Distinguishing summertime atmospheric production of nitrate across the East Antarctic Ice Sheet

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Abstract

Surface snow and atmospheric samples collected along a traverse from the coast to the ice sheet summit (Dome A) are used to investigate summertime atmospheric production of nitrate (NO3−) across East Antarctica. The strong relationship observed between δ15N and δ18O of nitrate in the surface snow suggests a large (lesser) extent of nitrate photolysis in the interior (coastal) region. A linear correlation between the oxygen isotopes of nitrate (δ18O and Δ17O) indicates mixing of various oxidants that react with NOx (NOx = NO + NO2) to produce atmospheric nitrate. On the plateau, the isotopes of snow nitrate are best explained by local reoxidation chemistry of NOx, possibly occurring in both condensed and gas phases. Nitrate photolysis results in redistribution of snow nitrate, and the plateau snow is a net exporter of nitrate and its precursors. Our results suggest that while snow-sourced NOx from the plateau due to photolysis is a significant input to the nitrate budget in coastal snow (up to ~35%), tropospheric transport from mid-low latitudes dominates (~65%) coastal snow nitrate. The linear relationship of δ18O vs. Δ17O of the snow nitrate suggests a predominant role of hydroxyl radical (OH) and ozone (O3) in nitrate production, although a high Δ17O(O3) is required to explain the observations. Across Antarctica the oxygen isotope composition of OH appears to be dominated by exchange with water vapor, despite the very dry environment. One of the largest uncertainties in quantifying nitrate production pathways is the limited knowledge of atmospheric oxidant isotopic compositions.

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1. INTRODUCTION

There is great interest in using the isotopic composition of nitrate (NO3−) in ice cores to track the history of atmospheric precursor (i.e., NOx = NO + NO2) sources and oxidation chemistry. However, NO3 can be lost from the snowpack by surface processes, and the extent of NO3 loss via post-depositional processing may be accumulation
dependent (Freyer et al., 1996; Röthlisberger et al., 2002; Grannas et al., 2007). In addition, the physical evolution of the snow influences the chemical composition and recent modeling of the co-condensation of HNO₃ and water vapor suggests that this could influence the deposition and preservation of NO₃ in surface snow (Bock et al., 2016). Post-depositional loss of NO₃ can be severe at low accumulation sites such as Dome C (<30 kg m⁻² a⁻¹) and is accompanied by isotopic modification of the residual NO₃ (Frey et al., 2009; Erbland et al., 2013). In contrast, NO₃ can be largely preserved under higher snow accumulation conditions such as at Summit, Greenland (>200 kg m⁻² a⁻¹) likely owing to the faster burial and possibly snow impurity content (Hastings et al., 2005; Fibiger et al., 2013; Zatko et al., 2013).

Thus, it has been suggested that high-accumulation sites with less post-depositional processing have great potential to deliver information regarding NO₃ sources and oxidation chemistry (Hastings et al., 2009; Erbland et al., 2013; Shi et al., 2015; Zatko et al., 2016). For lower accumulation sites, it can be difficult to interpret archived records due to surface modification, although the isotopic composition of NO₃ may be useful in this regard since post-depositional loss leaves a large isotopic imprint (Erbland et al., 2015). A number of field observations and laboratory experiments suggest that photolysis is the dominant NO₃ loss mechanism and leads to a large enrichment of ¹⁵N in the remaining snow NO₃, with local impacts on summertime atmospheric NO₃/OH mixing ratios via photoproducts (e.g., NO₂) (Davis et al., 2004; Jacobi et al., 2006; McCabe et al., 2007; Davis et al., 2008; Frey et al., 2009; Slusher et al., 2010; Erbland et al., 2013; Berhanu et al., 2014). Due to photolytic loss, isotopic enrichment in ¹⁸O and ¹⁷O of the residual snow NO₃ is also expected (Frey et al., 2009), but field and laboratory studies tend to show a decrease in δ¹⁸O and Δ¹⁷O (McCabe et al., 2005; Shi et al., 2015). δ(“delta”) is defined as (Rsample/Rreference − 1) × 1000‰, where R = ¹⁵N/¹⁴N for δ¹⁵N, R = ¹⁸O/¹⁶O for δ¹⁸O and R = ¹⁷O/¹⁶O for δ¹⁷O; Δ¹⁷O = δ¹⁷O – 0.52 × δ¹⁸O; and the reference is air-N₂ for δ¹⁵N and Vienna Standard Mean Ocean Water (VSMOW) for δ¹⁸O and δ¹⁷O. McCabe et al. (2005) determined in laboratory photolysis experiments that the decrease in Δ¹⁷O of NO₃ in water was due to reoxidation and O-exchange reactions between the photoproducts, OH and H₂O (Δ¹⁷O(H₂O) = 0‰).

Photoproducts from photolysis of NO₃ in snow can be reoxidized and recycled in the atmosphere before local re-deposition as NO₃ or transport away. Observations in coastal regions of Antarctica have suggested that snow-sourced NO₃/NOₓ from photolysis on the Antarctic plateau could be transported and deposited in the coastal zone (Davis et al., 2004; Savarino et al., 2007; Davis et al., 2008; Slusher et al., 2010; Grilli et al., 2013). Model simulations have suggested that most of the NO₃ in inland Antarctic snow is lost via photolysis (perhaps greater than 90%), leading to a large enrichment of ice core δ¹⁵N of NO₃ (up to 300–400‰), while the recycled NO₃ due to transported photoproducts contributes to a lowering of δ¹⁵N in coastal snow (Zatko et al., 2016). However, another modeling study concluded that tropospheric sources of NOₓ from mid-latitudes (i.e., fossil fuel combustion, soil, lightning, and thermal decomposition of peroxyacetyl nitrate (PAN)) are the main driver of NO₃ concentrations in snow except in summer (Lee et al., 2014). This latter modeling study did not include photolytic loss or recycling of snow NO₃ and suggested that observed summertime peaks (November–January) in snow NO₃ concentrations across Antarctica would likely be explained if this process were included. Previous observational studies had suggested that a stratospheric source of NO₃ was an important driver of seasonality in NO₃ concentrations in spring and early summer (Legrand and Delmas, 1986; Wagenbach et al., 1998; Savarino et al., 2007; Traversi et al., 2017). The potential mix of tropospheric and stratospheric sources, and the atmospheric transport of ‘secondary’ NO₃/NOₓ across the East Antarctic Ice Sheet (EAIS) adds additional complexity to the interpretation of NO₃ in ice cores.

In an effort to better discern the influence of production of ‘secondary’ NO₃ in Antarctica, we collected surface snow and atmospheric samples along a ~1300 km traverse from coastal East Antarctica to the summit of the ice sheet (Dome A). This traverse covers a variety of environments, e.g., from very low (<25 kg m⁻² a⁻¹) to high (>200 kg m⁻² a⁻¹) snow accumulation rates, from the coast to the ice sheet summit (with elevation ~4100 m). We utilize the full suite of NO₃ isotopic measurements (δ¹⁵N, δ¹⁸O and Δ¹⁷O) on snow and atmospheric samples to investigate processing of snow NO₃ and formation pathways of atmospheric NO₃ in different environments on the EAIS.

2. METHODOLOGY

2.1. Sample collection

In austral summer 2012–2013, surface snow samples were collected from 124 sites at ~10 km intervals along a traverse from Zhongshan Station on the coast to Kunlun Station at Dome A (Fig. 1). The topmost 3 ± 1 cm of snow was collected using 250 ml high-density polyethylene (HDPE) bottles pushed into the snow in the windward direction. The surface snow sampling was carried out upwind with respect to the traverse route, generally >500 m away from the route. The bottles were pre-cleaned with ultrapure Milli-Q water (18.2 MΩ), dried under a class 100 clean hood at room temperature and sealed in clean polyethylene (PE) bags until field sampling. Pre-cleaned bottles filled with Milli-Q water taken to the field and treated to the same conditions as samples represent field blanks. After sampling, the bottles were again sealed in clean PE bags and preserved frozen in a clean insulated cabinet. At individual sampling sites, the surface snow density (the topmost ~10 cm layer) was measured using a rectangular sampler (total volume = 1000 cm³).

In addition to surface snow, atmospheric NO₃, i.e., both particulate and gaseous NO₃, was collected along the traverse following similar protocols for previous work in East Antarctica (Savarino et al., 2007; Frey et al., 2009; Erbland et al., 2013). Briefly, the atmospheric samples were collected on Whatman G653 glass-fiber filters (8 × 10 in; prebaked at
with a flow rate of 1.0 m$^3$ min$^{-1}$ for 12–15 h. All sampling was performed ~200 m upwind from the temporary field camps. Two HVASs were operated at the same time to ensure sufficient amounts of NO$_3^-$ for isotopic analysis, and the two filters were combined to form one sample. In total, 34 atmospheric samples were collected on the traverse (Fig. 1).

Recent model simulations suggest that the tropospheric transport of NO$_x$ emitted as far north as 25°S is an important contribution to the Antarctic NO$_3^-$ budget (Lee et al., 2014), and characterizing the isotopic signatures of NO$_3^-$ in the southern mid-low latitudes would be of significance to the interpretation of NO$_3^-$ sources in Antarctic snow. Thus, marine atmospheric NO$_3^-$ was sampled in the Indian Ocean sector by the RV Xuelong during the 2015–2016 Chinese Antarctic Expedition cruise (Table S1). The sampling protocols were similar to those described here. To avoid contamination from the vessel’s emissions, the HVAS was situated on the top deck (~25 m above sea level) and operated only when the incoming wind direction was perpendicular to the vessel’s path and the wind velocity was greater than 1.5 m s$^{-1}$. The sampling durations were 24–48 h, with the typical sampling air volume for each sample ranging from about 1500 to 3500 m$^3$. In total, 10 atmospheric samples in the mid-low latitudes (~20–45°S) were collected. (We note that samples were collected along the entire cruise route and the full dataset is the subject of a forthcoming publication.) Four field blanks were collected from filters installed in the HVAS without pumping and treated as samples thereafter. All filters were kept in opaque PE bags before and after collection and stored at < −20 °C prior to extraction and analysis.

2.2. Sample analysis

The procedure for extracting filter NO$_3^-$ was similar to previous work (Xu et al., 2013). Each filter was cut into pieces using pre-cleaned scissors that were rinsed between samples, placed in ~100 ml of Milli-Q water, ultrasonicated for 40 min and leached for 24 h under shaking. The sample solutions were then filtered through 0.22 μm ANPEL PTFE filters for NO$_3^-$ concentration and isotopic analysis. Nitrate concentration ([NO$_3^-$]) in snow and extracted solutions was determined using a Dionex ion chromatograph (ICS 3000) following Shi et al. (2012). The pooled standard deviation ($\sigma_{p}$; Table S2) of replicate samples run at least twice in different sample sets was 1.5 ng g$^{-1}$ ($n = 25$). The detection limit (DL) of NO$_3^-$ is obtained from three standard deviations of Milli-Q water in the lab, which is typically run 10 times, and the DL is estimated to be ~3.0 ng g$^{-1}$. [NO$_3^-$] in the field blanks...
(n = 3) consisting of bottled Milli-Q water taken to Antarctica was near or below detection limit. For the glass fiber filter blanks (n = 4), [NO3] was generally two orders of magnitude lower than actual atmospheric sample extract solutions (hundreds to thousands of ng ml⁻¹).

Water oxygen isotope ratios ([³¹⁷O(H₂O)) of snow were determined by a Finnigan MAT253 isotope ratio mass spectrometer (IRMS) using the standard CO₂ equilibration method (Johnsen et al., 1997). The 1σ of reference material (VSMOW) measurements was 0.10‰ (n = 20).

Nitrogen and oxygen isotopic ratios in NO₃(δ¹⁵N, δ¹⁸O and Δ¹⁷O) were analyzed using the bacterial denitrifier method at Brown University (Sigman et al., 2001; Casciotti et al., 2002; Kaiser et al., 2007). Briefly, denitrifying bacteria (Pseudomonas aureofaciens) lacking the N₂O reductase enzyme quantitatively convert NO₃ to N₂O, using a Thermo Scientific Delta V + IRMS. Δ¹⁷O was measured separately via the thermal decomposition of N₂O to N₂ and O₂ in a heated gold tube (Kaiser et al., 2007). It is noted that δ¹⁸O and δ¹⁷O of NO₃ were determined independently at Brown, i.e., different aliquots of a sample are measured separately for δ¹⁸O (using N₂O) and Δ¹⁷O (using O₂ decomposed from N₂O; Fibiger et al., 2013). Additional details on the isotopic measurements are described in Shi et al. (2015). The 1σ of sample replicates depicts the analytical precision of the overall method (Fibiger et al., 2013; Buffen et al., 2014; Shi et al., 2015), and for this work was δ¹⁵N = 0.3‰ (n = 18), δ¹⁸O = 0.5‰ (n = 18) and Δ¹⁷O = 0.6‰ (n = 23) (Table S2).

3. RESULTS

3.1. Concentration and isotopic composition of NO₃

The concentration and isotopic composition of NO₃ in the snow and atmosphere are shown in Fig. 2. Snow [NO₃] ranges from 30.0 to 488 ng g⁻¹ (mean = 51.1 ng g⁻¹) with a coefficient of variation (CV, standard deviation/mean) of 0.5, indicating moderate variability. In general, [NO₃] in snow is comparable to other Antarctic traverses such as Dumont d’Urville (DDU)-Dome C, Talos Dome-Dome C, and Syowa-Dome F (Traversi et al., 2004; Bertler et al., 2005; Frey et al., 2009). Atmospheric [NO₃] varies between 6 and 118 ng m⁻³, with a mean of 38 ng m⁻³ (Fig. 2c).

Due to the wide range of accumulation rates (which are influenced by wind scouring and redistribution in addition to precipitation), the 3 cm of snow sampled at each site covers different periods of time. At inland sites (low accumulation: Fig. 2a), very high NO₃ concentrations have been observed in the uppermost ~1 cm of snow during austral summertime (concentrations at Dome C, for example, have been observed above 1000 ng g⁻¹ (Udisti et al., 2004; Erbland et al., 2013), so we expect that the NO₃ in our inland samples contains a significant or even dominant amount from this upper, and presumably more recent, deposition.

Snow δ¹⁵N(NO₃) ranges from –33.6 to 110.6‰ (mean = 14.7‰, Fig. 2d), and δ¹⁸O(NO₃) varies between 39.5 and 100.7‰ (mean = 76.3‰, Fig. 2e). CV of δ¹⁸O(NO₃) is 0.17, while CV = 2.4 for δ¹⁵N(NO₃), suggesting larger spatial variability of the latter. It is difficult to directly compare the observations here with previous isotopic data from the DDU-Dome C traverse, primarily due to difference in sampling depth. Frey et al. (2009) reported that δ¹⁵N and δ¹⁸O of NO₃ in the top 10 cm of snow along the DDU-Dome C traverse was –13.3 to 36.8‰ (mean = 8.2‰) and 62.5–85.7‰ (mean = 70.6‰), respectively. These ranges are generally smaller compared to our data, possibly related to the deeper surface snow sampling in that study, while shallower surface sampling on a later DDU-Dome C traverse suggests a larger range than found here. Erbland et al. (2013) report data from 19 locations sampled at ~2 cm depth along the DDU-Dome C traverse, with δ¹⁸O ranging between –31 and 186‰ (mean of 41‰). For these same samples, δ¹⁸O varies between 28 and 107‰ (mean = 63‰). It is likely that significant deposition to the near surface layer of snow influences the concentration and isotopic results (see above). In the atmosphere, the ranges of δ¹⁵N(NO₃) and δ¹⁸O(NO₃) are –46.9 to 12.6‰ (mean = –20.1‰; Fig. 2d) and 58.7–82.7‰ (mean = 71.2‰; Fig. 2e), respectively, and these values generally fall within the ranges measured at Dome C and DDU (Savarino et al., 2007; Erbland et al., 2013).

Snow Δ¹⁷O(NO₃) ranges from 23.7 to 36.5‰, with a mean of 31.1‰ and CV of 0.07 (Fig. 2f), showing much less spatial variability than either δ¹⁵N(NO₃) or δ¹⁸O(NO₃). Information regarding Δ¹⁷O(NO₃) in Antarctic surface snow is rather limited but data from a DDU-Dome C traverse range from 27 to 38‰ (Erbland et al., 2013). Atmospheric Δ¹⁷O(NO₃) ranges from 24.0 to 30.1‰, with a mean of 27.7‰. Similar to δ¹⁵N(NO₃) and δ¹⁸O(NO₃), Δ¹⁷O(NO₃) here is comparable to the austral summer observations at Dome C and DDU (Savarino et al., 2007; Erbland et al., 2013). Note that previous works on isotopes of atmospheric NO₃ are site-specific observations (i.e., focusing on temporal/seasonal variations; Wagenbach et al., 1998; Savarino et al., 2007; Erbland et al., 2013), and data on the spatial variation across Antarctica (e.g., spatial variability along a traverse) are unavailable thus far.

Atmospheric [NO₃] in the marine boundary layer in the southern mid-low latitudes (from about 20°S to 45°S) ranges from 50 to 1350 ng m⁻³, which is similar to the previous investigations along the same cruise (Xu et al., 2013; Xu and Gao, 2015). Means of δ¹⁵N, δ¹⁸O and Δ¹⁷O of atmospheric NO₃ are –7.0 ± 3.7, 70.7 ± 8.2 and 25.1 ± 2.6‰ (mean ± 1σ, n = 10), respectively (Table S1), comparable to the observations in the Atlantic Ocean over the same latitudinal range (Morin et al., 2009).

3.2. NO₃ concentration and isotopic composition spatial pattern

In general, both [NO₃] and δ¹⁵N in the snow and atmosphere increase from the coast towards the plateau while δ¹⁸O shows an opposite trend, with lower values inland (Fig. 2c-e). This is similar to surface snow observations along the DDU-Dome C traverse (Frey et al., 2009). Δ¹⁷O shows a generally similar but much weaker trend as with δ¹⁸O (Fig. 2e and f).

Fig. 2. Annual snow accumulation rate and water isotopes (a), and snow density and elevation (b), along the traverse from Zhongshan Station to Dome A, East Antarctica. Results for concentration and isotopic composition of NO$_3^-$ ((c)–(f)) in surface snow and atmosphere. Note that the atmospheric data of $\delta^{15}$N, $\delta^{18}$O and $\Delta^{17}$O on the secondary y-axis are presented with a different scale from the primary y-axis (snow NO$_3^-$ isotopic data) ((d)–(f)).
A significant correlation was found between δ¹⁸O and δ¹⁵N of NO₃ in the snow and atmosphere (Fig. 3), while δ¹⁸O and Δ¹⁵O of NO₃ are closely related in snow (Fig. 4). However, the concentration generally shows no relation to the isotopic parameters of NO₃ in snow, except the data on the plateau (i.e., 800 km – Dome A), where positive correlations were found between oxygen isotopes (δ¹⁸O and Δ¹⁵O) and concentration (R² = 0.31 and 0.41, respectively; Fig. S1). In the atmosphere, [NO₃] is well correlated with δ¹⁸O or δ¹⁵N, but not with Δ¹⁵O (Fig. S2).

Both δ¹⁵N and δ¹⁸O in the snow NO₃ are most strongly, and non-linearly, related to site distance from the coast and elevation (since elevation increases inland; Table 1). The same is true for [NO₃] and Δ¹⁵O but to a lesser degree. Interestingly, there are no significant trends from the coast to ~400 km inland for snow NO₃ isotopic compositions (R² < 0.1, p > 0.05; Figs. S3 and S4). In the coastal ~400 km, the snow accumulation rate is high, generally >100 kg m⁻² a⁻¹ (Fig. 2a), which may restrict the post-depositional alteration of snow NO₃, leading to no clear trend in isotopic composition (see Section 4.2 below).

Previous reports have pointed out that snow [NO₃] and/or isotopic composition across Antarctica are related to site accumulation rate (Freyer et al., 1996; Röthlisberger et al., 2002; Erbland et al., 2013). The weak relationships with accumulation observed in this work are likely related to the very strong wind scouring and snow redistribution that occurs on the plateau (Ding et al., 2011) (Fig. S5). When sites from the mid-traverse are not considered, the relationships with accumulation improve but do not exceed those with distance from the coast (Tables 1 and S3). We note that when these mid-traverse sites are not considered, there is very little change in the relationships among δ¹⁵N, δ¹⁸O, Δ¹⁵O and [NO₃]. In the following, the transition zone is excluded such that only the plateau (~800 km – Dome A, with snow accumulation decrease towards Dome A and elevation > ~3000 m) and coastal (coast – ~400 km) sites will be focused on.

4. DISCUSSIONS

4.1. Plateau snow NO₃: post-depositional processing and recycling

If it is assumed that photolytic loss of snow NO₃ follows a Rayleigh type process, a theoretical fractionation constant, ε (%), can be used to quantify the changes in δ¹⁵N or δ¹⁸O with NO₃ processing (Blunier et al., 2005). Under the summertime radiation conditions on the Dome A plateau, the ¹⁵ε (¹⁵N) and ¹⁸ε (¹⁸O) are calculated to be -53‰ and -34‰ respectively, following the model proposed by Frey et al. (2009). This negative ¹⁵ε value, close to that derived from both laboratory and field experiments (Berhanu et al., 2014, 2015), would explain the inland high snow δ¹⁵N(NO₃) values, with larger values corresponding to a higher degree of photolytic loss of NO₃ (Fig. 2a). Consequently, higher atmospheric [NO₃] values are observed on the plateau due to the strong photolytic loss of snow NO₃ (Fig. 2c), and the atmospheric NO₃ is expected to hold the isotopic imprint of snow-sourced NO₃ (i.e., secondary NO₃ from snow-sourced NO₃).

Upon photolysis of NO₃, the δ¹⁵N of emitted NOₓ can be calculated following the Rayleigh fractionation equation,

$$\delta^{15}N_{\text{emitted}} = (1 + \delta^{15}N_0)(1 - f^{(15\text{N})})/(1 - f) - 1,$$

where δ¹⁵N₀ denotes δ¹⁵N in initially deposited NO₃; f is the fraction of NO₃ remaining in the snow. If we take δ¹⁵N in initially deposited NO₃ at Dome A to be similar to that at Dome C (i.e., δ¹⁵N₀ = 18‰, top ~0.4 cm snow value; Erbland et al., 2013) and f = 0.63 (i.e., a ~37% loss of NO₃ in inland Antarctica; Shi et al., 2018), the δ¹⁵Nemitted is calculated to be ~26‰, i.e., very negative δ¹⁵N(NO₃) values would be expected in the atmosphere above the plateau snowpack. Assuming that secondary δ¹⁵N(NO₃) =

![Fig. 3. Relationship between δ¹⁵N and δ¹⁸O of NO₃ in the snow (a) and atmosphere (b), with colors corresponding to site distance from the coast.](image-url)

Table 1
Coefficient of determinations ($R^2$) for best-fit regressions of snow NO$_3$ concentration and isotopic composition vs. distance from coast, elevation (m above sea level; m a.s.l.), snow accumulation rate and inverse accumulation rate. The best non-linear fit type was shown after the $R^2$.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>[NO$_3$], ng g$^{-1}$</th>
<th>$\delta^{15}$N(NO$_3$), ‰</th>
<th>$\delta^{18}$O(NO$_3$), ‰</th>
<th>$\Delta^{17}$O(NO$_3$), ‰</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distance from coast, km</td>
<td>0.38*, P</td>
<td>0.62*, P</td>
<td>0.67*, P</td>
<td>0.22*, P</td>
</tr>
<tr>
<td>Elevation, m a.s.l.</td>
<td>0.33*, P</td>
<td>0.57*, P</td>
<td>0.64*, P</td>
<td>0.20*, P</td>
</tr>
<tr>
<td>Snow accumulation rate, kg m$^{-2}$</td>
<td>0.13, Exp$^b$</td>
<td>0.27*, P</td>
<td>0.25*, P</td>
<td>0.11*, P</td>
</tr>
<tr>
<td>$1/$Accumulation</td>
<td>0.12, Pow$^c$</td>
<td>0.30*, P</td>
<td>0.25*, P</td>
<td>0.09*, P</td>
</tr>
</tbody>
</table>

$^a$ P, polynomial.
$^b$ Exp, exponential.
$^c$ Pow, power.
* Significant at $p < 0.05.$

$\delta^{15}$N(NO$_3$), the observed atmospheric $\delta^{15}$N(NO$_3$) is much higher than the expected values from a Rayleigh fractionation for almost all of the plateau, with even positive values (>5‰) observed (Fig. 2d). These values are similar to the summer atmospheric observations at Dome C (Erbland et al., 2013).

Could another source, such as tropospheric inputs, explain this deviation from expectation? For instance, Lee et al. (2014)’s adjoint modeling study suggests tropospheric sources from the mid-low latitudes should be important. The tropospheric $\delta^{15}$N(NO$_3$) observed in samples collected in mid-low latitudes of the Indian Ocean sector in this study was found to be negative (~7.0 ± 3.7‰), while the data in mid-low latitudes in the Atlantic Ocean sector is about ~4‰ (Morin et al., 2009). Although the potential fractionation of $^{15}$N during transport is not well understood, it is unlikely that the tropospheric source contributes substantially to positive atmospheric $\delta^{15}$N(NO$_3$) on the plateau rather than on the coast (i.e., very low atmospheric $\delta^{15}$N (NO$_3$) on the coast; Fig. 2d). Stratospheric inputs of NO$_3$ have also been hypothesized as important on the plateau, and this source is expected to have a high, positive $\delta^{15}$N (NO$_3$) value (19 ± 3‰) (Moore, 1974; Savarino et al., 2007). A stratospheric source of NO$_3$, however, should also have a high $\delta^{18}$O and $\Delta^{17}$O of NO$_3$ due to the influence of stratospheric ozone (Krankowsky et al., 2007) and this is opposite to the observations (Figs. 3 and 4).

This brings us back to the possibility that the recycling of NO$_3$ on the plateau dominates the atmospheric NO$_3$ pool. In the campaigns of Investigation of Sulfur Chemistry in the Antarctic Troposphere (ISCAT) and Antarctic Tropospheric Chemistry Investigation (ANTCI) at South Pole during 1990s–2000s, elevated atmospheric NO$_3$ levels on the plateau were proposed to be associated with NO$_3$ recycling (Davis et al., 2004, 2008). Recent box model and global chemical transport model simulations suggest that NO$_3$ recycling at the low snow accumulation sites, e.g., Dome C, is rather strong (~4 times before burial below the photic zone) (Erbland et al., 2015; Zatko et al., 2016). During photolysis of NO$_3$, some of the photoproducts are emitted into the gas phase and can be transported away by katabatic winds, leading to a net loss of NO$_3$, and regionally, the Antarctic plateau regions are predicted to be subjected to the largest losses of NO$_3$ (Zatko et al., 2016). This NO$_3$ net loss process would result in a large enrichment of $^{15}$N in the snow, and subsequently the atmosphere on the plateau (i.e., the increased $\delta^{15}$N(NO$_3$) values in the surface snow due to loss then lead to positive $\delta^{15}$N (NO$_3$) via photolysis). The local production of secondary NO$_3$ in the atmosphere is also consistent with the oxygen isotopic composition observations (see below). It is possible that the imprint of stratospheric NO$_3$ could also help explain the positive values on the plateau; however, the model studies suggest that at such sites nearly 100% of the NO$_3$ should reflect a recycled signal. Thus, we propose that the observations of summertime atmospheric NO$_3$ on the plateau (Figs. 2c and 3b) are best explained by the recycling of photolysed NO$_3$ products across the plateau. Accordingly, this leads to a spatial redistribution of NO$_3$ driven by photochemistry that also contributes to depleted $^{15}$N(NO$_3$) in the coastal snow (Section 4.2).

As a mass-dependent process, it is expected that photolysis alone will not change the $\Delta^{17}$O of NO$_3$ remaining in the snow, but will increase $\delta^{18}$O following from the very negative calculated $\delta^{18}$O = −34‰, as is the case with $\delta^{15}$N (Frey et al., 2009). On the plateau, the high $\delta^{15}$N(NO$_3$) corresponds to low $\delta^{18}$O(NO$_3$) (Fig. 3), and $\Delta^{17}$O(NO$_3$) also shows low values (Figs. 2f and 4), opposite to the expectations. During photolysis, however, some of the photoproducts remain in the condensed phase (Jacobi and Hilker, 2007) and undergo reoxidation reactions where oxygen atoms from OH and/or H$_2$O (with very negative $\delta^{18}$O and $\Delta^{17}$O ≈ 0; case 1 in Table 2; Fig. 2a) can be incorporated into this secondary snow NO$_3$. In this case, both $\delta^{18}$O and $\Delta^{17}$O in remaining snow NO$_3$ will be lowered. This is supported by laboratory and theoretical work (McCabe et al., 2005; Jacobi and Hilker, 2007) and has been invoked to explain other East Antarctic snowpit observations (Frey et al., 2009; Erbland et al., 2013; Shi et al., 2015). Simultaneously, some fraction of the photoproducts must also escape the condensed phase to the firn air and overlying atmosphere. These products should also undergo reoxidation (but in the gas phase) by local oxidants (e.g., OH; see below). This reformed NO$_3$ will either be redeposited (where it may undergo further recycling) or be transported away. The combination of loss and reformation of NO$_3$ can explain higher $\delta^{15}$N corresponding to lower $\delta^{18}$O in the snowpack at plateau sites (Fig. 3).

During the production of atmospheric NO$_3$, oxygen atoms are incorporated from different source oxidants,
Fig. 4. $\Delta^{17}O$ vs. $\delta^{18}O$ of NO$_3$ in surface snow. The relationship between $\delta^{18}O$ and $\Delta^{17}O$ of NO$_3$ ($R^2 = 0.54, p < 0.001$) with colors corresponding to site distance from the coast is in (a). The best fit equation, coefficient of determinations ($R^2$), and significance level ($p$) for the three groups of data (based upon distance from the coast) are shown in (b). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 2
Different NO$_3$ production cases in both interior and coast of Antarctica.

| Plateau: 800 km-Dome A | Case 1 | Condensed phase, $\delta^{18}O$(OH) = $\delta^{18}O$(H$_2$O)$_b$ = [-40.0%e, -60.2%e];
| Coast: 0–400 km | Case 2 | OH-H$_2$O = 0.188 T, with T = temperature (K).
| | Condensed phase, $\delta^{18}O$(OH) = $\delta^{18}O$(H$_2$O)$_b$ = [-40.0%e, -77.6%e];
| | Condensed phase, $\delta^{18}O$(OH) = $\delta^{18}O$(H$_2$O)$_b$ = [-69.1%e, -86.2%e];
| | Gas phase, $\delta^{18}O$(OH) = $\delta^{18}O$(H$_2$O)$_b$ = [-92.9%e, -114.8%e];
| | Gas phase, $\delta^{18}O$(OH) = $\delta^{18}O$(H$_2$O)$_b$ = [-111.2%e, -135.3%e];
| | Gas phase, $\delta^{18}O$(OH) = $\delta^{18}O$(H$_2$O)$_b$ + $\delta_{\text{OH-H}_2\text{O}}$ = [-114.8%e, -135.3%e];
| | Gas phase, $\delta^{18}O$(OH) = $\delta^{18}O$(H$_2$O)$_b$ + $\delta_{\text{OH-H}_2\text{O}}$ = [-92.9%e, -114.8%e];
| | Gas phase, $\delta^{18}O$(OH) = $\delta^{18}O$(H$_2$O)$_b$ = [-69.1%e, -86.2%e];
| | Gas phase, $\delta^{18}O$(OH) = $\delta^{18}O$(H$_2$O)$_b$ = [-40.0%e, -60.2%e];
| | Case 2B | $\delta^{18}O$(OH) = $r * (1/2\delta^{18}O(OH) + 1/2\delta^{18}O(OH)) = [-77.6%e, -95.7%e];$
| | Case 1B | $\delta^{18}O$(OH) = $r * (1/2\delta^{18}O(OH) + 1/2\delta^{18}O(OH)) = [92.9%e, 99.3%e];$
| | Case 1A | $\delta^{18}O$(OH) = $r * (1/2\delta^{18}O(OH) + 1/2\delta^{18}O(OH)) = [95.7%e, 102.9%e];$
| | Case 2A | $\delta^{18}O$(OH) = $r * (1/2\delta^{18}O(OH) + 1/2\delta^{18}O(OH)) = [92.9%e, 99.3%e];$
| | Case 1A | $\delta^{18}O$(OH) = $r * (1/2\delta^{18}O(OH) + 1/2\delta^{18}O(OH)) = [92.9%e, 99.3%e];$
| | Case 2B | $\delta^{18}O$(OH) = $r * (1/2\delta^{18}O(OH) + 1/2\delta^{18}O(OH)) = [95.7%e, 102.9%e];$
| | Case 1A | $\delta^{18}O$(OH) = $r * (1/2\delta^{18}O(OH) + 1/2\delta^{18}O(OH)) = [92.9%e, 99.3%e];$
| | Case 2B | $\delta^{18}O$(OH) = $r * (1/2\delta^{18}O(OH) + 1/2\delta^{18}O(OH)) = [95.7%e, 102.9%e];$
| | Case 2A | $\delta^{18}O$(OH) = $r * (1/2\delta^{18}O(OH) + 1/2\delta^{18}O(OH)) = [92.9%e, 99.3%e];$
| | Case 1A | $\delta^{18}O$(OH) = $r * (1/2\delta^{18}O(OH) + 1/2\delta^{18}O(OH)) = [92.9%e, 99.3%e];$
| | Case 2B | $\delta^{18}O$(OH) = $r * (1/2\delta^{18}O(OH) + 1/2\delta^{18}O(OH)) = [95.7%e, 102.9%e];$
| | Case 2A | $\delta^{18}O$(OH) = $r * (1/2\delta^{18}O(OH) + 1/2\delta^{18}O(OH)) = [92.9%e, 99.3%e];$
| | Case 1A | $\delta^{18}O$(OH) = $r * (1/2\delta^{18}O(OH) + 1/2\delta^{18}O(OH)) = [92.9%e, 99.3%e];$
| | Case 2B | $\delta^{18}O$(OH) = $r * (1/2\delta^{18}O(OH) + 1/2\delta^{18}O(OH)) = [95.7%e, 102.9%e];$
depending on the NOx oxidation channels, resulting in different $\Delta^{17}$O values in the produced NO3 (Michalski et al., 2003; Morin et al., 2007). The $\Delta^{17}$O value of NO3 produced by different pathways can be calculated by the following expression,

$$
\Delta^{17}\text{O} (\text{NO}_3) = 2/3 \Delta^{17}\text{O} (\text{NO}_2) + 1/3 \Delta^{17}\text{O} (\text{Oxidant})
$$

(2)

Three groups of NO3 production pathways need to be considered for $\Delta^{17}$O(Oxidant): oxidation by OH, O3, and BrO ((R1)–(R11));

$$
\begin{align*}
\text{NO} + \text{O}_3 & \rightarrow \text{NO}_2 + \text{O}_2, \\
\text{NO}_2 + \text{hv} & \rightarrow \text{NO} + \text{O}_3, \\
\text{NO} + \text{RO}_2 (\text{oxygen}) & \rightarrow \text{NO}_2 + \text{RO} (\text{oxygen}), \\
\text{NO} + \text{BrO} & \rightarrow \text{NO}_2 + \text{Br}, \\
\text{NO}_2 + \text{OH} + \text{M} & \rightarrow \text{NO}_3 + \text{M}, \\
\text{NO}_2 + \text{BrO} & \rightarrow \text{BrONO}_2, \\
\text{BrONO}_2 + \text{H}_2\text{O} + \text{surface} & \rightarrow \text{HNO}_3 + \text{HOB}, \\
\text{NO}_2 + \text{O}_3 & \rightarrow \text{NO}_2 + \text{O}_2, \\
\text{NO}_3 + \text{DMS} & \rightarrow \text{HNO}_3 + \text{products}, \\
\text{NO}_3 + \text{NO}_2 + \text{M} & \rightarrow \text{NO}_5 + \text{M}, \\
\text{N}_2\text{O}_5 (g) + \text{H}_2\text{O} (g) + \text{surface} & \rightarrow 2\text{HNO}_3 (aq),
\end{align*}
$$

where RO2 is an organic peroxy radical, M is an unreactive third body such as N2, DMS is dimethyl sulfide, and HC is a hydrocarbon. The reaction between OH and NO2 (R5) is dominant during the day (Antarctic summer) while the reaction of O3 with NO2 ((R8)–(R11)) is more important at night (Antarctic winter). NO2 can be oxidized by BrO to form NO3 via hydrolysis of BrONO2 ((R6), (R7)). However, the oxidation of NO3 by BrO on the Antarctic plateau has been suggested to be negligible due to the very low observed BrO levels (2–3 pptv) (Frey et al., 2015; Savarino et al., 2016). During summertime, modeling predicts that (R5) should be the most important for NO3 deposited in Antarctica (Lee et al., 2014).

The linear relationship between $\delta^{18}$O and $\Delta^{17}$O of NO3 is generally interpreted as the result of mixing of various oxidants that react with NOx to produce atmospheric NO3 (Michalski et al., 2004; Fiebig et al., 2013). Thus, the close relationship between $\delta^{18}$O and $\Delta^{17}$O of NO3 on the plateau (Fig. 4b) is representative of a mixing between two major oxidants: a higher end-member that is assumed to be ozone (O3) representing transferrable terminal atom of O3, $\delta^{18}$O(O3) ≈ 130‰e, and $\Delta^{17}$O(O3) ≈ 39‰e in the troposphere; Vicars and Savarino, 2014; Savarino et al., 2016), and an oxidant with very low $\delta^{18}$O and $\Delta^{17}$O that is difficult to identify.

The x-intercept of the linear regression of $\delta^{18}$O versus $\Delta^{17}$O of NO3 is −78±2‰e (plateau data; Fig. 4b), which is comparable to those in surface snow (−93%e) and snowpit (−84%e) at South Pole (McCabe et al., 2007). Based on the secondary NO3 production during photolysis, the lower end-member of the mixing line could be associated with OH and/or H2O. OH in Antarctica during summertime is mainly from the reactions between (a) NO and HO2, and (b) O(hD) and H2O, which will result in different oxygen isotopic compositions (Morin et al., 2007). The presence of elevated mixing ratios of NO emitted by NO3 photolysis in snow will favor reaction (a), which explains large concentrations of OH across the high Antarctic plateau (Chen et al., 2001; Mauldin et al., 2001; Kukui et al., 2014). Thus, atmospheric OH in inland Antarctica is more likely associated with channel (a), due to the high degree of NO3 photolysis. In this case, $\delta^{18}$O(OH) could be close to or lower than the value of water vapor due to equilibrium between OH and H2O, while $\Delta^{17}$O should be close to zero (e.g., $\Delta^{17}$O(OH) calculated to be 1–3‰e at Dome C in summer) (Morin et al., 2007; Michalski et al., 2011; Savarino et al., 2016).

The $\delta^{18}$O of OH is largely dependent on the exchange reaction between OH and H2O (Dubey et al., 1997), and it can be approximated that OH is in equilibrium with H2O under most conditions. In this case, a fractionation constant of this exchange reaction, $\epsilon_{\text{OH-H}_2\text{O}}$, as a function of temperature has been proposed (Michalski et al., 2011). On the Antarctic plateau, where water vapor is at ppmv levels and OH is at <pptv levels (Kukui et al., 2014; Casado et al., 2016), it is unclear that this equilibrium fractionation would apply. There are no direct observations of $\delta^{18}$O(OH), but we may draw conclusions about its expected isotopic composition based upon the combined $\delta^{18}$O and $\Delta^{17}$O(OH3) observations here. If we take $\delta^{18}$O (OH) as close to that of H2O (water vapor) in the condensed phase (gas phase) (case 1A, Table 2), the range of $\delta^{18}$O(OH) seems to explain the observations well (i.e., x-intercept = −78%e; Fig. 4b). Note that the estimated $\delta^{18}$O of water vapor on the plateau (−62.8 to −86.2‰e; Table 2) is comparable to the observations at Dome C in summertime (Casado et al., 2016), where the $\delta^{18}$O of snow/ice is comparable to those of Dome A (Hou et al., 2009 and references therein). However, the OH pathway ((R1), (R5)) would lead to an expected $\Delta^{17}$O(NO3) ≤ 26‰e (case 1, Table 2), lower than most of $\Delta^{17}$O(NO3) values (30 ± 2‰e, mean ± 1σ) in the plateau snow (Fig. 2f). In this case, a higher primary $\Delta^{17}$O(NO3), i.e., a higher $\Delta^{17}$O(OH) is required to account for the observed values. If the observed $\Delta^{17}$O(NO3) is mainly associated with O3 ((R1), (R5)), then $\Delta^{17}$O(O3) of 58‰e (for calculation details see Table 2), corresponding to $\Delta^{17}$O = 38‰e of bulk O3, is required to account for the observed $\Delta^{17}$O(NO3) = 30‰e. Note that this expected $\Delta^{17}$O(O3) represents an upper limit, calculated by assuming $\Delta^{17}$O(OH) ≈ 0‰e (OH may retain the ozone $\Delta^{17}$O signature) and no NO3 production pathway via BrO (the $\Delta^{17}$O signature of NO3 produced via BrO pathway is identical to that of O3 channel; (R1) and (R6)). This calculated $\Delta^{17}$O of bulk O3 is greater than suggested by observations using a nitrite coated filter technique at Dome C ($\Delta^{17}$O(O3)bulk = 24.9‰e; Savarino et al., 2016), but falls within the ranges from laboratory experiments (Mauersberger et al., 2003; Michalski et al., 2014).
In summary, although the fractionation between OH and H$_2$O in the polar regions is poorly understood, our observations are best explained by $\delta^{18}$O(OH) = $\delta^{18}$O (H$_2$O). Thus, it can be inferred that the isotopic composition of OH appears to be dominated by exchange with water vapor across the plateau, despite the very dry environment, and a large fractionation between OH and H$_2$O (or water vapor) does not seem to occur.

### 4.2. Coastal snow NO$_3^-$ sources and oxidant chemistry

Compared to interior snow, photolytic loss of NO$_3^-$ likely occurs to a lesser extent near the coast (Zatko et al., 2016), possibly due to the faster burial of NO$_3^-$ below the photochemically active zone as a result of higher snow accumulation rate (Fig. 2a). The lesser extent of NO$_3^-$ photolysis seems to account for the coastal data extending towards the lower (higher) extent for $\delta^{15}$N ($\delta^{18}$O) of NO$_3^-$ (Fig. 3). Thus, information on the primary deposition of NO$_3^-$ (e.g., sources of NO$_3^-$) is likely preserved in the coastal snow, consistent with the snowpit observations on this traverse (Shi et al., 2015). This deduction also agrees well with the results of Dronning Maud Land and the traverse from Northern Victoria Land to Dome C, where the post-depositional losses of NO$_3^-$ were found to be insignificant at sites with snow accumulation rates $\sim$100 kg m$^{-2}$ a$^{-1}$ (Weller et al., 2004; Traversi et al., 2012).

On the coast, NO$_3^-$ is featured with negative $\delta^{15}$N(NO$_3^-$) values, with means in the snow and atmosphere of $-13.7\%$ and $-30.6\%$ respectively (Fig. 2d). These very negative values are generally lower than that attributed to most NO$_3^-$ sources except microbial production in soils (Yu and Elliott, 2017; and references therein), but the contribution of this source to Antarctica has been simulated to be minor (Lee et al., 2014). While lightning should be an important natural source of NO$_3^-$ in the troposphere (Murray et al., 2012; Lee et al., 2014), laboratory experiments suggested a $\delta^{15}$N of NO$_3^-$ of around 0$\%$ (Hoering, 1960). Stratospheric NO$_3^-$ (sum of reactive nitrogen compounds) has been suggested to have a positive $\delta^{15}$N (Savarino et al., 2007). Thus, it is hard to attribute the very low $\delta^{15}$N(NO$_3^-$) values ($<20\%$) to the known mid-latitude NO$_3^-$ sources (atmospheric $\delta^{15}$N(NO$_3^-$) in the mid-latitude atmospheres is $\sim$7.0$\%$; Section 3.1), although our knowledge of transport effects is very limited. Considering the large fractionation during photolysis ($^{15}e = -53\%$), the very negative $\delta^{15}$N(NO$_3^-$) is most likely associated with NO$_3^-$ that is formed from photoproducts from inland Antarctica carrying very low $\delta^{15}$N (see Section 4.1). This NO$_3^-$ source has also been proposed to be responsible for the depleted $^{15}$N of atmospheric NO$_3^-$ at DDU in summertime (Savarino et al., 2007).

Previous model simulations suggested that the primary source of NO$_3^-$ to Antarctica is tropospheric transport (Lee et al., 2014), and the recycled NO$_3^-$ is predicted to account for less of the annual NO$_3^-$ deposition flux along the Antarctic coast (Frey et al., 2009; Zatko et al., 2016). The coastal dataset here provides observations to test these hypotheses, if the information on the primary deposition of NO$_3^-$ is largely preserved. If it is assumed that the recycled NO$_3^-$ and tropospheric transport of NO$_3^-$ from mid-latitude regions dominate the NO$_3^-$ flux in coastal snow, the contribution from both sources can be estimated by isotopic mass balance:

$$\delta^{15}N(NO_3^-)_{\text{snow}} = f_R \delta^{15}N(NO_3^-)_{\text{R}} + (1 - f_R) \delta^{15}N(NO_3^-)_{\text{T}}$$

with $\delta^{15}N(NO_3^-)_{\text{R}}$ and $\delta^{15}N(NO_3^-)_{\text{T}}$ representing $\delta^{15}$N of recycled NO$_3^-$ and tropospheric NO$_3^-$ from mid-latitude sources, respectively, and $f_R$ of NO$_3^-$ the fraction from recycled NO$_3^-$.

As we assume that transport does not modify the isotopes markedly, we can roughly estimate $f_R$ via:

$$\delta^{15}N(NO_3^-)_{\text{R}} = \text{similar to the predictions from Eq. (1),}$$

$$\delta^{15}N(NO_3^-)_{\text{T}} = -7.0\%$$

from observations, and $\delta^{15}N(NO_3^-)_{\text{T}} = -13.7\%$ from the mean in coastal snow. The calculated $f_R \approx 35\%$, suggesting an important contribution of tropospheric sources NO$_3^-$ in the coastal snow. This estimation agrees fairly well with model simulations, considering both recycling of snow sourced NO$_3^-$ (20–40%) near the coast (Zatko et al., 2016) and tropospheric transport of mid-latitude sourced NO$_3^-$ (Lee et al., 2014). Thus, ice cores near the coast hold great potential to track past atmospheric NO$_3^-$/NO$_2^-$ sources.

Considering the permanent sunlight during summertime in Antarctica, snow NO$_3^-$ is expected to be mainly from the OH production channel (R1 and R5) and global modeling agrees with this expectation (Alexander et al., 2009; Lee et al., 2014). On the coast, if the $\delta^{18}$O(OH) values are close to those of H$_2$O$_{\text{vap}}$, in the atmosphere, i.e., without large fractionation between OH and H$_2$O$_{\text{vap}}$ (case 2A, Table 2), the range of $\delta^{18}$O(OH), $-28$ to $-47\%$, seems to account for the x-intercept of the linear regression between $\delta^{15}$O and $\Delta^{15}$O of NO$_3^-$ ($-24\%$; Fig. 4b). This is consistent with the expectation that the OH channel dominates NO$_3^-$ production in summertime. Similar to the plateau results, if an additional fractionation between OH and H$_2$O$_{\text{vap}}$ (i.e., fractionation between OH and H$_2$O$_{\text{vap}}$) is taken into account (case 2B, Table 2), the $\delta^{18}$O(OH) values ($-77.6$ to $-95.7\%$) are likely too negative to fit the observations.

Based on the $f_R$ calculation above, the tropospheric sources in mid-latitude regions can contribute significantly to snow NO$_3^-$. For the oxygen isotopes, we must consider two cases: a) where NO$_3^-$ is formed in the mid-latitude (i.e., oxidation takes place in the mid-latitude regions), and b) where NO$_3^-$ is oxidized closer to the coast of Antarctica. For case a), considering that most of southern mid-latitude atmospheres are open oceans and the sampling time is summer when dimethyl sulfide (DMS) levels are enhanced (Gabric et al., 2001; del Valle et al., 2009), we would expect the high end-member in Fig. 4b to be explained by NO$_3^-$ formation with O$_3$ as the primary oxidant (e.g. (R7)–(R11)). The DMS and BrO pathways ((R7) and (R9)) produce the highest $\Delta^{15}$O(NO$_3^-$) values, as the only oxidant is O$_3$ (Eq. (2)), and $\Delta^{15}$O(NO$_3^-$) values produced by the two pathways are approximately equal. The OH channel (R5) produces the lowest $\Delta^{15}$O(NO$_3^-$) values as $\Delta^{15}$O(OH) $\approx 0\%$, and N$_2$O$_5$ hydrolysis (R11) produces intermediate values ($\Delta^{15}$O(NO$_3^-$) = $2/3\Delta^{15}$O(NO$_2$) + $1/6\Delta^{15}$O(O$_3$)). An
observed mean $\Delta^{15}O(\text{NO}_3)$ of 32 ± 2‰ in coastal snow corresponds to the contribution of the OH pathway of ≤ 30% (the maximum, ~30%, calculated assuming no contribution of N$_2$O$_5$ hydrolysis, see Case 2 in Table 2), suggesting a predominant role of BrO and/or DMS pathways in NO$_3$ production. If the NO$_3$ is mainly produced via either of these channels, the marine atmospheric NO$_3$ in the mid-low latitudes should feature high $\Delta^{17}O$ values. However, the atmospheric $\Delta^{17}O(\text{NO}_3)$ mean in mid-low latitudes in the Indian Ocean sector is 25.1‰ (21.0–30.4‰; Table S1), much lower than $\Delta^{15}O$ values of NO$_3$ calculated via the DMS or BrO pathways. In addition, the oxidation of NO$_3$ by BrO in coastal East Antarctica has been suggested to be minor compared to the reaction with OH during summertime (Legrand et al., 2009; Kukui et al., 2012; Grilli et al., 2013). Lee et al. (2014) suggest that the degradation of PAN, a reservoir species of NO$_3$, that is highly temperature sensitive, is a major source of NO$_3$ to Antarctica. In this case (case b)), the oxygen isotopic composition of NO$_3$ would be determined by high latitude oxidation. Even with this assumption, it is difficult to match the high observed coastal snow $\Delta^{15}O(\text{NO}_3)$. One possible explanation, for either case (a) or (b), is that $\Delta^{15}O(\text{OH})$ is greatly underestimated. All of the existing $\Delta^{15}O(\text{OH})$ values are from calculations (e.g., Morin et al., 2007; Savarino et al., 2016), with no environmental observations available thus far. A contradiction between expectations and observations of oxygen isotopes of NO$_3$ was also observed at Summit, Greenland, and lack of understanding of isotopic composition of OH was proposed as a possible reason (Fibiger et al., 2016). However, given our results above, a high positive $\Delta^{15}O$ signal of OH seems unlikely due to the exchange of oxygen atoms with water in the atmosphere (Michalski et al., 2011). Another possibility is additional stratospheric input of NO$_3$ and/or an underestimation of $\Delta^{15}O(\text{O}_3)$. If we take $\Delta^{15}O(\text{O}_3) \approx 52$‰ (corresponding to $\Delta^{17}O \approx 35$‰ of bulk O$_3$, close to the result of laboratory experiments by Michalski et al. (2014)), the contribution of the OH pathway can be as much as or greater than 90%, consistent with expectations. Alternatively, if there are no systematic errors in the measurements of tropospheric O$_3$ using the nitrite coated filter technique ($\Delta^{15}O(\text{O}_3) \approx 26$‰) (Vicars et al., 2012; Vicars and Savarino, 2014), a stratospheric source with very high $\Delta^{15}O$ and/or an unknown NO$_3$ chemistry is needed to explain the observed $\Delta^{15}O(\text{NO}_3)$ in the snow. A similar issue (underestimation of $\Delta^{15}O(\text{NO}_3)$) was also found for year round observations at Dome C (Savarino et al., 2016). Better constraint on the $\Delta^{15}O(\text{O}_3)$ in high latitudes is needed to resolve this and allow for interpretation of ice core NO$_3$ records, even at the high-accumulation sites where most of the primary NO$_3$ deposition information is preserved.

In summary, the summer coastal observations of $\delta^{18}N$ (NO$_3$) are best explained by a contribution from secondary NO$_3$ via NO$_3$ sourced from the plateau (~35%). Based upon modeling and our observations, the remaining fraction is likely best explained by tropospheric nitrogen sources (~65%), although a stratospheric source of NO$_3$ cannot be ruled out. The oxygen isotopic composition of NO$_3$, both on the coast and the plateau, cannot be explained if OH exchanged with H$_2$O$_{18}$O in the atmosphere results in a large offset for $\delta^{18}O(\text{OH})$ from $\delta^{18}O$ of H$_2$O$_{18}$O. The formation of NO$_3$ is expected to be dominated by NO$_2$ + OH in summer, however, the isotopic observations require a high initial $\Delta^{17}O(\text{O}_3) (~ 35$‰) for bulk O$_3$ based on the current knowledge of NO$_3$ chemistry and the oxygen isotopes of oxidants.

5. CONCLUSIONS

The purpose of this investigation was to track the differences in summertime NO$_3$ atmospheric chemistry across the EAIS by means of the complete isotopic composition of NO$_3$ in the snow and atmosphere. Concentration and isotopic compositions of NO$_3$ in surface snow are dependent upon distance from the coast. On the plateau, snow NO$_3$ is heavily influenced by post-depositional processing and local oxidation, confirming previous isotopic studies at Dome C and recent modeling studies that suggest significant release and recycling of snow-sourced NO$_3$. The production of secondary NO$_3$ likely occurs both in the condensed phase (i.e., in the snow) and in the gas phase above the snowpack, based upon the isotopic composition of NO$_3$ in the snow and in the atmosphere. During snow NO$_3$ photolysis, some of the photoproducts are transported away, resulting in an enrichment of $\delta^{15}N$(NO$_3$) in the snowpack and subsequently in the atmosphere. A mixing line between the NO$_3$ oxidants O$_3$ and OH/H$_2$O can explain the linear relationship of $\delta^{15}O$ and $\Delta^{17}O$ of NO$_3$ on the plateau, if there is no significant fractionation between OH and H$_2$O$_{18}$O. A higher $\Delta^{17}O(\text{O}_3)$ value than observed predicts a better agreement between measured and expected $\Delta^{17}O$(NO$_3$) values in the plateau snow.

From our observations, it is possible to estimate the contribution of secondary NO$_3$ to coastal concentrations. In coastal snow, ~35% of NO$_3$ is determined to be from snow-sourced NO$_3$, from the interior (due to photolysis), while tropospheric transport from lower latitudes contributes about 65% to snow NO$_3$. The OH oxidation pathway plays an important role in gas phase NO$_3$ production and, as on the plateau, the relationship between the oxygen isotopes of NO$_3$ in coastal snow are best explained by $\delta^{15}O$ (OH) ≈ $\delta^{18}O$(H$_2$O)$_{18}$O. However, the current knowledge on $\Delta^{17}O$ of oxidants and NO$_3$ chemistry, and observations of mid-low latitude atmospheric NO$_3$, cannot account for the high observed snow $\Delta^{17}O$(NO$_3$) values. Again, a high $\Delta^{17}O$(O$_3$) (~35‰) reconciles the discrepancies in observations and expectations, based upon chemical transport modeling, that tropospheric transport also contributes importantly to coastal deposition.

From both the plateau and coastal observations, it appears that $^{18}$O fractionation for the equilibrium between OH and water vapor would be rather small or close to zero across the EAIS. Although the isotopic composition of O$_3$ has been analyzed recently at specific sites in Antarctica (e.g., Dome C; Savarino et al., 2016), further investigation is needed to determine the isotopes of OH and O$_3$ and/or the potential for missing NO$_3$ chemistry. Coastal ice cores hold the best promise for reconstructing and tracking oxidant chemistry in the present and in the past via snow/ice core NO$_3$. 

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APPENDIX A. SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.gca.2018.03.025.

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