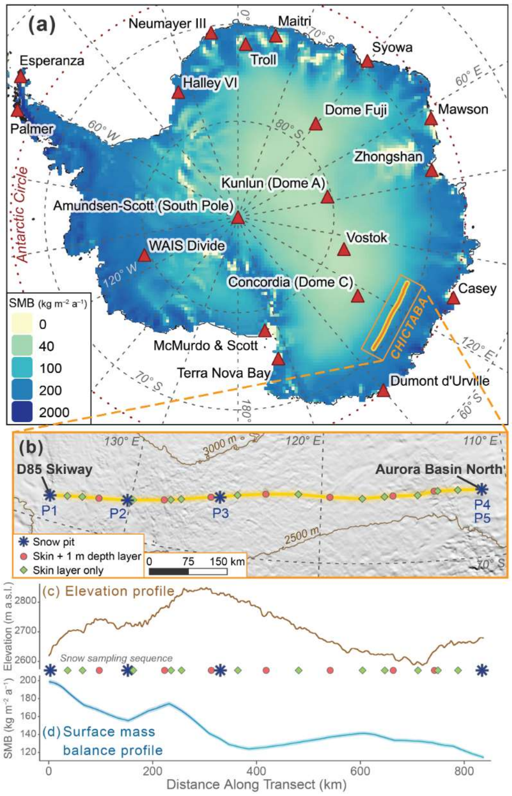

Figure 2. Maps and environmental profiles of the CHICTABA traverse. (a) Spatial variability in surface mass balance (SMB) across Antarctica shown by base color shading of MARv3.12.1 output data for the years 2011–2013 (Agosta et al., 2019; Amory et al., 2021). Major Antarctic stations are labeled (COMNAP, 2017), and the route of the CHICTABA transect is indicated by the orange and yellow line. (b) Zoomed map focused on the CHICTABA route (yellow line) overlaid on hillshaded topography with elevation contours shown in brown (Howat et al., 2019). Snow sampling locations along the transect and the sampling method are shown by colored icons with snow pit sites labeled. (c) Elevation (Howat et al., 2019) and (d) SMB (Agosta et al., 2019; Amory et al., 2021) profiles along CHICTABA starting from the D85 skiway and ending at Aurora Basin North, following the layout of (b), with the sequence of snow sampling sites along the transect provided. The resolution of the elevation profile reflects the 200 m REMA raster cell-size. The SMB values for the SMB profile were bilinearly interpolated at 1 km intervals from the original 35 km MAR output grid. MAR SMB uncertainty is included on (d) as a shaded zone around the profile line~~,~~ but ~~can be~~is difficult to see due to its ~~relatively~~ small ~~extent~~size.

Table 1. ~~Site details snow sampling~~Snow sampling site details ~~for nitrate isotope analysis on~~ along the CHICTABA traverse. Elevation is based on the Reference Elevation Model of Antarctica (REMA) (Howat et al., 2019) and surface mass balance (SMB) values are the mean annual SMB output and uncertainty of the MARv3.12.1 ~~forced with ERA5 data from~~for 2011–2013 (Agosta et al., 2019; Amory et al., 2021). Sites are ordered by distance along the traverse from the D85 starting point toward the ABN destination. Note that the sampling dates are not sequential because samples were taken on both the outbound and return trips.

Site	**Latitude (°)**	**Longitude (°)**	**Elevation (m a.s.l.)**	**SMB 2011–2013 (kg m^{-2} a^{-1})**	**Sampling date**	**Pit samples**	**Skin layer samples**	**Depth layer samples**
CHIC-01	~~-~~–70.431	134.138	2619	198.8- ± -2.2	2013-11-30	P1: 99 cm		
CHIC-02	~~-~~–70.500	133.264	2694	188.7~~±~~± 2.2	2013-12-26		SK23	
CHIC-03	~~-~~–70.551	132.506	2702	175.0~~±~~± 2.1	2013-12-01		SK01	
CHIC-04	~~-~~–70.597	131.646	2740	167.2~~±~~±	2013-12-25		SK22	D09

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CHIC-05	~~-~~−70.675	130.172	2731	155.8~~±~~± 2.0	2013-12-02	P2: 102 cm	SK02	
CHIC-06	~~-~~−70.700	129.891	2718	157.5~~±~~± 2.0	2013-12-25		SK21	
CHIC-07	~~-~~−70.804	128.282	2781	172.3~~±~~± 2.1	2013-12-24		SK20	D08
CHIC-08	~~-~~−70.826	127.944	2796	173.7~~±~~± 2.1	2013-12-03		SK03	
CHIC-09	~~-~~−70.867	127.408	2824	166.9~~±~~± 2.1	2013-12-24		SK19	
CHIC-10	~~-~~−70.979	125.863	2843	140.2~~±~~± 2.0	2013-12-23		SK18	D07
CHIC-11	~~-~~−70.998	125.388	2828	135.3~~±~~± 2.0	2013-12-04	P3: 102 cm	SK04	
CHIC-12	~~-~~−71.070	124.474	2806	126.4~~±~~± 2.0	2013-12-23		SK17	
CHIC-13	~~-~~−71.137	122.974	2755	125.9~~±~~± 2.0	2013-12-22		SK16	D06
CHIC-14	~~-~~−71.174	121.232	2713	131.2~~±~~± 2.0	2013-12-22		SK15	
CHIC-15	~~-~~−71.145	119.534	2666	137.2~~±~~± 2.1	2013-12-21		SK14	D05
CHIC-16	~~-~~−71.126	117.799	2631	141.3~~±~~± 2.1	2013-12-21		SK13	
CHIC-17	~~-~~−71.155	116.607	2623	136.4~~±~~± 2.0	2013-12-07		SK05	
CHIC-18	~~-~~−71.165	116.151	2617	133.6~~±~~± 2.0	2013-12-20		SK12	D04
CHIC-19	~~-~~−71.157	114.826	2697	132.6~~±~~± 2.0	2013-12-20		SK11	
CHIC-20	~~-~~−71.212	113.927	2638	129.8~~±~~± 2.0	2013-12-19		SK10	D03
CHIC-21	~~-~~−71.210	113.740	2652	129.0~~±~~± 2.0	2013-12-08		SK06	
CHIC-22	~~-~~−71.198	112.657	2666	123.9~~±~~± 2.0	2013-12-19		SK09	
ABN	~~-~~−71.167	111.367	2679	114.3~~±~~± 1.9	2013-12-12	P4: 102 cm		
ABN	~~-~~−71.167	111.367	2679	114.3~~±~~± 1.9	2013-12-14		SK07	D01
ABN	~~-~~−71.167	111.367	2679	114.3~~±~~±	2013-12-17	P5: 201 cm	SK08	D02

				1.9				

Apparent fractionation constants (${}^{z}\varepsilon_{app}$, where ${}^{15}\varepsilon$ = $\delta^{15}N_{NO3}$, ${}^{18}\varepsilon$ =$\delta^{18}O_{NO3}$, and ${}^{17}E$ = $\Delta^{17}O_{NO3}$) were calculated at all sites through linear regressions of skin layer samples with samples taken at 1 m depth and along the pit profiles. As the site CHIC-01 did not have a skin layer sample, we extrapolated skin layer values of $\omega(NO_3^-)$, $\delta^{15}N_{NO3}$, $\delta^{18}O_{NO3}$, and $\Delta^{17}O_{NO3}$ from other sites' skin layer data using linear regressions calculated between these variables and site-specific SMB. This extrapolated value was only used in the fractionation constant and pit cycle calculations and otherwise not included in statistical analyses and figures.

In line with previous studies (Blunier et al., 2005; Shi et al., 2015), ε_{app} values are calculated as the slope of a linear regression through Eq. (1):

$$\ln R_f = \varepsilon \cdot \ln \omega_f + \ln R_0 \tag{1}$$

where R_0 and R_f denote isotopic ratios in the initial and remaining NO_3^- and ω_f denotes the mass fraction of remaining NO_3^-. This equation can also be written with delta notation:

$$\ln(\delta_f + 1) = \varepsilon \cdot \ln \omega_f + \ln(\delta_0 + 1) \tag{2}$$

where δ_0 and δ_f denote the desired isotopic species in delta ~~value~~ notation versus a chosen standard (e.g., $\delta^{18}O_{NO3}$ vs. VSMOW). For the subset of skin layer sites that had a paired ~~with the~~ 1 m depth layer sample~~s~~, this regression is simple as it only has two points. In the pits, however, the regressions did not capture well the broader multi~~-~~annual photolytic trend due ~~largely~~ to the limited number of seasonal cycles recorded per pit and due to the irregular magnitude peaks of the $\omega(NO_3^-)$ cycle, which contributed large outlier points. We therefore created "pseudo-depth layer samples" for each of the five pits to represent an annually-averaged NO_3^- value from below the photic zone. These pseudo-depth layer samples are the $\omega(NO_3^-)$-weighted means of $\omega(NO_3^-)$, $\delta^{15}N_{NO3}$, $\delta^{18}O_{NO3}$, and $\Delta^{17}O_{NO3}$ for the deepest complete full seasonal cycle observed for P1–P4 and the deepest three complete cycles combined for P5.~~We therefore created "pseudo-depth layer samples" for each of the five pits by calculating the $\omega(NO_3^-)$-weighted means of $\omega(NO_3^-)$, $\delta^{15}N_{NO3}$, $\delta^{18}O_{NO3}$, and $\Delta^{17}O_{NO3}$ for the deepest complete full seasonal cycle observed in the pit data for P1–P4 and the deepest three complete cycles for P5.~~

The ε_{app} values produced in this manner give insight into the isotopic fractionation processes at work, but they also have limitations that are important to recognize. Namely, the most accurate ε_{app} determinations require many samples taken over a full photic zone profile to compensate for seasonal and environmental variability in $\omega(NO_3^-)$ and $\delta^{15}N_{NO3}$ values (Shi et al., 2015). This is of particular importance at sites where annual snow accumulation is greater than the NO_3^- sampling resolution, as is the case for our CHICTABA samples. Because our 1 m depth samples were taken as the mixed aggregate of a layer only 5–10 cm thick, each 1 m depth sample collects only part of a complete annual NO_3^- cycle. Assuming that the odds of the exact seasonal timing sampled by each 1 m depth sample is stochastic, our individual ε_{app} values should be viewed as having wide uncertainty with regards to the true site ε_{app} value, but ε_{app} values averaged across our dataset should reflect accurate regional ε_{app} values.

To examine spatial relationships in NO_3^- with SMB along the CHICTABA transect, we calculated ~~L~~linear regressions between NO_3^- variables and local SMB ~~were calculated~~ for both skin layer samples and 1 m depth layer samples (including the five pit pseudo-depth layer samples) ~~to examine spatial relationships in NO_3^- with SMB along the transect~~. Following the relationships defined in Akers et al. (2022), regressions were performed as $\omega(NO_3^-)$ or $\ln(\delta_f + 1)$ versus SMB^{-1}. The SMB values used in these regressions were the mean annual MAR output for the period 2011–2013 (i.e., the three years preceding sampling). This period was chosen because three years of snowfall at the CHICTABA sites is roughly equal to 1 m of accumulation and compaction.~~–~~ Additional regressions were calculated using the mean annual MAR output for the full data coverage period of 1979–2021 and for the sole year 2013 to determine if the choice of SMB data period substantially affected results. We again assume that any seasonal bias introduced by the 1 m depth sampling technique would be stochastic and that conclusions drawn from observations integrating all sites are generally accurate but admittedly more imprecise than if the individual 1 m depth samples had integrated full annual cycles. Statistical calculations and figure production were performed using the R programming language with packages *tidyverse, lubridate, RColorBrewer*, *gridExtra*, *cowplot*, *raster, rts, ncdf4, RMisc*, and *HMisc*. QGIS was used for spatial analyses and map creation using data produced here or cited in image captions~~, and~~ with Adobe Illustrator used for finalization of ~~graphic~~figures~~ figures~~.

4. Results

In total, 234 individual snow samples were analyzed for $\omega(NO_3^-)$ and NO_3^- isotopic ratios (Figure 3~~Figure 3~~). Skin layer samples have the highest $\omega(NO_3^-)$, with values from 124 to 501 ng g^{-1}, and 1 m depth layer samples have lower $\omega(NO_3^-)$ between 49 and 97 ng g^{-1}. . Each pit has a wide range of $\omega(NO_3^-)$ values that fall between the values observed in the skin layer and at 1 m depth (Figure 3a). ~~Each pit has a wide range of $\omega(NO_3^-)$ values, but each pits' average $\omega(NO_3^-)$ values are similar to or somewhat lower than the 1 m depth samples~~ (Figure 3~~Figure 3~~a). Skin layer samples have $\delta^{15}N_{NO3}$ values that are largely below 0 ‰ (mean: −8.9 ± 3.3 ‰) and within the range observed in atmospheric NO_3^- (Figure 1). In contrast, nearly all the $\delta^{15}N_{NO3}$ values from the 1 m depth layer (mean: +46.1 ± 12.3 ‰) and pit samples (mean: +36.0 ± 3.1 ‰) are much higher than the skin layer (Figure 3b). ~~Skin layer samples have very low $\delta^{15}N_{NO3}$ values that are largely below 0 ‰ (mean: −8.9 ± 3.3 ‰) and are lower than nearly all the $\delta^{15}N_{NO3}$ values from the 1 m depth layer (mean: +46.1 ± 12.3 ‰) and pit samples (mean: +36.0 ± 3.1 ‰) (Figure 3b).~~ Values of $\delta^{18}O_{NO3}$ and $\Delta^{17}O_{NO3}$ are broadly similar across all sample groups ($\delta^{18}O_{NO3}$ all samples mean: +70.7 ± 1.4 ‰, $\Delta^{17}O_{NO3}$ all samples mean: +30.9 ± 0.5 ‰), but drier pit sites (i.e., P3, P4, and P5) have somewhat lower values (Figure 3~~Figure 3~~c–d). For both $\omega(NO_3^-)$ and $\delta^{15}N_{NO3}$, the mean values between the skin layer and 1 m depth layer sample sets are strongly and significantly differentiated (Mann-Whitney U test, $p \ll 0.01$), while the differences between skin and 1 m depth layer samples for both $\delta^{18}O_{NO3}$ and $\Delta^{17}O_{NO3}$ are less clear but still statistically significant at $p = 0.01$ and 0.04, respectively (Mann-Whitney U test).

Data from the pits (n = ~~207~~202 pit + 5 site skin layer) show cyclical patterns in $\omega(NO_3^-)$ and isotopic values ~~with depth (Figure 4)~~ as well as ~~longer-term~~linear trends ~~with depth~~across the entire depths of the pits (Figure 4, Supplementary Table S1). The pits have 2–2.5 cycles in the top 100 cm with drier sites containing more cycles per unit depth. For the deeper P5, we observe five complete cycles over the total 201 cm depth. Linear regressions of NO_3^- variables with depth reveal that $\omega(NO_3^-)$ has statistically significant negative slopes at P3–P5 ($p < 0.01$) while $\delta^{15}N_{NO3}$ has a significant positive slope only at P5 ($p = 0.02$). Both $\delta^{18}O_{NO3}$ and $\Delta^{17}O_{NO3}$ have statistically significant negative slopes at all pits except P1 ($p < 0.01$). In the absence of other supplemental geochemical data, the residuals of the $\Delta^{17}O_{NO3}$ regression with depth were used to identify seasonal cycles with positive residuals representing colder months and negative residuals representing warmer months (Figure 4). This seasonal identification is based on NO_3^- monitoring data from Dome C (Figure 1) and previously reported seasonal $\Delta^{17}O_{NO3}$ cycles linked to snow $\delta^{18}O$ variability in a snow pit (Shi et al., 2015).

We investigated how the cycle timing of NO_3^- variables were interrelated by correlating values after we removed linear trends with depth (i.e., we correlated the residuals of the linear regressions). Values for $\delta^{18}O_{NO3}$ and $\Delta^{17}O_{NO3}$ values are well-correlated ($r = +0.72$, $p < 0.01$), as is typically observed for NO_3^-. The $\omega(NO_3^-)$ has a moderate negative correlation with $\delta^{18}O_{NO3}$ ($r = -0.34$, $p < 0.01$) and a weak negative correlation with $\Delta^{17}O_{NO3}$ ($r = -0.16$, $p = 0.03$), while $\omega(NO_3^-)$ and $\delta^{15}N_{NO3}$ do not have a statistically significant relationship ($r = -0.11$, $p = 0.16$). Although $\delta^{15}N_{NO3}$ has fairly strong positive correlation with $\Delta^{17}O_{NO3}$ ($r = +0.51$, $p < 0.001$), there is no significant relationship between $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ ($r = -0.06$,

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p = 0.43). This difference in correlation strength seems unusual since $\delta^{18}O_{NO3}$ and $\Delta^{17}O_{NO3}$ are so strongly correlated, but it appears to arise because the $\delta^{18}O_{NO3}$ cycle is slightly more irregular and offset from the $\delta^{15}N_{NO3}$ cycle compared with the $\Delta^{17}O_{NO3}$ values (Figure 4~~Figure 4~~). Additionally, $\Delta^{17}O_{NO3}$ values tend to peak higher than $\delta^{18}O_{NO3}$ values when coinciding with the highest $\delta^{15}N_{NO3}$ values (e.g., P2: 75 cm, P3: 35 cm, P4: 55 cm), and these shared extreme values promote a stronger correlation. The reason for these small differences between $\delta^{18}O_{NO3}$ and $\Delta^{17}O_{NO3}$ is not presently clear but may be due to $\delta^{18}O_{NO3}$ values being theoretically directly affected by photolytic mass loss while $\Delta^{17}O_{NO3}$ is not. Unfortunately, the impact of a theoretical fractionation of oxygen isotopes by photolytic mass loss is poorly constrained due to competing effects from oxygen atomic exchange during NO_3^- re-oxidation, which we examine in more detail later.

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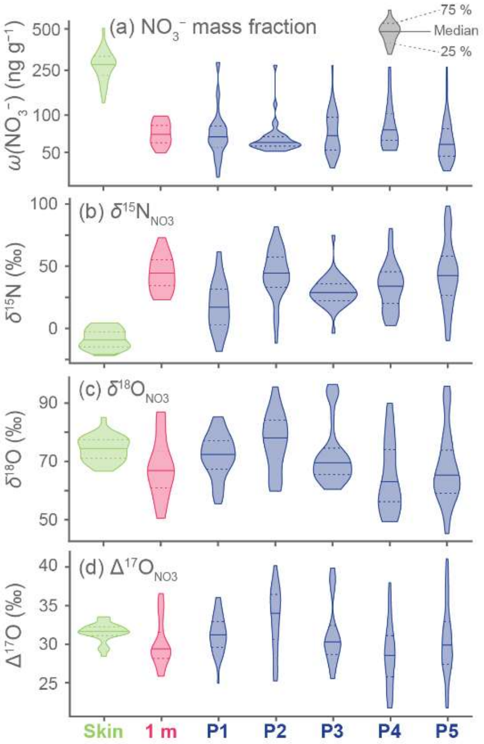

Figure 3. Violin plots showing the distributions of NO_3^- analytical results. Samples in each subplot are grouped and colored by sampling method: skin layer (green), 1 m depth layer (pink), or pits P1–P5 (blue). Data are plotted so that the total area of distribution is equivalent between groups, regardless of sample count. The median value per group is shown by a solid horizontal line, while the 25th and 75th percentiles are shown by dashed horizontal lines. Note that the y-axis for ω(NO_3^-) (a) is log-transformed to better display the much higher NO_3^- concentrations in the skin layer samples relative to other sample groups.

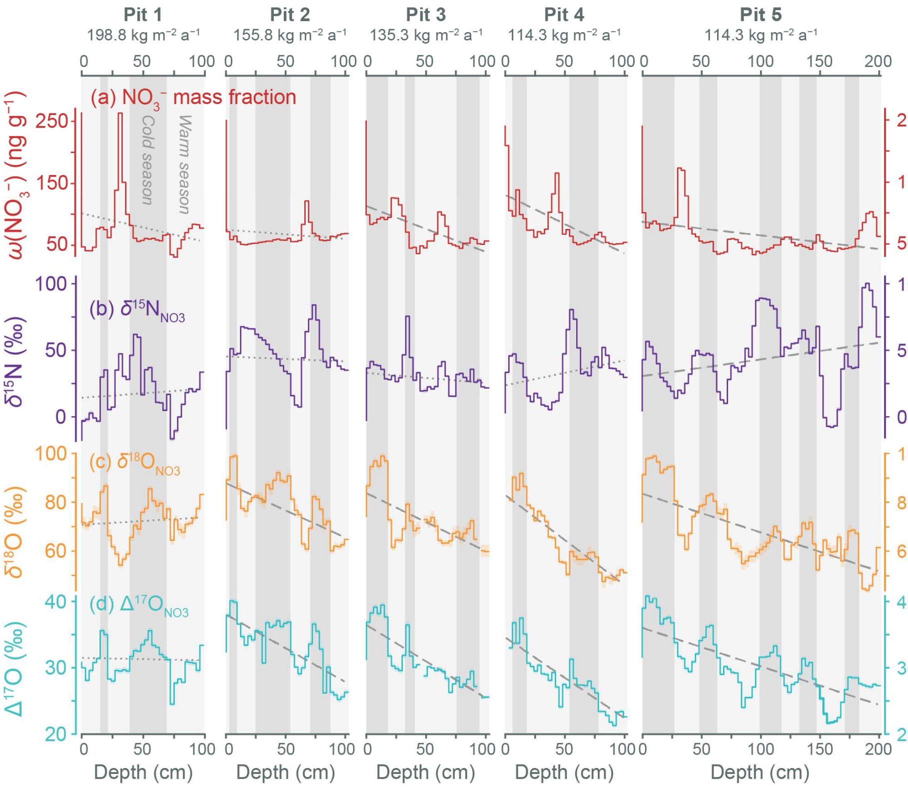

Figure 4. Changes in ω(NO_3^-) (a) and NO_3^-~~–~~ isotopic values (b–d) with snow depth for five pits sampled along the CHICTABA traverse. The modeled surface mass balances (Agosta et al., 2019; Amory et al., 2021) for different pit sites are given at the top of each plot. Dashed and dotted gray lines show a linear regression (variable vs. depth) fitted to each set of data (Supplementary Table S1). Dashed lines represent regressions whose f-statistic p-value < 0.05, and dotted lines represent regressions whose f-statistic p-value ≥ 0.05. Gray shaded backgrounds indicate inferred seasonal cycles (darker = colder months of ~May–Oct, lighter = warmer months of ~Nov–Apr) based primarily on when residuals of the $\Delta^{17}O_{NO3}$ regression are positive (i.e., $\Delta^{17}O_{NO3}$ peaks). Measurement uncertainties in isotopic values are displayed as colored shaded zones around the stepped lines~~,~~ but are too small to be visible on most data.

Across the full 1979–2021 dataset, we find interannual SMB variability to be very high, but the spatial pattern of variability is consistent year to year (Supplementary Figure S1, Supplementary Table S2). Model uncertainties in annual SMB values were estimated at ±1.6–2.5 kg m^{-2} a^{-1} by comparing model output to in situ observations (Supplementary Text S1). For the period 2011–2013, mean SMB values at sampling sites ranged from a high of 198.8±2.2 kg m^{-2} a^{-1} at the D85/CHIC-01 transect start to a low of 114.3±1.9 kg m^{-2} a^{-1} at the ending ABN site (Figure 2~~Figure 2~~d). Regressions performed with the 1979–2021 and 2013 SMB datasets produce very similar results to those of the 2011–2013 dataset (Supplementary Figure S2, Supplementary Table S3). Generally, slope values for the 1979–2021 and 2013 regressions have greater magnitude than 2011–2013 because the overall range in SMB values along CHICTABA in 2011–2013 was greater than during the other two time periods. ~~These mean SMB values for 2011–2013 are very similar to the overall mean values for 1979–2021 in the first half of the CHICTABA transect and 5–15 kg m⁻² a⁻¹ drier than the 1979–2021 means in the second half of the transect (Supplementary Table S2).~~

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Only some of the NO_3^- variables have statistically significant linear relationships with the 2011–2013 SMB^{-1} values (Figure 5~~Figure 5~~, Table 2~~Table 2~~). The $\delta^{15}N_{NO3}$ values decrease with higher SMB in both the skin layer and 1 m depth layer samples (Figure 5~~Figure 5~~b), but only the skin layer regression has a statistically significant *f-statistic* ($p < 0.01$, n = 23). For oxygen isotopes, only $\delta^{18}O_{NO3}$ in the 1 m depth samples has a statistically significant regression with SMB^{-1} (*f-statistic* $p = 0.04$, n = 14) with higher isotopic values associated with greater snow accumulation ~~rates~~ (Figure 5~~Figure 5~~c). The $\omega(NO_3^-)$ and $\Delta^{17}O_{NO3}$ values do not have statistically significant relationships with SMB^{-1} ~~(Figure 5a,d)~~ in either the skin layer or 1 m depth layer~~,~~ (Figure 5a, d). ~~although~~ Although ~~the~~ not reaching our defined level of statistical significance, we note that nonzero slope relationships with SMB^{-1} can also be observed in $\delta^{18}O_{NO3}$ in the skin layer and in $\delta^{15}N_{NO3}$ and $\Delta^{17}O_{NO3}$ at ~~skin layer~~1 m depth. ~~$\Delta^{17}O_{NO3}$ does display a trend of increasing value with higher SMB (*f-statistic* $p = 0.10$, n = 23).~~

~~Regressions performed with the 1979–2021 and 2013 SMB datasets produce very similar results to those of the 2011–2013 dataset (Supplementary Figure S2, Supplementary Table S3). Generally, slope values for the 1979–2021 and 2013 regressions have greater magnitude than 2011–2013 because the overall range in SMB values along CHICTABA in 2011–2013 was greater than the other two time periods. Despite these slope differences~~Comparing these results to regressions calculated with SMB from 1979–2021 and from 2013, we~~,~~ find that statistically significant variables are the same across all three time periods with the exception that the ~~skin~~ 1 m depth ~~layer~~ $\Delta^{17}O_{NO3}$ regression ~~just~~ reaches significance with both 1979–2021 (*f-statistic* $p = 0.04$, n = ~~23~~14) and 2013 (*f-statistic* $p = 0.05$, n = ~~23~~14) SMB values but not with 2011–2013 values (Supplementary Table S3).

Apparent fractionation constants for each of the isotopic ratios ~~are generally consistent~~have high variability across all sites (Table 3~~Table 3~~). This variability is likely due in part to the sampling methodology where the skin layer sample will have summer values (as we collected it in summer), but the 1 m depth samples reflect a random sampling from a buried seasonal cycle. While this reduces the precision of our overall ε_{app} estimate, general conclusions can be drawn from the range of ε_{app} values as well as their measures of central tendency. The $^{15}\varepsilon_{app}$ values are all negative and range between –65.6 ‰ and –24.8 ‰, with a mean value of –39.7 ± 6.1 ‰. Fractionation constants for oxygen isotopes are positive except at two sites, but smaller in magnitude than that of the nitrogen isotopes: $^{18}\varepsilon_{app}$ values range between −11.7 ‰ and +15.9 ‰ (mean: +5.0 ± 4.2 ‰) and $^{17}E_{app}$ range between −5.1 ‰ and +5.3 ‰ (mean: +1.2 ± 1.7 ‰). Fractionation constants do not have statistically significant linear regressions with either SMB or SMB^{-1}.

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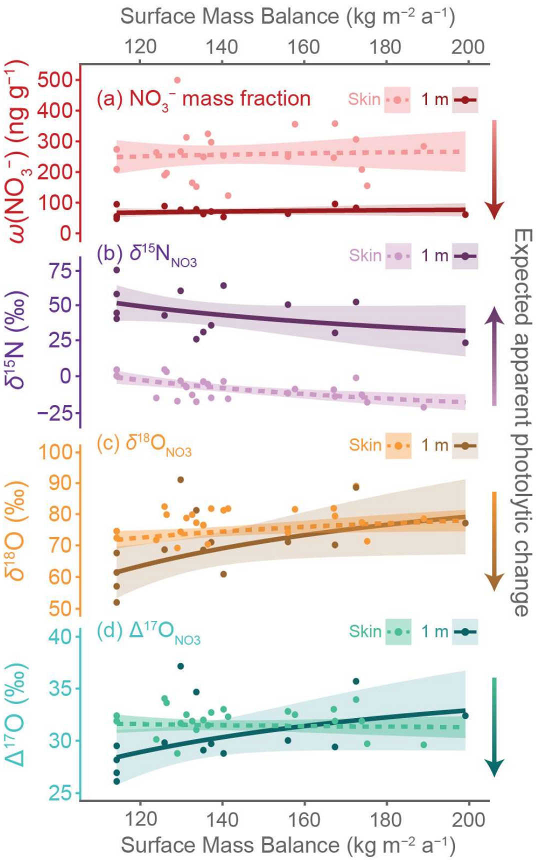

Figure 5. Spatial relationships between nitrate variables and site surface mass balance (SMB). Linear regressions of (a) ω(NO_3^-) and (b–d) ln(NO_3^- isotopic variable + 1) versus SMB^{-1} (Agosta et al., 2019) are shown by dashed (skin layer) and solid (1 m depth layer) lines with 95 % confidence intervals of the regression shown by shaded zones. The SMB values are mean annual values for 2011–2013 from MARv3.12.1 (Agosta et al., 2019; Amory et al., 2021). Individual points represent individual samples. The direction of expected changes to NO_3^- variables due to photolysis and associated re-oxidation is indicated by colored arrows. ~~Regression coefficients~~Coefficients and statistics for displayed regressions are given in Table 2~~Table 2~~.

Table 2. ~~Relationships between NO_3^- variables and surface mass balance (SMB) for skin layer and 1 m depth layer datasets. Coefficients and statistics are shown for the linear regressions of NO_3^- variables versus local site SMB^{-1}. Coefficient values are given with ± 1 standard error.~~ Coefficients and statistics ~~are shown~~ for the linear regressions of NO_3^- variables versus local site SMB^{-1}, with skin layer and 1 m depth layer samples separately analyzed. Coefficient values are given with ±1 standard error. Values of SMB used in regressions are the mean annual output of MARv3.12.1 forced with ERA5 data for the years 2011–2013 (Agosta et al., 2019; Amory et al., 2021). Regressions with statistically significant ~~($p < 0.05$)~~ *f-statistic* ($p < 0.05$) values are bolded.

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Skin layer samples				
Variable	***Slope***	***Intercept***	***F-statistic p-value***	***r^2***
	(ng g^{-1} · kg m^{-2} a^{-1} or kg m^{-2} a^{-1})	*(ng g^{-1} or unitless)*		
ω(NO_3^-)	−4227 ± 18373	290 ± 131	0.82	0.00

ln($\delta^{15}N_{NO3}$ + 1)	**4.0 ± 1.5**	**0.0 ± 0.0**	**0.01**	**0.26**
ln($\delta^{18}O_{NO3}$ + 1)	–1.4 ± 0.9	0.1 ± 0.0	0.11	0.11
ln($\Delta^{17}O_{NO3}$ + 1)	0.1 ± 0.3	0.0 ± 0.0	0.71	0.01
1 m depth layer samples				
Variable	***Slope***	***Intercept***	***F-statistic p-value***	***r^2***
	(ng g^{-1} · kg m^{-2} a^{-1} or kg m^{-2} a^{-1})	*(ng g^{-1} or unitless)*		
$\omega(NO_3^-)$	–2626 ± 3745	91 ± 28	0.50	0.04
ln($\delta^{15}N_{NO3}$ + 1)	5.1 ± 3.1	0.0 ± 0.0	0.12	0.19
ln($\delta^{18}O_{NO3}$ + 1)	**–4.4 ± 2.0**	**0.1 ± 0.0**	**0.04**	**0.30**
ln($\Delta^{17}O_{NO3}$ + 1)	–1.2 ± 0.7	0.0 ± 0.0	0.10	0.21

Table 3. Apparent NO_3^- isotopic fractionation constants ~~for NO_3^- calculated~~ for sites along the CHICTABA traverse. Values for $\delta^{15}N_{NO3}$ ($^{15}\varepsilon_{app}$), $\delta^{18}O_{NO3}$ ($^{18}\varepsilon_{app}$), and $\Delta^{17}O_{NO3}$ ($^{17}E_{app}$) were calculated from the paired skin layer and 1 m depth samples at individual sites. The MAR-estimated surface mass balance (SMB) (Agosta et al., 2019; Amory et al., 2021) is provided for each site for reference, and f~~. F~~urther site information is given in Table 1~~Table 1~~. For the five pit samples (P1–P5), a pseudo-depth layer sample was calculated by weight-averaging samples representing at least one full annual cycle and paired with a skin layer sample taken from the same site. Note that the site ABN was sampled four separate times within a five-day period.

Site	***$^{15}\varepsilon_{app}$ (‰)***	***$^{18}\varepsilon_{app}$ (‰)***	***$^{17}E_{app}$ (‰)***	***SMB 2011–2013 (kg m^{-2} a^{-1})***
CHIC-01 (P1)	–28.6	3.1	–0.4	198.8 ± 2.2
CHIC-04	–33.2	6.1	1.8	167.2 ± 2.1
CHIC-05 (P2)	–44.5	2.0	2.0	155.8 ± 2.0
CHIC-07	–39.4	0.3	–1.3	172.3 ± 2.1
CHIC-10	–41.7	11.6	2.6	140.2 ± 2.0
CHIC-11 (P3)	–24.8	5.1	2.0	135.3 ± 2.0
CHIC-13	–48.6	15.9	5.3	125.9 ± 2.0
CHIC-15	–34.9	6.6	2.0	137.2 ± 2.1
CHIC-18	–65.6	–5.3	–5.2	133.6 ± 2.0
CHIC-20	–48.8	–11.7	–4.2	129.8 ± 2.0
ABN (P4)	–29.3	10.4	4.6	114.3 ± 1.9
ABN (P5)	–34.4	7.3	2.2	114.3 ± 1.9
ABN (12-Dec)	–45.3	12.4	3.5	114.3 ± 1.9
ABN (17-Dec)	–36.6	5.8	2.1	114.3 ± 1.9
Mean ± 95 % CI	*–39.7 ± 6.1*	*5.0 ± 4.2*	*1.2 ± 1.7*	
Median	*–39.4*	*5.8*	*2.0*	

5. Discussion

5.1 Photolytic impacts observed in skin layer and 1 m depth samples

Our data reveal evidence of photolytic ~~loss~~ changes to~~of~~ NO_3^- in the photochemically active zone of the snowpack. The mean $\delta^{15}N_{NO3}$ of skin layer samples (−8.9 ± 3.3 ‰) ~~falls~~ is within the typical seasonal range (≈−~~20~~ 40 to +20 ‰) observed in atmospheric NO_3^- at both coastal and interior Antarctic stations (Savarino et al., 2007; Frey et al., 2009; Erbland et al., 2013; Winton et al., 2020; Shi et al., 2022a), suggesting that the skin layer NO_3^- is recently deposited from the atmosphere and has experienced little to no photolytic ~~mass loss~~effects. In contrast, the $\delta^{15}N_{NO3}$ values at 1 m depth are 49 ± 11 ‰ higher on average than the skin layer $\delta^{15}N_{NO3}$. This increase, combined with the average 71 ± 9 % ng g^{-1} drop in $\omega(NO_3^-)$ from the skin layer to the 1 m depth, strongly points to substantial photolytic mass loss (Savarino et al., 2007; Frey et al., 2009; Meusinger et al., 2014; Zatko et al., 2016). As further support, the range of $^{15}\varepsilon_{app}$ values (−65.6 ‰ to −24.8 ‰) at the CHICTABA sites is comparable to both modeled and field-observed values previously reported for photolytic fractionation across interior Antarctic transects (−76.8 ‰ to −31.5 ‰) (Frey et al., 2009; Erbland et al., 2013; Berhanu et al., 2015; Shi et al., 2015). While ~~we acknowledge that~~ HNO_3 volatilization ~~could be~~is not excluded as a minor source of mass loss at some sites due to the wide range in fractionation factors, photolytic mass loss alone can explain ~~our~~ the observed findings without needing to invoke additional, non-fractionating mass loss from volatilization.

Photolysti~~c~~s-related impacts on oxygen isotopes are also present but more subtle. Our ~~observed~~ apparent isotopic fractionation factors for $^{18}\varepsilon_{app}$ and $^{17}E_{app}$ are comparable to ~~NO_3^- photolytic~~ oxygen fractionation factors reported in other photolysis studies (Frey et al., 2009; Erbland et al., 2013; Berhanu et al., 2015; Shi et al., 2015) that are a combination of effects from both photolytic mass loss fractionation and oxygen exchange due to a cage effect during re-oxidation of photolytic products. As is expected from photolysis and the resulting NO_3^- re-oxidation, mean values for $\delta^{18}O_{NO3}$ and $\Delta^{17}O_{NO3}$ along the CHICTABA transect are lower at 1 m than in the skin layer. However, the difference between the mean skin layer and 1 m depth values is much smaller than observed in $\delta^{15}N_{NO3}$.~~In contrast to the $\delta^{15}N_{NO3}$ results, neither $\delta^{18}O_{NO3}$ nor $\Delta^{17}O_{NO3}$ have large differences in mean value between the skin layer and 1 m depth samples.~~ This ~~is likely because the~~is reflected in how the ~~fractionation factors~~apparent fractionation factors for $\delta^{18}O_{NO3}$ and $\Delta^{17}O_{NO3}$ are much closer to zero than the apparent fractionation factor for $\delta^{15}N_{NO3}$ (Frey et al., 2009; Erbland et al., 2013; Shi et al., 2015), and thus photolytic mass loss did not ~~produce~~ result in as large of a change in isotopic value for oxygen as for nitrogen. ~~Still, mean values for $\delta^{18}O_{NO3}$ and $\Delta^{17}O_{NO3}$ are, as expected from photolysis, lower at 1 m than in the skin layer, although only the difference in $\delta^{18}O_{NO3}$ means has a 95 % confidence interval that excludes zero. The difference in oxygen isotopic values between the skin layer and 1 m depth is larger at drier sites (Figure 5c–d), likely because NO_3^- is exposed to photolytic radiation for a longer time due to slower accumulation which serves to exaggerate the magnitude of isotopic change.~~

5.2 Annual nitrate cycle and photolytic evidence observed in pit samples

We interpret the cyclical variability of $\omega(NO_3^-)$ and NO_3^- in the depth profiles of the CHICTABA snow pits (Figure 4~~Figure 4~~) as a relic of the annual cycles observed in atmospheric and skin layer NO_3^- (Figure 1~~Figure 1~~) that has been partially preserved through NO_3^- deposition and initial burial. The cycles in $\delta^{18}O_{NO3}$ and $\Delta^{17}O_{NO3}$ are clear and well-synchronized in each pit, which allows us to differentiate between the winter darkness season (peaks) and summer sunlit season (troughs) (Savarino et al., 2007; Frey et al., 2009; Shi et al., 2015). Peaks in $\omega(NO_3^-)$ generally coincide with the summer minima in the oxygen isotopic cycles due to enhanced deposition of recycled NO_3^- (Figure 4~~Figure 4~~a), as similarly observed in NO_3^-

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monitoring at Dome C (Figure 1~~Figure 1~~) and in three snow pits reported in a previous study (Shi et al., 2015). However, a few minor peaks observed in winter (e.g., in P1 and P4) could represent NO_3^- deposition from stratospheric denitrification. Additionally, the annual $\omega(NO_3^-)$ peak corresponding to summer 2012–2013 (i.e., the summer before sampling occurred) is particularly large relative to other $\omega(NO_3^-)$ peaks in most pits. This may represent a particularly heavy local NO_3^- deposition that year, although atmospheric and skin layer NO_3^- monitoring at Dome C captured no unusually high NO_3^- at that time (Erbland et al., 2013; Winton et al., 2020). Overall, the range and cycles in $\omega(NO_3^-)$ values observed in these CHICTABA pits are similar to those reported from pits with similar SMB on a transect from Zhongshan station to Dome A (Shi et al., 2018b).

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Following that each complete oxygen isotopic cycle is equivalent to one year, the pits cover roughly 2–3.5 years of snow accumulation in the top 100 cm, with five years of accumulation at the 201 cm deep P5. This accumulation is similar to rough estimates (P1: 2.0 yr; P2: 2.5 yr; P3: 2.9 yr; P4: 3.4 yr; P5: 7.0 yr) calculated from modeled SMB for 2011–2013 and snow density profiles taken from two shallow cores along the transect (where 1 m snow depth = 38.9 cm water equivalent and 2.25 m snow depth = 90.4 cm water equivalent). Differences between the modeled estimates and the dating from NO_3^- oxygen isotope cycles could be due to interannual snowfall variability, surface roughness, and/or localized differences in snow density profiles. ~~An example of a~~ A surface roughness effect may explain the exceptionally broad $\delta^{15}N_{NO3}$ peak and lack of $\omega(NO_3^-)$ spike in the upper 50 cm of P2~~, where~~ as a localized high rate of drifted snow accumulation that ~~might have~~ "stretched" the typical cycle frequency. Otherwise, the general regularity of the isotopic cycles suggests that limited physical mixing or snow layer disturbance occurred after initial deposition.

Although photolysis only occurs during sunlit periods, it affects NO_3^- deposited in all seasons. For the pit data, the cyclical patterns of $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ are offset 10–80 ‰ higher and 5–15 ‰ lower, respectively, compared to the mean seasonal cycle values reported from the skin layer at Dome C (Erbland et al., 2013). Because it takes over two years for newly deposited NO_3^- to be buried below 1 m along the CHICTABA traverse, NO_3^- that is deposited in winter darkness will still be exposed to summer sunlight and partially photolyzed before being fully buried below the photic zone. We also find that NO_3^- deposited in the late winter and early spring has the greatest $\delta^{15}N_{NO3}$ increase relative to its corresponding seasonal skin layer values, with pit $\delta^{15}N_{NO3}$ values of 50–100 ‰ compared to skin layer mean values of 10–30 ‰. The ^{15}N enrichment maximum at this time can be expected because the NO_3^- deposited during late winter and early spring will typically have been buried perhaps 5–20 cm beneath the surface by the time intense summer insolation returns. At this depth, the late winter/early spring NO_3^- is still shallow enough to be readily photolyzed, but also deep enough that newly recycled, isotopically light NO_3^- deposited onto the surface will not be mixed in.

~~The very clear negative trends in~~ The oxygen isotope values have very clear negative trends with depth in P2–P5 (Figure 4~~Figure 4~~c–d). ~~are an expression of the cumulative effect of greater photolytic NO_3^- loss with depth.~~ While the $\delta^{18}O_{NO3}$ and $\Delta^{17}O_{NO3}$ value ranges in the first 25 cm are similar to skin layer values observed at Dome C (Figure 1~~Figure 1~~g–h), the pit values at 75–201 cm are 20–40 ‰ lower for $\delta^{18}O_{NO3}$ and 8–14 ‰ lower for $\Delta^{17}O_{NO3}$ than the Dome C skin layer. This agrees with previous observations where increased photolysis and its resulting oxygen exchange during NO_3^- re-oxidation produce lower oxygen isotopic ratios (Erbland et al., 2013; Shi et al., 2015). However, it is notable that only P4 and P5 have visibly increasing $\delta^{15}N_{NO3}$ trends with depth as would be expected from cumulative photolytic mass loss. ~~While the difference in mean isotopic value between the top and bottom of the pits is smaller and not as easily distinguishable for nitrogen as with the oxygen isotopes, $\delta^{15}N_{NO3}$ values in P4 and P5 have visibly increasing trends with depth as would be expected from cumulative photolytic mass loss.~~ This suggests that substantial oxygen exchange may be occurring regardless of photolytic mass loss, perhaps due to photolytic NO_x being produced and re-oxidized in place without the ventilated transport that leads to mass loss to the atmosphere. In this case of in situ photolysis and re-oxidation, no isotopic effect of photolysis would be

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observed in nitrogen, but there could be an isotopic change in oxygen due to the chance of an atomic exchange with the local snow grain matrix.

Possible oxygen isotopic changes not triggered by photolysis must also be considered. We expect photolysis to drive the greatest rate of isotopic change in the uppermost depths where radiation is strongest and increasingly less change toward the bottom of the photic zone. We observe this in the $\delta^{15}N_{NO3}$ where $\delta^{15}N_{NO3}$ values greatly increase between each skin layer and ≈6–9 cm depth, even for the P2 and P3 pits where no clear additional photolytic change is present beneath this uppermost zone (Figure 4b). In contrast, the oxygen isotopes have a remarkably consistent rate of isotopic change with depth for P2–P5 (Figure 4c–d). Competition between photolytic mass loss fractionation and oxygen exchange isotopic effects is discussed in the following section as one possible explanation for this difference between nitrogen and oxygen profiles. However, the $\delta^{18}O_{NO3}$ and $\Delta^{17}O_{NO3}$ values in P5 continue to decline steadily from 100–201 cm. These depths are well beneath the photic zone, and therefore the NO_3^- should be isotopically stable. No current mechanism in our current understanding of Antarctic NO_3^- dynamics has been described for oxygen isotopic changes in the snowpack without photolysis, and it is difficult to make strong hypotheses or conclusions at this time in the absence of deeper and/or replicated pits. Further and more extensive field observations will be needed to clarify this uncertainty.

The relative timing of isotopic cycles in the pits has some small but important differences from the cycles observed in the atmosphere and skin layer at Dome C. As best seen in the P2–P5 pits, the $\delta^{15}N_{NO3}$ cycle generally aligns in phase with oxygen isotopes, but with a slight offset so that the $\delta^{15}N_{NO3}$ maxima and minima are 0–10 cm shallower (~0–3.5 months later) than the corresponding oxygen isotope cycles (Figure 4~~Figure 4~~b–d). The delayed $\delta^{15}N_{NO3}$ minima, in particular, is unexpected because the early summer $\delta^{15}N_{NO3}$ minima in atmospheric and skin layer NO_3^- precedes the mid-summer minima in oxygen isotopes by 1–2 months (Figure 1~~Figure 1~~b–d) (Savarino et al., 2007; Erbland et al., 2013; Winton et al., 2020). A similar "delayed" relationship between $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ can be observed in three snow pits sampled from the wetter section of the Zhongshan to Dome A traverse route (Shi et al., 2015), suggesting that this phenomenon is not unique to CHICTABA and may be typical for intermediate SMB regions of Antarctica.

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This discrepancy between observations in snow pits versus the observations in the atmosphere and skin layer may be explained by the seasonality of photolytic loss (Figure 6). The early summer atmospheric $\delta^{15}N_{NO3}$ minima is due to the photolytic production and subsequent re-oxidation of NO_x with low $\delta^{15}N$ from the snowpack NO_3^-, and the skin layer NO_3^- shares a similarly timed $\delta^{15}N_{NO3}$ minima as the re-oxidized NO_3^- is deposited back onto the surface (Figure 1). However, as this skin layer NO_3^- is buried by additional snow, it will be exposed to sunlight in the photic zone for the entire summer season with subsequent photolytic losses and an increase in $\delta^{15}N_{NO3}$ values.

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~~I~~In contrast, while NO_3^- deposited toward the end of summer may not initially have $\delta^{15}N_{NO3}$ values as low as in early summer, this NO_3^- will experience far less photolytic-inducing radiation before winter darkness and will likely be buried and protected relatively deep in the photic zone before the next summer begins. In this manner, the late summer $\delta^{15}N_{NO3}$ values could end up as the lowest $\delta^{15}N_{NO3}$ values simply because they are photolytically elevated the least from initial atmospheric values. Likewise, the minimum values in pit oxygen isotope cycles may be shifted slightly earlier in the summer because ~~photolysis~~ re-oxidation of photolytic products lowers $\delta^{18}O_{NO3}$ and $\Delta^{17}O_{NO3}$ values through oxygen atomic exchange. Thus, we would observe the oxygen isotopic minima occurring before the nitrogen isotopic minima in the pit profiles, despite the atmospheric and skin layer cycles not exhibiting this pattern.

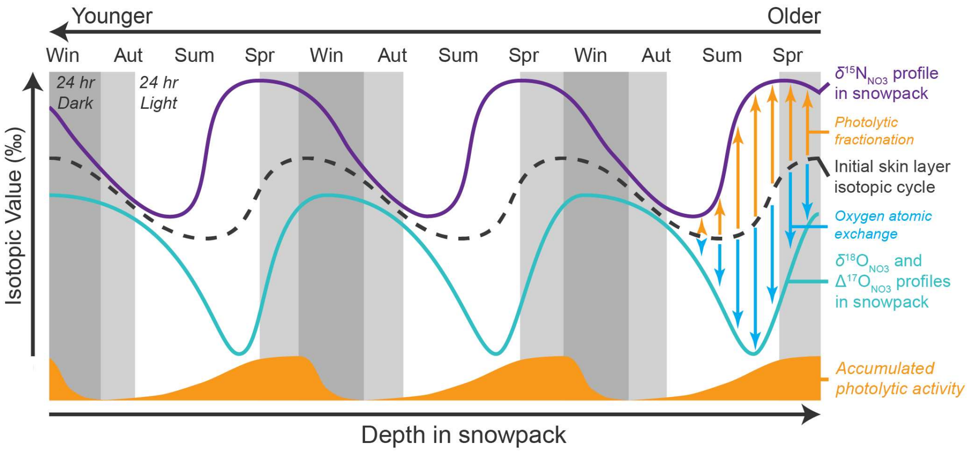

Figure 6. The proposed mechanism for observed isotopic cycle offsets in snow pit $\mathrm{NO_3^-}$. Even if $\delta^{15}\mathrm{N}_{\mathrm{NO3}}$, $\delta^{18}\mathrm{O}_{\mathrm{NO3}}$, and $\Delta^{17}\mathrm{O}_{\mathrm{NO3}}$ have synchronous seasonal isotopic cycles when deposited in the skin layer (black dashed line), post-depositional photolysis will skew $\delta^{15}\mathrm{N}_{\mathrm{NO3}}$ values (purple solid line) differently than $\delta^{18}\mathrm{O}_{\mathrm{NO3}}$ and $\Delta^{17}\mathrm{O}_{\mathrm{NO3}}$ values (teal solid line). Photolysis increases isotopic values for nitrogen due to photolytic fractionation (orange arrows) but decreases values for oxygen due to oxygen atomic exchange (blue arrows). Because the typical amount of photolytic activity experienced by $\mathrm{NO_3^-}$ deposited on the snow surface (orange solid curve) also changes seasonally in a cycle not aligned with the skin layer isotopic value cycles, photolysis will enhance or subdue the existing skin layer isotopic cycle differently for $\delta^{15}\mathrm{N}_{\mathrm{NO3}}$ than for $\delta^{18}\mathrm{O}_{\mathrm{NO3}}$ and $\Delta^{17}\mathrm{O}_{\mathrm{NO3}}$. This produces the observed cyclical offsets between nitrogen and oxygen isotopes (Figure 4), even if the magnitude of isotopic value changes due to photolysis (i.e., the size of the arrows) is the same for all isotopic species at a given point in the cycle.

5.3 Links between $\delta^{15}\mathrm{N}_{\mathrm{NO3}}$ and SMB

The linear relationships between $\mathrm{NO_3^-}$ variables and ~~snow accumulation rate~~SMB (Figure 5~~Figure 5~~) match what is expected based on photolysis-dominated $\mathrm{NO_3^-}$ dynamics on the East Antarctic Plateau. While not all the regressions are statistically significant at $p < 0.05$, their combined evidence supports increased photolysis with lower SMB. At drier sites, $\mathrm{NO_3^-}$ will remain within the photic zone for a longer period due to slower snow accumulation, and as a result the $\mathrm{NO_3^-}$ will experience more photolysis before being buried in the archived zone (Akers et al., 2022). For the 1 m depth layer samples, $\delta^{15}\mathrm{N}_{\mathrm{NO3}}$ values increase while $\delta^{18}\mathrm{O}_{\mathrm{NO3}}$ and $\Delta^{17}\mathrm{O}_{\mathrm{NO3}}$ values decrease with lower SMB (Figure 5~~Figure 5~~b–d), which reflects the negative apparent isotopic fractionation factor of nitrogen with $\mathrm{NO_3^-}$ photolysis and the positive apparent fractionation factors for oxygen (Erbland et al., 2013; Shi et al., 2015).

An improved sampling method for the 1 m depth samples might produce stronger and more precise linear regressions with SMB^{-1} for all isotopic ratios. Each seasonal isotopic cycle typically covers 30–50 cm depth in the upper snowpack as observed in the pit records (Figure 4). However, each 1 m depth sample taken along the CHICTABA transect likely represents only part of an annual isotopic cycle because our sampling methodology mixed snow from only a 5–10 cm thick layer at 1 m depth. If a seasonal maximum or minimum happened to fall at 1 m depth, the resulting $\delta^{15}\mathrm{N}_{\mathrm{NO3}}$, $\delta^{18}\mathrm{O}_{\mathrm{NO3}}$, and $\Delta^{17}\mathrm{O}_{\mathrm{NO3}}$ values could be offset from the true annual mean value by 20–50 ‰, 10–20 ‰, and 5–6 ‰, respectively (Figure 4). For example, although the oxygen isotopic values for 1 m depth samples at CHIC-18 and CHIC-20 are much higher than expected (see high values near 130 kg $\mathrm{m^{-2}\ a^{-1}}$ in Figure 5), their values are similar to winter maximum values and may simply be a result of seasonally-biased sampling. Future sampling of 1 m depth samples should ideally mix snow from at least a 50 cm range (i.e., from 1.0 to 1.5 m depth) to reduce the chance of seasonal bias and provide more accurate $\omega(\mathrm{NO_3^-})$ and $\mathrm{NO_3^-}$ isotopic values, and ideally the exact mixing depth could be adapted in advance for any site based on modeled accumulation and compaction rates.

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The skin layer samples also show an increase in $\delta^{15}N_{NO3}$ ~~and decrease in $\delta^{18}O_{NO3}$~~ with lower SMB (Figure 5~~Figure 5~~b–c) despite not having much photolytic mass loss that would drive this pattern. ~~Instead, T~~This spatial relationship between ~~NO_3^- isotopes~~$\delta^{15}N_{NO3}$ and SMB in the skin layer likely results from NO_3^- recycling (Erbland et al., 2015; Winton et al., 2020), where some of the NO_3^- deposited on the skin layer is derived from re-oxidized photolytic NO_x ventilated from the local snowpack. Because NO_3^- in the snowpack beneath the skin layer has higher $\delta^{15}N_{NO3}$ ~~and lower $\delta^{18}O_{NO3}$ and $\Delta^{17}O_{NO3}$ values~~ at drier sites due to increased photolytic mass loss, the isotopic ratios of photolyzed NO_x~~Nox~~ products and resulting re-oxidized NO_3^- coming from the snowpack will also ~~share similar isotopic relationships with SMB~~tend to have higher $\delta^{15}N_{NO3}$ values at drier sites. ~~Nitrate at drier sites also experiences more NO_3^- recycling (Erbland et al., 2013, 2015; Winton et al., 2020) which drives skin layer NO_3^- isotopes to be closer to the high $\delta^{15}N_{NO3}$ and low $\delta^{18}O_{NO3}$ that we observe deeper in the snowpack.~~ Additionally, the skin layer NO_3^- would sit at the surface for a slightly longer period at the drier sites than the wetter sites, potentially also giving a slightly greater photolytic imprint on skin layer $\delta^{15}N_{NO3}$ for sites with lower SMB.

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This shared spatial relationship with SMB for both the skin layer and 1 m depth ~~NO_3^-~~$\delta^{15}N_{NO3}$ samples might be seen as evidence that the ~~NO_3^- isotopic~~$\delta^{15}N_{NO3}$ values at ~~depth~~ 1 m are simply preserving an already existing spatial relationship in NO_3^- isotopes present in the skin layer. If photolytic impacts were indeed the same at all sites, regardless of SMB, we would expect the slope of the 1 m depth samples to match the slope of the skin layer samples, because the degree of isotopic fractionation per unit depth would be the same at every site. However, comparing the spatial regressions of the skin layer samples to the 1 m depth samples reveals that ~~the isotopic differences between the two sample sets is greater at drier sites (Table 2). For nitrogen,~~ both skin layer and 1 m depth samples have higher $\delta^{15}N_{NO3}$ values as SMB decreases, but the $\delta^{15}N_{NO3}$ values in the 1 m samples increase at a greater rate than the skin layer samples (i.e., the magnitude of the regression's slope is greater for the 1 m depth dataset than for the skin layer dataset) (Table 2). As a result, the greater photolytic action at drier sites enhances and exaggerates the pre-existing $\delta^{15}N_{NO3}$ trend with SMB observed in the skin layer.

~~Similarly, the~~ The oxygen isotope regressions with SMB ~~also~~also provide some evidence of greater photolytic ~~mass loss~~activity at drier sites. Making definitive conclusions from the oxygen isotope regressions is more difficult than for nitrogen isotopes because the ~~uncertainty~~ uncertainties of the 1 m depth layer regressions largely overlap and encompass the regressions for skin layer samples. Still, the regressions suggest that at sites with the highest SMB (180–200 kg m^{-2} a^{-1}), there will not be a significant difference in the oxygen isotopic ratios between the skin layer and the 1 m depth layer while, in contrast, the skin layer has higher $\delta^{18}O_{NO3}$ and $\Delta^{17}O_{NO3}$ values than 1 m depth at the driest SMB sites (110–130 kg m^{-2} a^{-1}). This divergence is also expressed through the regression slopes where the 1 m depth samples have a more positive relationship with SMB than the skin layer samples (Figure 4c–d).

~~(Frey et al., 2009)(McCabe et al., 2005; Erbland et al., 2015)(Zatko et al., 2016)~~Compared to nitrogen isotopes, it thus appears that a greater degree of photolytic activity (i.e., a drier site) is needed to observe a clear divergence between skin layer and 1 m samples for oxygen isotopic values. This is a reasonable observation because the apparent isotopic fractionation factors for oxygen isotopes are much smaller than for nitrogen, and we would expect based on these observations that photolytic impacts become obvious more quickly for $\delta^{15}N_{NO3}$ than for $\delta^{18}O_{NO3}$ or $\Delta^{17}O_{NO3}$. However, the reduced photolytic impact in oxygen isotopes compared to nitrogen isotopes may seem surprising given that the isotopic trends with depth in the pit data are much clearer in the oxygen isotopes than $\delta^{15}N_{NO3}$ (Figure 4).

The relatively limited photolytic signal in the oxygen isotopes is likely due in part to summer bias in our skin layer sampling whereas the 1 m depth samples draw from the full range of the annual cycle. During summer, skin layer NO_3^- has maximum $\omega(NO_3^-)$ and minimum isotopic values (Figure 1). An annual mean skin layer sample, however, would have lower $\omega(NO_3^-)$ and higher isotopic values, although still weighted heavily toward summer values due to summer's much higher NO_3^- concentrations. Adjusting our observed skin layer values to reflect annual values increases our calculated ε_{app} values for all isotopic species by 3–10 ‰. This slightly weakens the observed $^{15}\varepsilon_{app}$ values for nitrogen but more impactfully shifts the $^{18}\varepsilon_{app}$ and $^{17}\varepsilon_{app}$ of the oxygen isotopes to clearly positive values that better reflect our observations of oxygen isotopic change in the pit profiles.

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The snow pit isotopic trends reveal another unusual characteristic that may also help explain why skin layer and 1 m depth sample values only diverge at drier sites for oxygen isotopes. In the snow pits, $\delta^{15}N_{NO3}$ values rapidly increase in the uppermost 5–10 cm coinciding with the rapid decline in $\omega(NO_3^-)$ (Figure 4a–b). This follows our expectations as photolytic activity is concentrated near the surface due to rapid attenuation of solar radiation in the snowpack. However, $\delta^{18}O_{NO3}$ and $\Delta^{17}O_{NO3}$ values exhibit a steady decline throughout the entire 100–200 cm depth of the pits with no obvious signs of a greater rate of decline at shallow depths where photolytic activity should be strongest (Figure 4c–d). Re-examining the drivers of NO_3^- oxygen isotopic change may help explain this inconsistency.

The seeming insensitivity of oxygen isotopic values to changing photolytic activity may instead reflect changes in the balance between two competing isotopic effects. Although it has not been experimentally observed, photolytic mass loss is theoretically predicted to have a direct isotopic fractionation effect on oxygen that would increase $\delta^{18}O_{NO3}$ values in the remaining NO_3^-, similar to $\delta^{15}N_{NO3}$ (Frey et al., 2009). This is counter-balanced by an opposing isotopic effect resulting from oxygen exchange from a cage effect during NO_3^- re-oxidation (McCabe et al., 2005). In uppermost 5–10 cm of the snowpack, the proximity of the atmosphere makes it relatively easy for photolyzed NO_3^- to be lost from the snowpack. This leads to the rapid change observed in $\delta^{15}N_{NO3}$, but the lack of corresponding substantial change in $\delta^{18}O_{NO3}$ suggests that the isotopic effect of mass loss fractionation is balanced by the competing effect from oxygen exchange in these uppermost depths.

Deeper within the snow, however, photolyzed NO_3^- lacks this nearby interface with the atmosphere, and it is more likely that photolytic products will re-oxidize back into NO_3^- in place or somewhere within the photic zone. This increase in intra-snowpack NO_3^- recycling will reduce photolytic mass loss fractionation, but oxygen exchange can still occur. The balance in competing isotopic effects will thus shift increasingly toward oxygen exchange with greater depth. Although photolytic activity and NO_3^- recycling is decreasing with depth due to radiation attenuation, the increased dominance of the oxygen exchange effect appears to compensate for the decreasing radiation to produce the steady lowering in $\delta^{18}O_{NO3}$ values. Therefore unlike $\delta^{15}N_{NO3}$, the greatest degree of isotopic change for $\delta^{18}O_{NO3}$ should occur beneath the immediate uppermost snowpack layers once the oxygen exchange effect is predominant. Presumably, the quicker burial of NO_3^- at wetter sites would limit the amount of oxygen exchange that could occur in the deeper photic zone, and thus we observe little difference in $\delta^{18}O$ values between skin layer and 1 m depth samples. In contrast, the greater photolytic activity at drier sites would enhance the imbalance between competing isotopic effects and produce distinctly lower $\delta^{18}O_{NO3}$ values at 1 m depth compared to the surface.

This proposed concept works well to explain the patterns observed in $\delta^{18}O_{NO3}$, but it struggles to fully explain the similar patterns also observed in $\Delta^{17}O_{NO3}$. Unlike $\delta^{18}O_{NO3}$, photolytic mass loss is not expected to affect $\Delta^{17}O_{NO3}$ values (McCabe et al., 2005). Thus, there is no isotopic effect counter-balancing the oxygen exchange brought by NO_3^- re-oxidation and the cage effect, yet we still observe an unusually steady lowering of $\Delta^{17}O_{NO3}$ values with depth in the pit data. As previously mentioned, periods with high photolytic mass loss observed in the pit data (as indicated by the highest $\delta^{15}N_{NO3}$ values) often have $\Delta^{17}O_{NO3}$ peaks that are higher than would be expected compared to the coinciding $\delta^{18}O_{NO3}$ values. In other words, $\Delta^{17}O_{NO3}$ values decline from skin layer values to a lesser extent than $\delta^{18}O_{NO3}$ values during times of high photolytic mass loss, which is in fact the opposite expected from our proposed “balanced competing effects” concept and difficult to explain mechanistically. Overall, this suggests that substantial complexities and unknowns still exist with regards to photic zone processes and NO_3^- dynamics at the snow-atmosphere interface in Antarctica and resolving these issues will be necessary to properly interpret NO_3^- oxygen isotopes archived in Antarctic ice.

~~In contrast, at the driest SMB sites (110–130 kg m^{-2} a^{-1}) the regressions show that $\delta^{18}O_{NO3}$ and $\Delta^{17}O_{NO3}$ values are notably higher in the skin layer than at 1 m depth. Compared to nitrogen isotopes, it appears that a greater degree of photolytic mass loss (i.e., a drier site) is needed to observe a clear divergence between skin layer and 1 m samples for oxygen isotopic values. This is a reasonable observation because the isotopic fractionation factors for oxygen isotopes are much smaller than for nitrogen, and we would expect that photolytic impacts become obvious much quicker for $\delta^{15}N_{NO3}$ than for $\delta^{18}O_{NO3}$ or $\Delta^{17}O_{NO3}$.~~

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~~An improved sampling method for the 1 m depth samples might produce stronger and more precise linear regressions with SMB^{-1}. The methodology used to collect 1 m depth samples during CHICTABA was to mix snow in a 5–10 cm thick layer at 1 m depth. However, each seasonal isotopic cycle typically covers 30–50 cm depth in the upper snowpack as observed in the pit records (Figure 4). As a result, each 1 m depth sample taken along the CHICTABA transect likely represents only part of full isotopic cycle. If a seasonal maximum or minimum happened to fall at 1 m depth, the resulting $\delta^{15}N_{NO3}$, $\delta^{18}O_{NO3}$, and $\Delta^{17}O_{NO3}$ values could be offset from the true annual mean value by 20–50 ‰, 10–20 ‰, and 5–6 ‰, respectively (Figure 4). For example, although the oxygen isotopic values for 1 m depth samples at CHIC-18 and CHIC-20 are much higher than expected (see high values near 130 kg m^{-2} a^{-1} in Figure 5), their values are similar to winter maximum values and may simply be a result of seasonally-biased sampling. Future sampling of 1 m depth samples should ideally mix snow from at least a 50 cm range (i.e., from 1.0 to 1.5 m depth) to reduce the chance of seasonal bias and provide more accurate $\omega(NO_3^-)$ and NO_3^- isotopic values.~~

6. Conclusions

Our analysis of NO_3^- in snow samples taken along the CHICTABA ~~traverse~~ transect reveals the environmental drivers of NO_3^- concentration and isotopic variability at an unprecedented spatial resolution for a region of East Antarctica with intermediate SMB values (110–200 kg m^{-2} a^{-1}). We find that seasonal geochemical cycles observed in atmospheric NO_3^- are preserved in NO_3^- buried in the snowpack. However, these cycles are clearly altered by post-depositional ~~photolytic mass loss~~changes as shown by NO_3^- isotopic values ~~changes~~ and calculated apparent isotopic fractionation factors that match ~~previous~~ observations from elsewhere in Antarctica attributed to photolysis ~~from elsewhere in Antarctica~~. ~~We find no strong evidence that HNO_3 volatilization or physical snow mixing substantially affected NO_3^- after deposition.~~ Additionally, we observe that the isotopic changes are greater at drier sites along the transect. This ~~supports~~ is consistent with photolysis as a causative factor in NO_3^- isotopic change because slower burial rates at dry sites expose NO_3^- to more cumulative photolytic radiation before the NO_3^- is buried ~~deeper~~ beneath~~than~~ the reach of sunlight.

Because photolysis does not entirely wipe out the initial seasonal NO_3^- cycles like it does at very dry sites in the Antarctic interior (e.g., Erbland et al., 2013; Shi et al., 2015), the interpretation of NO_3^- is complicated in firn and ice cores from regions with intermediate SMB values~~similar to the CHICTABA transect~~. If sampled at a high enough resolution, seasonal cycles in NO_3^- concentration and isotopes may be recoverable far into the past, but these values are not representative of the exact NO_3^- character~~istics~~ at the time of deposition. Photolysis will reduce $\omega(NO_3^-)$ while increasing $\delta^{15}N_{NO3}$ values and~~, to a lesser degree,~~ decreasing $\delta^{18}O_{NO3}$ and $\Delta^{17}O_{NO3}$ values from their initial atmospheric values. The ~~amount~~ degree of photolytic change is not likely consistent from year to year as it will depend strongly upon local SMB. Because regions in East Antarctica with intermediate SMB are generally found on the sloped transition between the high elevation interior plateau and low-lying coastal zone, katabatic winds drive intense irregular erosion and deposition of the snow surface (Frezzotti et al., 2002; Agosta et al., 2012). Additionally, ~~and~~ intrusions by atmospheric rivers and lower latitude moisture

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bring infrequent but regular extreme accumulation events to these transitional regions (Gorodetskaya et al., 2014; Wille et al., 2021; Djoumna and Holland, 2021). ~~This~~ As a result, the regions have ~~produces~~ very high interannual SMB variability that ~~will~~ leads to very high interannual variability in ~~interannual~~ photolytic impacts that~~, and this variability~~ makes it difficult or impossible to reconstruct precise initial atmospheric NO_3^- characteristics at a seasonal resolution from NO_3^- archived in firn and glacial ice.

However, relative to the interannual variability introduced by local SMB changes, interannual differences in ~~initial~~ mean atmospheric NO_3^- isotopic values are likely to be relatively small, at least in the recent past. Atmospheric and skin layer NO_3^- samples at Dome C are generally consistent year to year (Erbland et al., 2013; Winton et al., 2020), and atmospheric NO_3^- observed at other sites have similar patterns and values (Wagenbach et al., 1998; Savarino et al., 2007; Frey et al., 2009). Regular sampling of atmospheric and skin layer NO_3^- over one or more full years at an ~~moderate~~ intermediate SMB site would greatly aid our comprehensive spatial understanding of NO_3^- depositional dynamics, but unfortunately no permanent scientific stations exist in ~~moderate~~ intermediate SMB regions far from the coast. ~~Atmospheric and skin layer NO_3^- samples at Dome C are generally consistent year to year (Erbland et al., 2013; Winton et al., 2020), and atmospheric NO_3^- observed at other sites have similar patterns and values (Wagenbach et al., 1998; Savarino et al., 2007; Frey et al., 2009).~~ The most practical approach to NO_3^- interpretation in firn and ice cores from intermediate SMB sites may be to assume atmospheric NO_3^- isotopic values can be considered "constant" when aggregated over multiple years. As a result, observed isotopic variability at this multiannual resolution will reflect changes in photolytic activity driven by ~~local~~ SMB, with stronger and more detectable effects at drier sites and more accuracy with more years of accumulation aggregated per sample.

Recognizing the importance of SMB in determining the isotopic composition of NO_3^- may allow us to investigate other drivers of isotopic change. Ice cores from intermediate accumulation regions can preserve seasonal ion and water isotope cycles well enough to produce highly precise chronologies (Buizert et al., 2015). Coupled with physical measurements of the ice core's volume and mass, we can model SMB based on physical changes in ice density and/or annual layer thickness (e.g., Fudge et al., 2016; Akers et al., 2022). This physical SMB reconstruction could then be used to remove the SMB signal from a parallel NO_3^- isotope record, and the residual NO_3^- isotopic variability should reflect past changes in other environmental factors, such as insolation, total column ozone, snow optical properties, and atmospheric NO_3^- sourcing and chemistry (Zatko et al., 2016; Cao et al., 2022; Shi et al., 2022b). This would be most effective for $\delta^{15}N_{NO3}$ which has a more clear relationship with SMB (Akers et al., 2022) than $\delta^{18}O_{NO3}$ or $\Delta^{17}O_{NO3}$, but additional investigation into the mechanisms behind the apparent impacts of photolysis on oxygen isotopic composition is likely to provide valuable insight into past and present NO_3^- dynamics as well. Additionally, ice cores taken from high SMB regions nearer the coast (i.e., regions with limited photolytic mass loss) should better preserve the seasonal and interannual variability of atmospheric NO_3^- and can provide an interesting comparison for ice core NO_3^- records from drier inland settings.

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Our NO_3^- work as part of CHICTABA adds to the growing body of literature on NO_3^- isotopes that point the way forward for future improvements to NO_3^- interpretation in Antarctica. This knowledge is particularly critical for understanding the environmental changes archived in deep Antarctic ice cores, including new projects such as Beyond EPICA-Oldest Ice (Lilien et al., 2021). Based on our CHICTABA findings and other recent studies (Erbland et al., 2013; Shi et al., 2015, 2018a), we highlight in particular the value of NO_3^- isotopic profiles from snow pits in understanding the transition of NO_3^- from the atmosphere into archived glacial ice. We argue for additional dedicated pit sampling of NO_3^- isotopes with particular emphasis on extending profile depth below 1 m with paired chronological and snow density profiles to constrain SMB changes. Replication of pit profiles at individual sites will also improve our understanding of the natural range of local spatial NO_3^- variability. Expansion of atmospheric NO_3^- monitoring beyond Dome C and Zhongshan stations will also help constrain spatial variability in seasonal NO_3^- cycling. Finally, the potential spatial variability in snow optical properties and photic zone depths remain one of the greatest unknowns in Antarctic NO$_3^-$ dynamics (France et al., 2011, 2020; Winton et al., 2020), and improved field observations and modeling will be required to precisely interpret NO$_3^-$ isotopic variability for paleoenvironmental reconstructions. ~~(Akers et al., 2022)Ice cores taken from high SMB regions nearer the coast (i.e., regions with limited photolytic mass loss) likely preserve the seasonal and interannual variability of NO$_3^-$ at deposition better and can provide an interesting comparison for ice core NO$_3^-$ records from drier inland settings.~~ Overall, the NO$_3^-$ samples from the CHICTABA mission confirm the general understanding of NO$_3^-$ dynamics in East Antarctica that has developed in the past two decades and suggest that the understudied regions between the coasts and interior dome summits hold much untapped potential to improve our understanding of the Antarctic environment.

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Data availability

Data are ~~currently under review for inclusion in the~~available through the PANGAEA online repository at https://doi.org/10.1594/PANGAEA.948355. ~~Data needed for reviewers to recreate analyses and plot creation are included with the code at the link provided below.~~

Code availability

All code used to analyze data and produce figures is available at https://doi.org/10.5281/zenodo.7287413. ~~https://github.com/pete-d-akers/chictaba-nitrate. This code and data package will be formally published with a DOI prior to final publication.~~

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Formal analysis: PDA

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