The importance of alkyl nitrates and sea ice emissions to atmospheric NOx sources and cycling in the summertime Southern Ocean marine boundary layer

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Abstract. Atmospheric nitrate originates from the oxidation of nitrogen oxides (NOx=NO+NO2) and impacts both tropospheric chemistry and climate. NOx sources, cycling, and NOx to nitrate formation pathways are poorly constrained in remote marine regions, especially the Southern Ocean where pristine conditions serve as a useful proxy for the preindustrial atmosphere. Here, we measured the isotopic composition (δ15N and δ18O) of atmospheric nitrate in coarse-mode (> 1μm) aerosols collected in the summertime marine boundary layer of the Atlantic Southern Ocean from 34.5°S to 70°S, and across the northern edge of the Weddell Sea. The δ15N-NO3 decreased with latitude from -2.7‰ to -42.9‰. The decline in δ15N with latitude is attributed to changes in the dominant NOx sources: lightning at the low latitudes, oceanic alkyl nitrates at the mid latitudes, and photolysis of nitrate in snow at the high latitudes. There is no evidence of any influence from anthropogenic NOx sources or equilibrium isotopic fractionation. Using air mass back trajectories and an isotope mixing model, we calculate that oceanic alkyl nitrate emissions have a δ15N signature of -21.8‰ ± 7.6‰. Given that measurements of alkyl nitrate contributions to remote nitrogen budgets are scarce, this may be a useful tracer for detecting their contribution in other oceanic regions. The δ18O-NO3 was always less than 70‰, indicating that daytime processes involving OH are the dominant NOx oxidation pathway during summer. Unusually low δ18O-NO3 values (less than 31‰) were observed at the western edge of the Weddell Sea. The air mass history of these samples indicates extensive interaction with sea ice covered ocean, which is known to enhance peroxy radical production. The observed low δ18O-NO3 is therefore attributed to increased exchange of NO with peroxy radicals, which have a low δ18O, relative to ozone, which has a high δ18O. This study reveals that the mid- and high-latitude surface ocean may serve as a more important NOx source than previously thought, and that the ice-covered surface ocean impacts the reactive nitrogen budget as well as the oxidative capacity of the marine boundary layer.
1 Introduction

Atmospheric nitrate (NO$_3^-$), hereafter defined as gas phase nitric acid (HNO$_3$) and particulate NO$_3^-$ (p-NO$_3^-$), impacts air quality and climate by contributing to atmospheric particulate matter (Park and Kim, 2005), and influencing the Earth’s radiative heat budget (IPCC, 2013). It also plays a major role in the biogeochemical cycling of reactive nitrogen (Altieri et al., 2021). NO$_3^-$ aerosols originate from the oxidation of nitrogen oxides, collectively referred to as NO$_x$ (NO$_x$ = NO + NO$_2$). NO$_x$ cycling controls the chemical production of tropospheric ozone (O$_3$), a greenhouse gas and pollutant (Finlayson-Pitts and Pitts, 2000), which in turn contributes to the oxidising capacity of the atmosphere (Alexander and Mickley, 2015). Globally, fossil fuel combustion is the primary NO$_x$ source (van der A et al., 2008), which far exceeds natural emissions such as biomass burning (Finlayson-Pitts and Pitts, 2000), soil processes (Davidson and Kingerlee, 1997) and lightning (Schumann and Huntrieser, 2007).

Due to its remoteness, the summertime Southern Ocean (SO) marine boundary layer (MBL) can be representative of preindustrial-like atmospheric conditions (Hamilton et al., 2014). The chemical composition of the Southern Ocean MBL is characterised by low NO$_3^-$ concentrations (Virkkula et al., 2006), representative of a background aerosol environment (i.e., minimal anthropogenic influence). Furthermore, the South Atlantic sector of the Southern Ocean is primarily influenced by natural NO$_x$ sources. During summer, high lightning activity over South America and southern Africa results in NO$_x$ production between approximately 40° S and the intertropical convergence zone (ITCZ) (Nesbitt et al., 2000). As such, lightning is expected to be the dominant NO$_x$ source in the low latitude MBL (Schumann and Huntrieser 2007, van der A et al., 2008). Because of its pristine nature, the summertime Southern Ocean serves as a unique region in which to study atmospheric chemistry and is a useful preindustrial reference point for comparing the magnitude of anthropogenic aerosol impacts on climate (Haywood and Boucher 2000; Hamilton et al., 2014).

The atmospheric chemistry of the polar MBL at the high southern latitudes differs from that of the mid- and low-latitude MBL. During summer, high levels of photochemistry result in the emission of reactive gases from sea ice and snow cover in the Antarctic. As a result, highly elevated concentrations of hydrogen oxide radicals (HO$_x$ = OH + peroxy radicals), halogens, nitrous acid (HONO), and NO$_x$ have been observed during spring and summer in the polar regions (Brough et al., 2019). Furthermore, photochemical production of NO$_x$ within the surface snow of Antarctica and subsequent oxidation in the overlying atmosphere represents a significant NO$_3^-$ source to the Antarctic troposphere (Jones et al., 2000, 2001). NO$_3^-$ photolysis near the surface-air interface of ice crystals produces NO$_2$ (Grannas et al. 2007; Jones et al., 2000), which can be released to the firn (i.e., the intermediate stage of ice between snow and glacial ice) air and escape the snowpack to the overlying atmosphere (Erbland et al., 2013; Shi et al., 2015; Shi et al., 2018). During winter, additional NO$_x$ sources to the Antarctic atmosphere may include long-range transported peroxyacetyl nitrates (PAN) and stratospheric inputs (Savarino et al., 2007; Lee et al., 2014; Walters et al., 2019).

Emission of alkyl nitrates (a group of nitrogen gases collectively referred to as RONO$_2$) from the surface ocean have been recently proposed as a potential NO$_x$ source to the MBL in remote regions (Williams et al., 2014; Fisher et al., 2018).
Observations of elevated MBL alkyl nitrate concentrations suggest that a direct oceanic source exists in both the tropics (Atlas et al., 1993; Blake et al., 2003), and the high-latitude Southern Ocean (Blake et al., 1999; Jones et al., 1999). Although the exact mechanism remains unclear, experimental evidence suggests that oceanic RONO₂ production occurs via photochemical processes involving the aqueous phase reaction of RO₂, derived from the photolysis of oceanic dissolved organic matter and NO, derived from seawater nitrite photolysis (Dahl et al., 2003; Dahl and Saltzman, 2008). Supersaturated RONO₂ conditions in the surface ultimately drive a net flux from the ocean to the atmosphere (Chuck et al., 2002; Dahl et al., 2005). The photolysis of emitted RONO₂ and subsequent OH oxidation in the overlying atmosphere leads to NOₓ formation (Fisher et al., 2018), and/or RONO₂ can form aerosol NO₃⁻ directly by hydrolysis (Rindelaub et al., 2015).

Current global atmospheric models suggest that oceanic RONO₂ represents a significant source of nitrogen (N) to the Southern Ocean MBL, accounting for 20% to 60% of the reactive N pool at the high-latitudes (60° S to 90° S) (Fisher et al., 2018). However, only one shipborne dataset with coincident ocean-atmosphere RONO₂ concentration measurements exists to substantiate this notion (Hughes et al., 2008). Additionally, the NOₓ source from RONO₂ degradation dominates relative to model defined primary NOₓ emission sources over the SO, which include shipping, aircraft and lightning (Fisher et al., 2018). However, the lack of seawater observations available to constrain Southern Ocean RONO₂ distributions hamper the validation of model fluxes. Better understanding of the Southern Ocean RONO₂ source is required to improve simulations and accurately evaluate its contribution to the Southern Ocean MBL NOₓ budget.

1.1 Natural abundance isotopes of atmospheric nitrate

Measurements of the oxygen (O) and N stable isotope ratios of atmospheric NO₃⁻ can be used to constrain NOₓ sources, NO-NO₂ cycling, and NOₓ to NO₃⁻ oxidation pathways, which are critical for understanding the reactive N budget in the atmosphere. This technique has been applied in polluted (Elliot et al., 2007; Zong et al., 2017), open ocean (Hastings et al., 2003; Morin et al., 2009; Kamezaki et al., 2019; Gobel et al., 2013; Altieri et al., 2013), and polar environments (Morin et al., 2009; Walters et al., 2019). Stable isotope ratios are reported as a ratio of the heavy to light isotopologues of a sample relative to the constant isotopic ratio of a reference standard, using delta (δ) notation in units of “per mil” (‰) following Eq. (1):

\[ \delta = \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000 \]  

(1)

where R represents the ratio of ¹⁵N/¹⁴N or ¹⁸O/¹⁶O in the sample and in the reference standard, respectively. The reference for O is Vienna Standard Mean Ocean Water (VSMOW) and for N is atmospheric N₂ (Bøhlke et al., 2003).

When NOₓ is converted to NO₃⁻, the N atom is conserved. As such, it is generally expected that the N stable isotope ratio of atmospheric NO₃⁻ (δ¹⁵N-NO₃⁻) reflects the δ¹⁵N of the source NOₓ, (Kendall et al., 2007) plus any isotopic fractionation associated with NO/NO₂ cycling or NOₓ to NO₃⁻ conversion. For example, the δ¹⁵N of lightning generated NOₓ is close to 0‰ (Hoering, 1957) and is distinct from stratospheric and snowpack NOₓ. Savarino et al., (2007) used the degree of N₂O destruction in the stratosphere and the associated isotopic fractionation to derive an Antarctic stratospheric δ¹⁵N-NOₓ source signature of 19‰ ± 3‰ (Savarino et al., 2007). In contrast, snow emitted NOₓ typically has a very low δ¹⁵N signature due to
the large fractionation ({$^{15}\epsilon$}) of ~ -48‰ (Berhanu et al., 2014, 2015) associated with NO$_3^-$ photolysis in the snowpack, where

{$^{15}\epsilon$} = (KIE -1) x 100‰ and the kinetic isotope effect (KIE) is the ratio of the rates with which the two isotopes of N are converted from reactant to product. If equilibrium isotope fractionation during NO/NO$_2$ cycling occurs, it results in the $^{15}$N enrichment of NO$_2$ such that the NO$_3^-$ formed from this NO$_2$ will have a higher $^{15}$N-NO$_3^-$ than the initial NO$_3$ source (Freyer et al., 1993; Walters et al., 2016). Equilibrium isotope fractionation during the transformation of NO$_3$ to NO$_2^-$ also results in higher $^{15}$N-NO$_2^-$ compared to the original NO$_3$ source (Walters and Michalski, 2015).

In contrast to N, the O stable isotope ratio of atmospheric NO$_3^-$ ($^{18}$O-NO$_3^-$) is reflective of the oxidants involved in NO$_3$ cycling prior to NO$_3^-$ formation, as well as the dominant NO$_3^-$ formation pathway (Hastings et al., 2003; Michalski et al., 2003; Alexander et al., 2020). The O atoms of NO$_3$ are rapidly exchanged with oxidising agents in the atmosphere to produce NO$_3^-$.

Tropospheric NO$_3$ recycles rapidly with O$_3$ following the equations below:

\[ \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \] (R1)

\[ \text{NO}_2 + \text{O}_2 + \text{hv} \rightarrow \text{NO} + \text{O}_3 \] (R2)

The oxidation of NO to NO$_2$ requires an atmospheric oxidant, typically O$_3$ throughout most of the troposphere (R1), while the breakdown of NO$_2$ back to NO is photolytic and requires light (R2). Therefore, under nighttime/dark conditions (R2) shuts down and NO$_3$ is comprised almost entirely of NO$_2$.

The dominant daytime sink for NO$_3$ is the oxidation of NO$_2$ by OH, which produces nitric acid (HNO$_3$) via (R3), where M is a non-reacting molecule.

\[ \text{NO}_2 + \text{OH} + \text{M} \rightarrow \text{HNO}_3 + \text{M} \] (R3)

Under nighttime/dark conditions, the photolytic production of OH cannot occur and NO$_2$ is oxidised by O$_3$ (R4). HNO$_3$ is ultimately formed via the hydrolysis of dinitrogen pentoxide (N$_2$O$_5$), following the reactions (R5) and (R6) below:

\[ \text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 \] (R4)

\[ \text{NO}_3 + \text{NO}_2 + \text{M} \leftrightharpoons \text{N}_2\text{O}_5 \text{(g)} + \text{M} \] (R5)

\[ \text{N}_2\text{O}_5 \text{(g)} + \text{H}_2\text{O} \text{(l)} \rightarrow 2\text{HNO}_3 \text{(aq)} \] (R6)

NO$_3$ can also react with hydrocarbons (HC) (e.g., dimethylsulphide (DMS)) to form HNO$_3$ following reaction (R7) below:

\[ \text{NO}_3 + \text{HC/DMS} \rightarrow \text{HNO}_3 + \text{products} \] (R7)

Lastly, in regions with elevated halogen concentrations, NO$_2$ can be oxidised by reactive halogens, for example bromine oxide (BrO), to form HNO$_3$ following (R8) and (R9) below:

\[ \text{NO}_2 + \text{BrO} \rightarrow \text{BrONO}_2 \] (R8)

\[ \text{BrONO}_2 + \text{H}_2\text{O} + \text{surface} \rightarrow \text{HNO}_3 + \text{HOBr} \] (R9)

Typically, aerosol $^{18}$O-NO$_3^-$ is interpreted as being determined by the dominant NO$_3$ oxidation pathways, (R3) versus (R4) to (R9). If some combination of R4-R9 occurs, then O$_3$ is the main oxidant, whereas during (R3), one of the O atoms originates from OH. The OH radical exchanges with H$_2$O vapor in the troposphere, therefore the $^{18}$O of OH is a function of the $^{18}$O of H$_2$O vapour, which generally ranges from -27.5‰ to 0‰ in the subtropics and over the Southern Ocean (Michalski et al., 2012; Guilpart et al., 2017; Dar et al., 2020), and equilibrium isotope exchange between OH and H$_2$O (Walters and
Michalski, 2016). In contrast the $\delta^{18}$O of tropospheric O$_3$ is much higher, the most recent estimate being 114.8±10.4‰ (Vicars and Savarino, 2014). Therefore, a higher $\delta^{18}$O for atmospheric NO$_3^-$ reflects the increased influence of O$_3$ on NO$_x$ to NO$_3^-$ conversion (R4-R9), and the $\delta^{18}$O-NO$_3^-$ is lower when (R3) is favoured, due to the lack of exchange of O atoms with O$_3$ (Hastings et al., 2003; Fang et al., 2011; Altieri et al., 2013).

Here, we present the concentration and isotopic composition of coarse mode (> 1 μm) atmospheric NO$_3^-$ collected in the MBL of the Southern Ocean between Cape Town, South Africa and coastal Antarctica, as well as across the Weddell Sea gyre, during summer. Using air mass back trajectories, surface ocean nitrite measurements, and the aerosol $\delta^{15}$N- and $\delta^{18}$O-NO$_3^-$; we address 1) the major NO$_x$ sources as well as the main oxidants in NO/NO$_2$ cycling and NO$_x$ to NO$_3^-$ conversion across a large latitudinal transect of the Atlantic Southern Ocean and within the Weddell Sea gyre, and 2) the influence of sea-ice and snowpack emissions on NO$_x$/NO$_3^-$ chemistry in the high-latitude MBL.

2) Methods

2.1) Sample collection

Samples were collected on board the Research Vessel (R/V) SA Agulhas II during one cruise subdivided into three legs. Leg one refers to the voyage south from Cape Town (33.9° S, 18.4° E) to Penguin Bukta (71.4° S, 2.5° W) in early summer (7 to 19 December 2018) as part of the South African National Antarctic Expedition’s annual relief voyage (SANAE 58). Leg two is the Weddell Sea Expedition (WSE) from 4 January to 21 February 2019. All data were recorded in GMT. The WSE refers to the voyage west from Penguin Bukta to the northern edge of the Weddell Sea gyre to Larsen C ice shelf, followed by a detour to King George Island before returning to the Weddell Sea and sailing back to Penguin Bukta. Leg three refers to the SANAE 58 return voyage north from Penguin Bukta to Cape Town in late summer (27 February to 15 March 2019). From here on, legs one, two and three will be referred to as early summer, the Weddell Sea, and late summer, respectively.

Size-segregated atmospheric aerosols were collected on the ninth floor above the bridge (approximately 20 m above sea level), using a high-volume air sampler (HV-AS; Tisch Environmental). Air was pumped at an average flow rate of 0.82 m$^3$ min$^{-1}$ though a five-stage cascade impactor (TE-235; Tisch Environmental), loaded with combusted (400°C for 4 hours) glass fibre filters (TE-230-GF; Tisch Environmental) that have a surface area of approximately 119 cm$^2$. Aerosol nitrate in the MBL is predominantly present in the coarse mode (> 1 μm), therefore only filter stages 1 through 4 were analysed, where the aerodynamical diameter of particles collected are as follows: stage 1 (> 7 μm); stage 2 (3 to 7 μm); stage 3 (1.5 to 3 μm) and stage 4 (1 to 1.5 μm).

A sector collector was used to restrict HV-AS activity to avoid contamination from ship stack emissions (Campbell Scientific Africa). The HV-AS only began operating if the wind was blowing at an angle less than 75° or greater than 180° from the bow of the ship for a minimum of ten minutes at a speed of at least 1 m s$^{-1}$. Filters were removed from the cascade impactor inside a laminar flow cabinet (Air Science), placed in individual zip-sealed plastic bags and stored at -20°C until analysis.
Given that the MBL of the Southern Ocean is characterised by low atmospheric NO$_3^-$ concentrations, an attempt was made to ensure that at least 24 hours of in-sector sampling had passed before filters were removed from the cascade impactor. However, this was not always possible as on occasion the filters had to be removed early to avoid contamination due to unusual ship manoeuvres or stagnant conditions. Therefore, sampling times ranged between 13 and 88 hours across the three legs. The details of each cruise leg can be found in the supplemental information (Table S1).

During the research voyage, a field blank was collected by fitting the cascade impactor with a set of filters and walking the cascade impactor from the laboratory to the HV-AS in the same way that atmospheric samples were deployed. The cascade impactor was placed into the HV-AS and then immediately removed without the HV-AS turning on, after which the filters were removed from the cascade impactor and stored in the same manner as the atmospheric samples. All chemical analyses performed on samples were also performed on the field blank filters to assess possible contamination during filter deployment or sample handling.

### 2.2) Sample analysis

Filter stages 1 to 4 were extracted using ultra-clean deionised water (DI; 18.2 MΩ) under a laminar flow cabinet (Air Science). The extraction ratio was approximately 30 cm$^2$ of filter in 25 mL of DI. Extracts were immediately sonicated for one hour and then stored at 4°C for at least 12 hours. Thereafter, extracts were filtered (0.2 μm) using an acid washed syringe into a clean 30 mL HDPE bottle and stored at -20°C until analysis (Baker et al., 2010).

Aerosol nitrate concentrations ([NO$_3^-$]) were determined using a Thermo Scientific Dionex Aquion Ion Chromatography (IC) system (precision of ± 0.3 μmol L$^{-1}$). The anion IC contained an AG22 RFIC 4 x 50 mm guard column and AG22 RFIC 4 x 250 mm analytical column. A six-point standard curve that encompassed the range of sample concentrations (extract [NO$_3^-$]: 1.3 to 27.7 μmol L$^{-1}$) was run on each day of analysis (Dionex Seven Anion-II Standard) and an R$^2$ value > 0.999 was required for sample analysis to proceed. Final aerosol [NO$_3^-$] were corrected by subtracting the field blanks, which represented 35% of the total [NO$_3^-$] on average. Aerosol samples were also analysed for [NO$_3^-$] using a Lachat QuikChem® flow injection autoanalyzer (precision of ± 0.8 μmol L$^{-1}$). The average [NO$_3^-$] measured using the Lachat QuikChem® flow injection autoanalyzer and the IC system is reported (Table S3).

Nitrogen and oxygen isotopic ratios were measured using the denitrifier method (Sigman et al., 2001 and Casciotti et al., 2002). To determine the $^{15}$N/$^{14}$N and $^{18}$O/$^{16}$O of NO$_3^-$, a natural strain of denitrifying bacteria, *Pseudomonas aureofaciens*, that lack the terminal nitrous oxide (N$_2$O) reductase enzyme were used to convert aqueous NO$_3^-$ quantitatively to N$_2$O gas. The product N$_2$O was analysed by continuous flow isotope ratio mass spectrometry (IRMS) using a Delta V Advantage IRMS interfaced with an online N$_2$O extraction and purification system. Individual analyses were referenced to injections of N$_2$O from a pure gas cylinder and then standardized through comparison to the international reference materials of IAEA-N3 and USGS34 for $\delta^{15}$N-NO$_3^-$, and IAEA-N3, USGS34 and USGS35 for $\delta^{18}$O-NO$_3^-$ (Table S2) (Böhlke et al., 2003). The $^{15}$N/$^{14}$N of samples was corrected for the contribution of $^{17}$O to the peak at mass 45 using an average reported $\Delta^{17}$O value of 26‰ from atmospheric nitrate collected in the Weddell Sea (Morin et al., 2009). The pooled standard deviation for all measurements of
IAEA-N3 and USGS34 for $\delta^{15}$N-NO$_3^-$, and IAEA-N3, USGS34 and USGS35 for $\delta^{18}$O-NO$_3^-$ are reported (Table S2). All samples were measured in triplicate in separate batch analyses. The pooled standard deviation from all replicate analyses of samples was 0.25‰ for $\delta^{15}$N-NO$_3^-$ and 0.64‰ for $\delta^{18}$O-NO$_3^-$. The average $\delta^{15}$N-NO$_3^-$ and $\delta^{18}$O-NO$_3^-$ computed for each filter deployment was weighted by the [NO$_3^-$] observed for each stage and error was propagated according to standard statistical practises (Table S3).

Seawater samples were collected in triplicate every two hours from the ship’s underway system (position at depth approximately 5 m) for the analysis of surface ocean nitrite concentrations ([NO$_2^-$]). [NO$_2^-$] was analysed using the colorimetric method of Grasshof et al. (1983) using a Thermo Scientific Genesys 30 visible spectrophotometer (detection limit of 0.05 μmol L$^{-1}$) (Table S4).

2.3) Air mass back trajectory analysis

To determine the air mass source region for each aerosol sample, air mass back trajectories (AMBTs) were computed for each hour in which the HV-AS was operational for at least 45 minutes of that hour. Given that the ship was moving, a different date, time and starting location was used to compute each AMBT. An altitude of 20 m was chosen to match the height of the HV-AS above sea level and 72-hour AMBTs were computed to account for the lifetime of NO$_3^-$ in the atmosphere. All AMBTs were computed with NOAA’s Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT v 4), using NCEP Global Data Assimilation System (GDAS) output, which can be accessed at https://www.arl.noaa.gov/ready/hysplit4.html (NOAA Air Resources Laboratory, Silver Spring, Maryland) (Stein et al., 2015; Rolph 2016).

3) Results

The coarse mode (> 1 μm in diameter) aerosol [NO$_3^-$] computed by summing the [NO$_3^-$] of stages 1 through 4, ranged from 15.1 to 235.0 ng m$^{-3}$ (Fig. 1a and Table 1). The mass-weighted $\delta^{15}$N of coarse mode aerosol NO$_3^-$ ranged from -43.1‰ to -2.7‰ (Figs. 1b, 2 and Table 1). There were no clear trends in atmospheric [NO$_3^-$] or $\delta^{15}$N-NO$_3^-$ with aerosol size (Table S5).

The highest nitrate concentrations occurred between 34°S and 45°S, and then decreased with increasing latitude. Similarly, higher values characterized $\delta^{15}$N-NO$_3^-$ between 34°S and 45°S (-4.9 ± 1.3‰), and then decreased with increasing latitude (Fig. S2). At the high latitudes (south of 60°S), median values of 26.21 ng m$^{-3}$ and -22.2‰ were observed for nitrate concentration and $\delta^{15}$N, respectively. Coincident mass-weighted $\delta^{18}$O-NO$_3^-$ values ranged from 16.5‰ to 70‰ (Figs. 1c, 3 and Table 1). No latitudinal trend in $\delta^{18}$O-NO$_3^-$ was apparent, although distinctly low $\delta^{18}$O-NO$_3^-$ values were observed in the Weddell Sea, as discussed in section 4.3 below. The difference between $\delta^{18}$O-NO$_3^-$ observed in the Weddell Sea (during January to February) and $\delta^{18}$O-NO$_3^-$ observed at corresponding latitudes (56°S to 70°S) during the early and late summer transects is statistically significant (p-value = 0.009). The early and late summer cruise transects were similar spatially in that both took place along the same hydrographic line (i.e., the Good Hope line), apart from the deviation to South Georgia during late summer (Fig. 2a & b). Even though the early and late summer cruise transects occurred in December and March,
respectively, there is no statistically significant difference in $[\text{NO}_3^-]$ (p-value = 0.43), $\delta^{15}\text{N-NO}_3^-$ (p-value = 0.53) or $\delta^{18}\text{O-NO}_3^-$ (p-value = 0.67) between them. Therefore, the early and late summer legs are discussed together and collectively referred to as the latitudinal transect.

Table 1: The average (Avg), standard deviation (SD) and range of total coarse-mode (> 1μm) atmospheric nitrate concentration ($[\text{NO}_3^-]$; ng m$^{-3}$) and the mass weighted average N and O isotopic composition of coarse mode nitrate ($\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$; ‰) are shown. Cruise legs are denoted as follows: early summer (ES), Weddell Sea (WS) and late summer (LS).

| Leg | $[\text{NO}_3^-]$ (ng m$^{-3}$) | $\delta^{15}\text{N-NO}_3^-$ (%o vs. N$_2$) | $\delta^{18}\text{O-NO}_3^-$ (%o vs. VSMOW) |
|-----|-----------------------------|---------------------------------|---------------------------------|
|     | Avg (SD) | Range | Avg (SD) | Range | Avg (SD) | Range |
| ES  | 88.1 (70.2) | 20.0 to 235.0 | -19.5 (16.4) | -42.9 to -2.7 | 47.1 (17.8) | 16.5 to 70.0 |
| WS  | 29.4 (12.1) | 15.1 to 59.5 | -22.7 (7.2) | -38.1 to -11.6 | 38.4 (12.9) | 18.8 to 60.3 |
| LS  | 59.7 (59.4) | 16.9 to 177.4 | -15.0 (8.1) | -25.6 to -4.6 | 50.3 (6.3) | 43.1 to 58.9 |
Figure 1. (a) The average (± 1 SD) coarse mode (> 1 μm) nitrate concentration [NO₃⁻] (ng m⁻³), and the weighted average (± 1 SD) δ¹⁵N (b) and δ¹⁸O (c) of atmospheric nitrate (δ¹⁵N-NO₃⁻ (‰ vs. N₂) and δ¹⁸O-NO₃⁻ (‰ vs. VSMOW), respectively), as a function of latitude (°S). Early and late summer latitudinal transects are denoted by the red triangles and green squares, respectively. Weddell Sea samples are denoted by blue circles. Where error bars (± 1 SD) are not visible, the standard deviation is smaller than the size of the marker.
Figure 2. 72-hour AMBTs (grey lines) computed for each hour of the voyage when the HV-AS was operational for more than 45 minutes of the hour during early summer (a), late summer (b), and in the Weddell Sea (c). The colour bar represents the weighted average δ¹⁵N of coarse mode (> 1 µm) atmospheric nitrate (δ¹⁵N-NO₃⁻). Individual AMBTs for each aerosol sample from the Weddell Sea are shown in Fig. S1. The white represents the location of the sea ice determined using satellite derived sea-ice concentration data, obtained from passive microwave sensors AMSR2 (Advanced Microwave Scanning Radiometer 2, Spreen et al., 2008).
Figure 3. 72-hour AMBTs (grey lines) computed for each hour of the voyage when the HV-AS was operational for more than 45 minutes of the hour during early summer (a), late summer (b), and in the Weddell Sea (c). The colour bar represents the weighted average δ¹⁸O of coarse mode (> 1 µm) atmospheric nitrate (δ¹⁸O-NO₃⁻). Individual AMBTs for each aerosol sample from the Weddell Sea are shown in Fig. S1 The white represents the location of the sea ice (see Fig. 2 caption).

4) Discussion

Our observations reveal a latitudinal gradient in atmospheric NO₃⁻ concentration and δ¹⁵N-NO₃⁻, which we hypothesize may be attributed to the varying contribution of the dominant NOₓ sources present between Cape Town and coastal Antarctica. In contrast, δ¹⁸O-NO₃⁻ depicts no latitudinal trend; however, relatively low δ¹⁸O-NO₃⁻ values are observed in the Weddell Sea,
which we hypothesize may be attributed to the influence of sea ice emissions on NO\textsubscript{x} cycling. Below, we first discuss the extent to which anthropogenic NO\textsubscript{x} sources may influence the observed atmospheric NO\textsubscript{3\textsuperscript{-}} concentrations and δ\textsuperscript{15}N signatures. Then we discuss the dominant NO\textsubscript{x} sources to low, mid and high latitude Southern Ocean MBL NO\textsubscript{3\textsuperscript{-}}, determined in part from 72-hour AMBTs, as well as the role of various oxidants in NO/NO\textsubscript{2} cycling and NO\textsubscript{2} oxidation.

### 4.1) Minimal influence of anthropogenic NO\textsubscript{x} sources

Aerosol NO\textsubscript{3\textsuperscript{-}} concentrations were low (< 100 ng m\textsuperscript{-3}; Fig. 1a) for most air masses sampled along the latitudinal transect and in the Weddell Sea, consistent with the expectation of minimal influence from anthropogenic NO\textsubscript{x} sources. For comparison, [NO\textsubscript{3\textsuperscript{-}}] in a polluted urban airshed over South Africa can be > 500 ng m\textsuperscript{-3} (Collett et al., 2010). Interestingly, NO\textsubscript{3\textsuperscript{-}} concentrations were higher (± 200 ng m\textsuperscript{-3}; Fig. 1a) in samples collected near the South African coast at the beginning of the latitudinal transect (i.e., above 43° S). However, 72-hour AMBTs computed for all latitudinal transect samples indicate that sampled air masses originated from over the South Atlantic sector of the Southern Ocean (Fig. 2a and 2b), with no continental influence and limited opportunity for direct anthropogenic NO\textsubscript{x} emissions to contribute to aerosol NO\textsubscript{3\textsuperscript{-}}, assuming NO\textsubscript{3\textsuperscript{-}} has a lifetime of 72 hours (Alexander et al., 2020). Furthermore, contamination from ship stack emissions was avoided by using a sector collector to restrict HV-AS activity to certain wind directions (Sect. 2.1). As such, the higher atmospheric NO\textsubscript{3\textsuperscript{-}} concentrations observed near South Africa are best explained by greater lightning NO\textsubscript{x} production, which generally occurs between 40° S and the ITCZ during summer (Nesbitt et al., 2000; van der A et al., 2008).

### 4.2) Interpretation of natural NO\textsubscript{x} sources using the N isotopic composition of atmospheric NO\textsubscript{3\textsuperscript{-}}

Aerosol δ\textsuperscript{15}N-NO\textsubscript{3\textsuperscript{-}} ranged from -2.7‰ for low-latitude air masses to -42.9‰ for high-latitude air masses (including those sampled in the Weddell Sea; Fig. 1b). As discussed in section 1.1, the δ\textsuperscript{15}N-NO\textsubscript{3\textsuperscript{-}} reflects the δ\textsuperscript{15}N of the source NO\textsubscript{x} plus any isotopic fractionation imparted from NO/NO\textsubscript{2} cycling or NO\textsubscript{x} to NO\textsubscript{3\textsuperscript{-}} conversion. Similar to previous studies, we surmise that NO\textsubscript{x} equilibrium fractionation is unlikely to be relevant in our system, as NO\textsubscript{x} concentrations are significantly lower than O\textsubscript{3} concentrations (Elliott et al., 2007; Morin et al., 2009; Walters et al., 2016; Park et al., 2018). Typical O\textsubscript{3} concentrations observed at coastal sites in Antarctica are on the order of 20 ppbv (parts per billion by volume) (Nadzir et al., 2018), whereas the sum of NO and NO\textsubscript{2} rarely exceeds 0.04 ppbv (Jones et al., 2000; Weller et al., 2002; Bauguitte et al., 2012). Under these conditions NO\textsubscript{x} isotopic exchange occurs at a much slower rate than (R1) and (R2), such that little to no equilibrium isotope fractionation is expressed and the δ\textsuperscript{15}N of the NO\textsubscript{3\textsuperscript{-}} should reflect the δ\textsuperscript{15}N of the NO\textsubscript{x} source (Walters et al., 2016). Additionally, equilibrium isotope effects are temperature dependent (increasing with decreasing temperature) and here ambient temperatures decline with increasing latitude. Therefore, if equilibrium isotope fractionation were occurring during NO-NO\textsubscript{2} cycling and/or NO\textsubscript{x} to NO\textsubscript{3\textsuperscript{-}} conversion, one would expect δ\textsuperscript{15}N-NO\textsubscript{3\textsuperscript{-}} to increase with latitude, as both fractionation processes produce NO\textsubscript{3\textsuperscript{-}} with a δ\textsuperscript{15}N signature higher than the source NO\textsubscript{x}. However, the opposite trend is observed here whereby δ\textsuperscript{15}N-
NO$_3^-$ decreases with increasing latitude (Fig. 1b). Therefore, we discount the hypothesis that equilibrium isotope effects can explain the latitudinal gradient in $\delta^{15}$N-NO$_3^-$. NO$_3^-$ in the Antarctic troposphere may also derive from stratospheric denitrification, whereby HNO$_3$ is injected into the troposphere from the stratosphere via the subsidence and penetration of polar stratospheric clouds (PSC). However, this phenomenon typically occurs in winter when the tropospheric barrier is weak and the lower stratosphere is cold enough for PSC formation (Savarino et al., 2007; Walters et al., 2019). Furthermore, $\delta^{15}$N-NO$_3^-$ originating from stratospheric inputs is estimated to be 19$\%$ ± 3$\%$ (Savarino et al., 2007), a value substantially greater than the atmospheric $\delta^{15}$N-NO$_3^-$ observed here for high-latitude air masses; thus, we discount a direct influence from stratospheric NO$_3^-$. We propose that the observed variation in atmospheric $\delta^{15}$N-NO$_3^-$ across the Southern Ocean is best explained by the changing contribution of three dominant NO$_x$ sources: lightning, surface ocean alkyl nitrate emissions, and photochemical production on snow and ice, determined using AMBT analyses and typical NO$_x$ source signatures where possible, as discussed below.

4.2.1) High-latitudes: Photochemical NO$_x$ source

Aerosol $\delta^{15}$N-NO$_3^-$ was relatively low in air masses from the southern high-latitudes, including in the Weddell Sea (average of -24.3$\%$; Figs. 1b & 2). The latitudinal gradient in lightning NO$_x$ production suggests that lightning NO$_x$ is greatly reduced at high latitudes (Nesbitt et al., 2000). Similar to other studies in the region (Savarino et al., 2007; Morin et al., 2009), we suggest that photochemical NO$_x$ production on snow or ice accounts for the low aerosol $\delta^{15}$N-NO$_3^-$ in high-latitude air masses, where high-latitude air mass samples are defined as those exposed to the Antarctic continent or the surrounding sea ice (with sea ice concentration being at least 50$\%$). Antarctic estimates for isotopic fractionation associated with snow NO$_3^-$ photolysis during summer range from -47.9$\%$ to -55.8$\%$ for laboratory and field experiments, respectively (Berhanu et al., 2014, 2015), resulting in the emission of low $\delta^{15}$N NO$_x$ to the overlying atmosphere (Savarino et al., 2007; Morin et al., 2009; Shi et al., 2018; Walters et al., 2019). Therefore, NO$_3^-$ photolysis explains the very low $\delta^{15}$N-NO$_3^-$ observed in high-latitude air masses in early and late summer that crossed snow-covered continental ice or sea ice before being sampled (Figs. 2a & b). During early summer, air masses spent significantly more time over the snow-covered continent compared to late summer and the sea ice extent was greater in early summer compared to late summer (Figs. 2a & b). Combined, these dynamics resulted in a much lower $\delta^{15}$N-NO$_3^-$ for high-latitude air masses during early summer compared to late summer (minimum value of -42.9$\%$ vs -25.6$\%$). Similarly low MBL $\delta^{15}$N-NO$_3^-$ values (< -30$\%$) were recently observed for the southern high latitudes of the Indian ocean (Shi et al., 2021). Our data are also consistent with year-round studies of atmospheric NO$_3^-$ at coastal Antarctica (Savarino et al., 2007) and the South Pole (Walters et al., 2019), where $\delta^{15}$N-NO$_3^-$ was reported to range from -46.9$\%$ to 10.8$\%$ and from -60.8$\%$ to 10.5$\%$, respectively. Both studies observed a seasonal cycle in $\delta^{15}$N-NO$_3^-$ whereby the lowest values occurred during sunlit periods (i.e., summer) due to snowpack NO$_x$ emissions and the highest values occurred during dark periods (i.e., winter) due to stratospheric inputs (Savarino et al., 2007; Walters et al., 2019).


4.2.2) Low- to Mid-latitudes: Oceanic NO\textsubscript{x} source

At the northern extent of our transects, the low-latitude aerosol samples, defined as those with air mass back trajectories originating from anywhere north of 43° S in early summer and 41° S in late summer (Fig. 2), had the highest average \(\delta^{15}\text{N-NO}_3^-\) signature (-4.9 ± 1.3‰; \(n = 5\)). These values can be attributed to lightning-generated NO\textsubscript{x}, which has a \(\delta^{15}\text{N}\) signature close to 0‰ (Hoering 1957). Lightning activity at the low latitudes is also consistent with the higher atmospheric [NO\textsubscript{3}^-] observed (Fig. 1a) and is further supported by co-occurring high [NO\textsubscript{3}^-] and relatively high \(\delta^{15}\text{N-NO}_3^-\) (Fig. S2). An average atmospheric \(\delta^{15}\text{N-NO}_3^-\) signature of -4‰ was previously reported for the low latitude Atlantic Ocean, between 45° S and 45° N, and similarly attributed to a combination of natural NO\textsubscript{x} sources including lightning (Morin et al., 2009).

Aerosol samples across the mid-latitudes had an average \(\delta^{15}\text{N-NO}_3^-\) of -13.2‰ (Figs. 1b & 2). Mid-latitude air masses are defined as those originating from anywhere south of 43° S in early summer and south of 41° S in late summer that made no contact with Antarctica or any surrounding sea ice (Fig. 2a & b), therefore these samples were unlikely to be influenced by snow emitted NO\textsubscript{x} with its light isotopic signature. The beginning of the mid-latitude zone (i.e., 43°S and 41°S in early and late summer, respectively) was defined by the presence of non-zero sea surface nitrite concentrations in early and late summer (Fig. 4). However, the observed aerosol \(\delta^{15}\text{N-NO}_3^-\) was too low (-14.5‰ to -11.2‰) to be explained solely by lightning generated NO\textsubscript{x}. In the absence of any signature of anthropogenic NO\textsubscript{x} emissions (Sect. 4.1), we argue that the dominant NO\textsubscript{x} source for the mid-latitude samples originates from seawater.

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[Diagram showing air mass back trajectories for Early Summer and Late Summer with color bars indicating [NO\textsubscript{3}^-] and \(\delta^{15}\text{N-NO}_3^-\) values.]
Figure 4. 72-hour AMBTs computed for each hour of the voyage during early (a) and late (b) summer, when the HV-AS was operational for more than 45 minutes of the hour. AMBTs are colour coded by the weighted average δ¹⁵N of atmospheric nitrate (δ¹⁵N-NO₃⁻), represented by the horizontal colour bar. Over-layered are the surface ocean nitrite concentrations (circles; [NO₂⁻]; μmol L⁻¹), measured along each transect and represented by the vertical colour bar.

As mentioned in section 1, the most likely mechanism for an oceanic NOₓ source is via the photolysis of surface ocean derived RONO₂ in the MBL. NO derived from seawater nitrite is thought to limit RONO₂ production (Dahl and Saltzman 2008; Dahl et al., 2012), such that non-zero nitrite concentrations are required for RONO₂ production to occur. Here, surface ocean nitrite concentrations were relatively high, in particular from ~ 41° S to 50° S (Fig. 4). Furthermore, the latitudinal extent of mid-latitude air masses with low δ¹⁵N-NO₃⁻ signatures corresponds well with the same latitudinal extent in which non-zero surface ocean nitrite concentrations occurred (Fig. 4). As such, we suggest that in this region oceanic RONO₂ emission is the main source to the Southern Ocean MBL, ultimately resulting in the low δ¹⁵N-NO₃⁻ values observed for mid-latitude air masses.

No estimates exist for the δ¹⁵N of oceanic RONO₂, however RONO₂ photolysis may yield isotopically light NOₓ given that NO₃⁻ photolysis produces low δ¹⁵N products (e.g., Frey et al., 2009). Therefore, once oxidised in the overlying atmosphere, NOₓ derived from oceanic RONO₂ photolysis may form atmospheric NO₃⁻ with a low δ¹⁵N signature. Aerosol δ¹⁵N-NO₃⁻ values have been observed to range from -14.1‰ to -7.3‰ in the eastern equatorial Pacific (Kamezaki et al., 2019) and from -6‰ to ~0‰ (average = -3.4‰) in the western equatorial Pacific (Shi et al., 2021). Observed δ¹⁵N-NO₃⁻ is higher in the western compared the eastern equatorial Pacific, which could be attributed to the proximity of the western equatorial Pacific to continental/anthropogenic NOₓ sources, resulting in NO₃⁻ having a higher δ¹⁵N signature. The low average δ¹⁵N-NO₃⁻ observed for the mid-latitude air masses of the Southern Ocean MBL sampled in the present study (-14.5‰ to -11.2‰), are remarkably similar to those observed in the eastern equatorial Pacific (Kamazaki et al., 2019). Kamezaki et al., (2019) also concluded that such low δ¹⁵N-NO₃⁻ values cannot be explained solely by lightning NOₓ and given the lack of considerable influence from any continental NOₓ sources, they invoked the contribution of oceanic N emissions in the form of ammonia (NH₃) and/or RONO₂. However, NH₃ flux data for the summertime Atlantic Southern Ocean derived from situ ocean/atmosphere observations suggest that the ocean in this region is a net sink of NH₃ (Altieri et al., 2021).

The latitudinal extent of our sampling campaign enabled us to estimate a range of likely values for the N isotopic composition of NO₃⁻ derived from oceanic RONO₂. We split the latitudinal transect into three regions, each characterised by the dominance of a different natural source of NO₃⁻, i.e., lightning NOₓ at the low-latitudes (Fig. 5 light orange), oceanic RONO₂ emissions at the mid-latitudes (Fig. 5 dark orange) and snowpack emissions at the high-latitudes (Fig. 5 red).
Assuming that the dominant natural source of NO$_3^-$ is the only source relevant in each latitudinal zone, we estimate the contribution of each source to total NO$_3^-$ formation by ascertaining the amount of time air masses spent in each zone. We further assume that atmospheric $\delta^{15}$N-NO$_3^-$ reflects at most a combination of two sources based on the AMBTs of each sample, either lightning NO$_x$ and oceanic RONO$_2$ emissions near South Africa, or oceanic RONO$_2$ emissions and snowpack NO$_x$ emissions near Antarctic (Fig. 5 and Table S6). Using a two-end member mixing model the $\delta^{15}$N signature of the source NO$_3^-$ derived from mid-latitude Southern Ocean RONO$_2$ emissions was calculated for all samples where air masses from the mid-latitude region contributed at least 10% (Table S6). This 10% threshold was chosen as the isotopic endmember of oceanic RONO$_2$ is harder to determine with confidence when its contribution to total NO$_3^-$ is less than 10%. As an example, the AMBTs for sample ES 4 spent 3% of the time in the low-latitude zone and 97% in the mid-latitude zone. Using the measured $\delta^{15}$N-NO$_3^-$ for ES 4 of -14.5‰ and assuming lightning NO$_x$ has a $\delta^{15}$N signature of 0‰, we calculate the $\delta^{15}$N signature of the RONO$_2$-derived NO$_3^-$ to be -14.9‰. It is important to note that using this approach to estimate the $\delta^{15}$N-NO$_3^-$ from oceanic RONO$_2$ emissions relies heavily on AMBTs generated using HYSPLIT. While HYSPLIT is a frequently used tool for assessing air mass origin in the Southern Hemisphere and over Antarctica (Morin et al., 2008; Walters et al., 2019; Shi et al., 2021), it is important to note that a spatial uncertainty of 15% to 30% of the trajectory path distance can be expected (Scarchilli et al., 2011). AMBTs also become increasingly uncertain the further back in time they are used (Sinclair et al., 2013). Some of this uncertainty is alleviated by the fact that the AMBTs generated here are relatively short (< 5 days). Additionally, the spatial scale of the low-, mid- and high-latitude zones is large, such that some variation in sample AMBTs will not significantly alter the expected dominant NO$_3^-$ source.
Using this approach for each filter deployment along the latitudinal transect, an average $\delta^{15}$N-NO$_3^-$ from oceanic RONO$_2$ emissions of $-21.8 \pm 7.6\%_o$ was estimated. Furthermore, the contribution of RONO$_2$ emissions can explain the lowering of $\delta^{15}$N from 0\% for the low-latitude air mass samples. For example, the highest $\delta^{15}$N observed in the study was $-2.7\%_o$, and this sample has a $< 5\%$ contribution from the mid-latitude zone. The other two low-latitude samples have 30\% to 40\% contribution from the mid-latitude zone and their $\delta^{15}$N is lower (Table S3), as expected due to the influence of RONO$_2$ emissions.

The influence of low $\delta^{15}$N-NO$_3^-$ from RONO$_2$ emissions is not limited to the Southern Ocean, and this estimate of the N isotopic composition for the RONO$_2$ derived NO$_3^-$ source may be useful to constrain the contribution of RONO$_2$ emissions to NO$_3^-$ formation in other ocean regions with elevated surface ocean nitrite concentrations, such as the tropical Pacific.

4.3) The O isotopes of atmospheric nitrate

The corresponding $\delta^{18}$O values allow us to determine the pathways of NO$_3^-$ formation from NO$_x$. However, an assumption must first be made regarding the oxidation of NO to NO$_2$. While the dominant oxidant of NO to NO$_2$ is O$_3$ (R1) in most of the troposphere, over the open ocean there can be a significant contribution via the reaction of NO with peroxy radicals (HO$_2$ and its organic homologues RO$_2$) (Alexander et al., 2020). Peroxy radicals compete with O$_3$ to convert NO into NO$_2$ via R10:

$$\text{NO} + \text{HO}_2 \ (\text{or RO}_2) \rightarrow \text{NO}_2 + \text{OH} \ (\text{or RO}) \quad \text{(R10)}$$

The $\delta^{18}$O of peroxy radicals is much lower than that of O$_3$ because the O atoms derive from atmospheric O$_2$, which has a well-defined $\delta^{18}$O of 23.9\% (Kroopnick and Craig, 1972). The $\delta^{18}$O-NO$_2$ can then be calculated using Eq. (2),

$$\delta^{18}$O-NO$_2 = (\delta^{18}$O-O$_2)(1-f) + (\delta^{18}$O-O$_3*)(f) \quad \text{(2)}$$

where f is the fraction of NO$_2$ formed from R1, (1-f) is the fraction formed from R10, and the terminal $\delta^{18}$O-O$_3$ value ($\delta^{18}$O-O$_3*$) is 130.4 ± 12.9\% (Vicars and Savarino, 2014).

The $\delta^{18}$O-NO$_3^-$ is then determined using Eq. (3) in which two thirds of the O atoms in NO$_3^-$ come from NO$_2$ and one third comes from OH i.e., R3, or using Eq. (4) in which three sixths of the O atoms in NO$_3^-$ come from O$_3$, two sixths come from NO$_2$ and one sixth comes from H$_2$O i.e., R4-R6 (Hastings et al., 2003; Alexander et al., 2020).

$$\delta^{18}$O-NO$_3^-$ (R3) = (2/3)(\delta^{18}$O-NO$_2^-$) + (1/3)(\delta^{18}$O-OH) \quad \text{(3)}$$

$$\delta^{18}$O-NO$_3^-$ (R4-R6) = (1/2)(\delta^{18}$O-O$_3^*$) + (1/3)(\delta^{18}$O-NO$_2^-$_) + (1/6)(\delta^{18}$O-H$_2$O) \quad \text{(4)}$$

We assume that 15\% of NO to NO$_2$ conversion occurs via HO$_2$/RO$_2$ oxidation and 85\% by O$_3$ oxidation as is suggested by global models (Alexander et al., 2020), and use the minimum and maximum $\delta^{18}$O-H$_2$O range of -27.5\% to 0\%, the temperature-dependent equilibrium isotope exchange between OH and H$_2$O (Walters and Michalski, 2016), and the resulting minimum and maximum estimates for $\delta^{18}$O-OH of -67.4\% to -41.0\%. Using these assumptions and Eq. (3) and (4), the expected $\delta^{18}$O-NO$_3^-$ for the daytime OH oxidation pathway (R3) is 46.5\% to 71.4\%, and for the dark reactions (R4-R6) is 88.7\% to 113.5\%. The observed $\delta^{18}$O-NO$_3^-$ values were all less than 70\% (Figs. 1c and 3), suggesting that NO$_x$ oxidation by OH (R3) was indeed the dominant pathway for atmospheric NO$_3^-$ formation during summer. The low $\delta^{18}$O-NO$_3^-$ values observed suggest a minimal influence of O$_3$ in the oxidation chemistry, ruling out both the halogen (R8 to R9) and DMS (R7) related NO$_3^-$ formation pathways in addition to N$_2$O$_5$ hydrolysis (R4-6). This is consistent with previous year-round studies of
atmospheric NO$_3^-$ at coastal Antarctica (Savarino et al., 2007) and the South Pole (Walters et al., 2019) where $\delta^{18}$O-NO$_3^-$ was at a minimum in summer (59.6‰ and 47.0‰, respectively). Both studies confirm the importance of HO$_x$ oxidation chemistry in summer when solar radiation enhances the production of these oxidants, followed by a switch to O$_3$ dominated oxidation chemistry in winter (Savarino et al., 2007; Ishino et al., 2017; Walters et al., 2019).

Interestingly, most aerosol samples have a $\delta^{18}$O-NO$_3^-$ less than 46.5‰ (n=19), the lower limit estimated above for the OH pathway. This suggests that there is more NO to NO$_2$ conversion via HO$_2$/RO$_2$ oxidation occurring than the global average. A maximum HO$_2$/RO$_2$ contribution to NO oxidation of $\sim$63% is required to explain the lowest $\delta^{18}$O-NO$_3^-$ value, which was observed over the mid-latitudes during early summer. Increased RO$_2$ production over the mid-latitudes could derive from RONO$_2$ photolysis in the MBL, which we hypothesise is happening in this region based on the $\delta^{15}$N-NO$_3^-$ (Sect. 4.2.2). Although the lowest $\delta^{18}$O observation occurred in the mid-latitudes, the majority of low $\delta^{18}$O-NO$_3^-$ values were observed in the Weddell Sea, away from the region of maximum RONO$_2$ emissions. Approximately half of the Weddell Sea samples have a $\delta^{18}$O-NO$_3^-$ < 31‰, which would require a HO$_2$/RO$_2$ contribution to NO oxidation upwards of 40% (more than double the contribution estimated by global models (Alexander et al., 2020)). These $\delta^{18}$O-NO$_3^-$ observations are unusually low compared to previous observations for the same region in spring (Morin et al., 2009). We hypothesize that the large contribution of HO$_2$/RO$_2$ to NO/NO$_2$ oxidation (i.e., a decrease in f in Eq. (2)) resulting in these low $\delta^{18}$O-NO$_3^-$ values is due to the influence of sea ice emissions. The 72-hour AMBTs for these low $\delta^{18}$O-NO$_3^-$ Weddell Sea samples indicate that all the air masses either originated from, or spent a significant amount of time recirculating, over the sea ice covered region of the western Weddell Sea (Fig. 6b). By contrast, aerosol samples from the Weddell Sea with $\delta^{18}$O-NO$_3^-$ values greater than 31‰ have air masses that experienced significantly more oceanic influence (Fig. 6a). There is evidence that sea ice can lead to enhanced peroxy radical production (Brough et al., 2019). In that work, increased HO$_2$ + RO$_2$ concentrations were observed during spring at a coastal Antarctic site when air masses arrived from across a sea ice covered zone. This was attributed to the oxidation of hydrocarbons by chlorine atoms, which leads to increased RO$_2$ concentrations via R11 and R12:

\[
\begin{align*}
\text{RH} + \text{Cl} & \rightarrow \text{R} + \text{HCl} \\
\text{R} + \text{O}_2 & \rightarrow \text{RO}_2
\end{align*}
\]
Figure 6. 72-hour AMBTs (light blue lines) computed for each hour of the voyage in the Weddell Sea, when the HV-AS was operational for more than 45 minutes of the hour. The vertical colour bar represents the weighted average $\delta^{18}$O of atmospheric nitrate ($\delta^{18}$O-NO$_3^-$), where $\delta^{18}$O-NO$_3^-$ was $> 3.1\%o$ (a) and $< 3.1\%o$ (b). The white represents the location of the sea ice (see Fig. 2 caption).

Cl atoms are much more reactive with hydrocarbons than OH (Monks, 2005) and can enhance hydrocarbon oxidation even when present at low concentrations. Brough et al. (2019) suggest that air masses that traversed the sea ice zone contained photolabile chlorine compounds that built up at night until photolysis occurred during the next day (Brough et al., 2019). Although our study was conducted in summer (the season of minimum sea ice extent), the sampling locations were uniquely
positioned at the western edge of the Weddell Sea gyre where significant sea ice remained (Fig. 6). Therefore, we suggest that chlorine chemistry over the sea ice increased RO₂ concentrations at the time of our sampling, allowing the NO + RO₂ pathway to play a more significant role in the Weddell Sea and resulting in low δ¹⁸O-NO₃⁻ values. We note that the only other estimates of δ¹⁸O-NO₃⁻ from the Weddell Sea ranged from ~ 50‰ to 110‰ during springtime, and these samples were associated with air masses that spent almost no time over the sea ice and therefore had limited potential for this peroxy radical chemistry to drive down the δ¹⁸O-NO₃⁻ to the low values we observe (Morin et al., 2009).

5) Conclusions

Our observations across a large latitudinal gradient of the summertime Southern Ocean MBL suggest it is dominated by natural NOₓ sources with distinct isotopic signatures. Aerosol NO₃⁻ was predominantly formed from lightning generated NOₓ with a δ¹⁵N of ~ 0‰ at the lower latitudes, whereas snowpack NOₓ emissions with a δ¹⁵N ~ -48‰ dominated the MBL inventory at higher latitudes. Over the mid-latitudes, NO₃⁻ derived primarily from oceanic RONO₂ emissions, with an estimated δ¹⁵N signature of ~ -22.0‰. Additional research is needed to improve our mechanistic and isotopic understanding of surface ocean RONO₂ formation, flux, and conversion to aerosol nitrate in order to constrain the contribution of oceanic RONO₂ emissions to NO₃⁻ formation in other ocean regions where this source has been invoked, such as the tropical Pacific (Kamezaki et al., 2019). The isotopic composition of NO₃⁻ observed here can further inform interpretations of Antarctic ice core NO₃⁻ isotope records to understand aerosol climate forcing and controls on the atmospheric oxidation budget over millennia (Freyer et al., 1996; Jiang et al., 2019) – the interpretation of which relies on knowledge of the NOₓ isotopic source signatures in the polar atmosphere.

The δ¹⁸O-NO₃⁻ values were consistently lower than 70‰, which confirms NOₓ oxidation by OH (R3) to be the dominant pathway for atmospheric NO₃⁻ formation during summer. However, unusually low δ¹⁸O-NO₃⁻ values observed at the mid-latitudes and in the Weddell Sea indicate the increased importance of peroxy radicals (and decreased importance of O₃) in NO oxidation to NO₂ in the MBL. At the mid-latitudes peroxy radicals (RO₂) may derive from RONO₂ photolysis, while in the Weddell Sea, sea ice appears to play an important role in the formation of this oxidant via its influence on chlorine chemistry (Brough et al., 2019). This implies that snow covered sea ice is not only a source of NOₓ but also other species that have the potential to change the composition of the atmosphere above the ice and impact NOₓ oxidation chemistry. These results also highlight the utility of δ¹⁸O-NO₃⁻ to identify the major oxidants in NO oxidation, as well as NOₓ to NO₃⁻ conversion. In particular, δ¹⁸O-NO₃⁻ can serve as a useful tool for testing our understanding of the relative importance of HO₂/RO₂ in NO/NO₂ cycling, which can be difficult to constrain in some environments.

Our study challenges the traditional paradigm that considers the ocean as a passive recipient of N deposition, as the Southern Ocean mid-latitude NO₃⁻ source may derive almost entirely from oceanic RONO₂ emissions. In the tropical equatorial Pacific atmosphere, Kamezaki et al. (2019) also suggested evidence for a low δ¹⁵N-NO₃⁻ source derived from the ocean. In the subtropical Atlantic Ocean MBL, Altieri et al. (2016) found that biogeochemical cycling in the surface ocean can directly
influence the lower atmosphere serving as a source of aerosol organic N and ammonium. This study suggests that the surface waters of the Southern Ocean may also serve as a NO$_x$ source, ultimately resulting in NO$_3^-$ aerosol formation. As such, the surface ocean may play a bigger role in atmospheric oxidative capacity over remote marine regions than previously thought.

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**Competing interests.** The authors declare that they have no conflict of interest.

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