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Nitrogen and oxygen isotopic constraints on the origin of atmospheric nitrate in coastal Antarctica

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Abstract

Throughout the year 2001, size-segregated aerosol samples were collected continuously for 10 to 15 days at the French Antarctic Station Dumont d'Urville (DDU) (66°40' S, 140°01' E, 40 m above mean sea level). The nitrogen and oxygen isotopic ratios of particulate nitrate at DDU exhibit seasonal variations that are among the most extreme observed for nitrate on Earth. Associated with a late winter increase in the concentration of particulate nitrate, $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ reach as high as 111.5‰ versus VSMOW and 41.1‰, respectively. These are best explained as a signal of stratospheric input, with halogen radicals extracting 17O- and 18O-rich terminal oxygen from ozone and incorporating it into the nitrogen oxides, even if we are unable to reproduce this high $\Delta^{17}\text{O}$ value with the current knowledge of isotopic anomaly transfers during chemical reactions. This failure calls for the evaluation of polar ozone isotopic composition. During the late springtime peak in particulate nitrate, its $\delta^{15}\text{N}$ falls to -46.9‰ versus atmospheric N₂, suggesting that this peak results from snow re-emission, which has been shown previously to enrich in $\delta^{15}\text{N}$ the retained nitrate fraction in continental Antarctic sites.

1 Introduction

Inorganic particulate nitrate (p-NO_3^-) and nitric acid (HNO₃) are ubiquitous in the atmosphere. Because of their high solubility and chemical stability, wet and dry depositions are the ultimate sinks of these species. Being the end-product of atmospheric nitrogen oxide (NO_x=NO+NO₂) oxidation, nitrate is formed via (1) hydroxyl radical (OH) oxidation of NO₂, (2) NO₂ oxidation to N₂O₅ followed by hydrolysis on particles and/or (3) NO₂ oxidation to NO₃ followed by H abstraction from reduced species (Finlayson-Pitts and Pitts, 2000), with some contributions from (4) BrONO₂/ClONO₂ hydrolysis (von Glasow et al., 2004).

NO_x acts as an important catalyst, modulating the oxidative capacity of the atmo-

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sphere by the control it exerts on ozone levels. At the global scale, NO_x sources are well established, although a precise quantification is difficult (Warneck, 2000). Lightning, fossil fuel combustion, soil exhalation, biomass burning and ammonia oxidation are the major tropospheric sources. N₂O oxidation and N₂ photo-dissociation and photo-ionization constitute the upper atmospheric sources (Brasseur and Solomon, 1986). Despite decades of intense research, the source partitioning of nitrate in polar regions remains unclear (Wolff, 1995). The recent nitrate concentration increase observed in Greenland ice cores is attributed to industrial NO_x emissions in the northern hemisphere (Mayewski et al., 1990). Such an increase has not been observed in Antarctica, suggesting that nitrate in this region of the world is still dominated by natural influences (Wolff, 1995). The low ratio of peroxyacetyl nitrate (PAN, CH₃C(O)OONO₂) to NO_x and the low PAN concentration at Antarctic costal sites argue for a weak influence of continental sources (Jacobi et al., 2000). Jones et al. (1999) demonstrated that methyl nitrate (CH₃ONO₂) is the most concentrated oxidized nitrogen (NO_y) species in the Antarctic troposphere (37 pmol mol⁻¹) and suggested an oceanic source for this species. They also showed that predominance of organic nitrate (PAN + alkyl nitrate ≈60 pmol mol⁻¹) over inorganic nitrate (HNO₃+p-NO₃⁻≈20 pmol mol⁻¹). Zeller and co-workers (Dreschhoff and Zeller, 1998, 1990; Laird et al., 1982; McCracken et al., 2001a, b; Zeller and Dreschhoff, 1995; Zeller et al., 1986; Zeller and Parker, 1981) have proposed Solar Proton Events (SPE) as a possible source of nitrate above Antarctica. However, this suggestion remains controversial (Herron, 1982; Jackman et al., 1990; Legrand and Delmas, 1986; Legrand and Kirchner, 1990; Palmer et al., 2001) and in any case, SPE will have only a discrete, time-limited impact on the nitrate budget. As a result, stratospheric N₂O destruction and unspecified tropospheric sources for background NO_x (presumably biomass burning, lightning, and or ocean) are believed to be the only significant sources of Antarctic nitrate (Wagenbach et al., 1998; Wolff, 1995). It should be borne in mind that none of the degradation products of organic nitrates are expected to form directly inorganic nitrate (Finlayson-Pitts and Pitts, 2000; Shallcross et al., 1997) but they are most probably a source of NO_x.

The quantification of nitrate sources in polar regions is complicated by the fact that nitrate is not irreversibly trapped in snow. Neubauer and Heumann (1988) were the first to recognize that nitrate in surface snow undergoes strong post-depositional processes such as photolysis and evaporation leading to its loss from the snow, which has been confirmed by a number of other studies (Dibb and Whitlow, 1996; Mulvaney et al., 1998; Röthlisberger et al., 2002; Wagnon et al., 1999). Beyond its effect on the preservation of nitrate in snow, nitrate photolysis is now recognized as an important source of NO_x and HONO (Beine et al., 2002; Cotter et al., 2003; Davis et al., 2004a, b; Dibb and Whitlow, 1996; Domine and Shepson, 2002; Honrath et al., 2000a, 2002, 1999; Jones et al., 2000; Mulvaney et al., 1998; Wagnon et al., 1999), with a possible enhancement in emissions since the appearance of the stratospheric ozone “hole” (Jones and Wolff, 2003). Although the South Pole boundary layer is the most pristine on Earth (see for instance ISCAT special issue – Davis et al., 2004b), these emissions make it as oxidative as urban atmospheres (Monks, 2005). An intense research effort is currently devoted to understand and quantify such emissions, including the post-depositional effects leading to remobilization of nitrate in snow (Beine et al., 2002; Burkhardt et al., 2004; Dibb and Whitlow, 1996; Honrath et al., 2002, 2000b; Jones et al., 2000; Mulvaney et al., 1998; Nakamura et al., 2000; Röthlisberger et al., 2000, 2002; Cotter et al., 2003; Wolff et al., 2002).

With the recent advances of online mass spectrometry techniques (Brand, 1996; Casciotti et al., 2002; Sigman et al., 2001), the stable isotope composition of polar nitrate has emerged as a new tool of investigation, complementing concentration measurements. Because the nitrogen atom is conserved between NO_x sources and nitrate sinks, the nitrogen isotope composition is generally viewed as fingerprint of NO_x sources (Freyer, 1978, 1991; Hastings et al., 2004; Heaton, 1990; Moore, 1977), whereas the oxygen isotope composition is related to NO_x oxidation pathways (Hastings et al., 2003, 2005; Michalski et al., 2003; Morin et al., 2006).

In an effort to resolve the origin and fate of nitrate in Antarctica, we report here on a year-long isotopic survey of nitrate aerosols collected at Dumont d’Urville. This

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study represents the first comprehensive picture of nitrate isotopes that combines the three isotopic ratios $^{15}\text{N}/^{14}\text{N}$, $^{17}\text{O}/^{16}\text{O}$ and $^{18}\text{O}/^{16}\text{O}$. The nitrogen and oxygen isotopes are used to probe potential sources of nitrate in Antarctica. The core of this study is dedicated to the understanding the seasonal cycle of particulate nitrate (p-NO_3^-) concentrations at coastal Antarctic stations.

2 Sampling site and experimental procedure

2.1 Sampling site

A detailed description of the sampling location can be found in Wolff et al. (1998). We provide here the principal characteristics. Dumont d'Urville (DDU) ($66^{\circ}40' \text{S}, 140^{\circ}01' \text{E}$)
10 is located on a small island (Île des Pétrels, 0.45 km^2), 1 km North of the Antarctic mainland. The site is located in the Pacific sector of Antarctica, facing Australia. During summer, the island is partly snow-free with gneiss rock outcrops. Such rocks produce little mineral aerosols in the sub-micrometer size range.

Some 12 000 Adélie penguins nest on this inland during the summer, from the end
15 of October to late February. A large population of Adélie penguins is also present on islands around DDU, with a total population estimated at 60 000 individuals. In addition, some 7000 Emperor penguins sit through the winter at this site. Technical and scientific staff numbers fluctuate between about 60 in the summer to about 20 in the winter. There is no “clean sector” defined due to the small size of the island, but
20 analyses have shown only sporadic nitrate contamination by station activities and no nitrate contamination by the penguin population (Wagenbach et al., 1998).

The meteorological climatology at DDU is described in detail by König-Langlo et al. (1998). In summer, DDU is surrounded by open ocean water. The average surface air temperatures range from -1°C in January to -17°C in winter, with a mean annual temperature of -11°C . The annual mean surface wind speed is 9.5 m s^{-1} , with no clear seasonal variations. Strong katabatic winds dominate at DDU, favoring the $120\text{--}160^{\circ}$

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wind sector. Southerly air mass advection from the Antarctic interior occurs up to 2 km altitude throughout the year, isolating the marine boundary layer from lower latitude air masses above it. The tropopause is located between 9 and 11 km altitude, slightly higher from September to October. DDU is at the edge of the polar vortex and strong zonal winds ($>50 \text{ m s}^{-1}$) prevail above 10 km from late autumn to end of winter.

2.2 Sample collections

A Thermo Andersen (formerly Graseby-Andersen) high-volume air sampler (HVAS; model GL 2000H) equipped with a four-stage cascade impactor and a backup glass fiber filter was used to collect size-segregated atmospheric particles. The cascade impactor was mounted with four slotted $12.7 \text{ cm} \times 17.8 \text{ cm}$ glass fiber filters in series with an additional $20.3 \text{ cm} \times 25.4 \text{ cm}$ backup fiber glass filter to collect the finest particles. The primary purpose of the cascade impactor is to separate and analyze sea-salt and non sea-salt sulfate aerosols (to be analyzed in the future).

The HVAS was situated on a platform, 1 m above ground, 50 m away from the shore and 20 m away from the closest building (Labo 3). It was usually operated at 1.3 to 1.5 m^3 per minute (calibrated prior to deployment) for 10 to 15 successive days (20 000 to 30 000 m^3/sample) to ensure sufficient amount of aerosols (nitrate, sulfate) for isotopic analysis. During the brief periods of waste incineration at the station, the HVAS was stopped by the operators. One blank was incorporated into the collection process. The blank was treated identically to the samples, i.e. the cascade impactor was loaded with regular filters, except that the HVAS was not turned on.

2.3 Nitrate extraction and analysis

All glass fiber filters were pre-cleaned by an overnight soak and several rinses with ultra pure water (Millipore, 18 $\text{M}\Omega \text{ cm}$), dried in a class 10 000 clean room and finally stored in clean plastic food storage bags (Ziploc) before being shipped to Antarctica. After each collection, filters were removed from the cascade impactor in a clean hood

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and stored in clean 50 ml-centrifuge tubes at –20°C. Samples were transported frozen back to our laboratory in Grenoble for extraction of soluble species.

Before sample extraction in Grenoble, the filters were inspected visually. In some cases, penguin feathers or brown ornithological soil were found on the first stage of the impactor. These filters were disregarded. The four slotted filters (SF) were grouped together while the backup filter (BF) was treated individually. In this manner, filters were processed according to the diameter of the aerosols collected, with BF representing particle sizes smaller than 1 μm cutoff and SF greater than 1 μm . Filters were placed with 40 ml of ultra-pure water in a centrifugal filter unit (Millipore Centricon plus-70) for 15 min, shaken a few times and filtered at 3000 g in a centrifuge. Thus, more than 98% of the initial water volume can be recovered. Small quantities (200 μl) of sample solution were taken and diluted 200 times for ion chromatography analysis. NO_3^- concentrations were determined using the ion-chromatography system described in Preunkert et al. (2001) and used to calculate atmospheric nitrate mass concentrations.

After quantification, a predetermined volume of sample was extracted (0.5 to 8 ml) to secure 200 nmol of nitrate for isotopic analysis. The remainder of the sample was kept frozen and archived for future analysis.

$^{15}\text{N}/^{14}\text{N}$ and $^{18}\text{O}/^{16}\text{O}$ isotope ratio analyses were performed by conversion of nitrate to N_2O using the denitrifier method and direct isotope analysis of the N_2O (Casciotti et al., 2002; Sigman et al., 2001). The triple oxygen isotopic composition ($^{17}\text{O}/^{16}\text{O}$, $^{18}\text{O}/^{16}\text{O}$) was measured with a novel method based on on-line conversion of N_2O (from the denitrifier method) to O_2 in a gold furnace at 800°C (Kaiser et al., 2006b¹). For the denitrifier method alone, we used a nominal nitrate amount of 20 nmol N, whereas the N_2O decomposition method required 50 nmol N to ensure good reproducibility.

¹Kaiser, J., Hastings, M. G., Houlton, B. Z., Röckmann, T., and Sigman, D. M.: Triple oxygen isotope analysis of nitrate using the denitrifier method and thermal decomposition of N_2O , Anal. Chem., submitted, 2006b.

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2.4 Isotopic expressions

Isotopic compositions are reported as delta values relative to an international reference material:

$$\delta = \frac{R_{\text{spl}}}{R_{\text{ref}}} - 1 \quad (1)$$

where R_{spl} is the elemental isotope ratio of the sample and R_{ref} the elemental isotope ratio of the reference material. In case of nitrate, R can refer to either $^{15}\text{N}/^{14}\text{N}$, $^{17}\text{O}/^{16}\text{O}$ or $^{18}\text{O}/^{16}\text{O}$. Atmospheric nitrogen (N_2) has been established as the international reference for $^{15}\text{N}/^{14}\text{N}$ ratios (Mariotti, 1983, 1984). For oxygen isotopes, Vienna Standard Mean Ocean Water (VSMOW) is the international reference material.

The oxygen isotopic system offers three stable isotopes, allowing a comparison of their respective behavior. Most kinetic and equilibrium processes, such as isotopic exchange or diffusion, fractionate isotopes according to their relative mass differences and form linear arrays in a three-isotope plot of $\delta^{17}\text{O}$ versus $\delta^{18}\text{O}$ with a slope of approximately 0.52. This is called a mass-dependent isotope effect (Bigeleisen, 1952; Matsuhisa et al., 1978). Thiemens and Heidenreich III (1983) discovered that ozone formation does not follow a mass-dependent relationship and that ^{17}O had an anomalous enrichment in comparison to ^{18}O . Explaining the cause of the ^{17}O isotope anomaly in ozone remains a major challenge in physical chemistry (Brenninkmeijer et al., 2003). Since ozone is a strong oxidant and found nearly everywhere in the atmosphere, many other atmospheric species, including nitrate (Michalski et al., 2003), have been shown to possess anomalous $^{17}\text{O}/^{16}\text{O}$ ratios (Thiemens et al., 2001), inherited from O_3 .

Several expressions have been proposed for the quantification of ^{17}O isotope anomaly (Farquhar et al., 2000; Kaiser et al., 2004; Miller, 2002; Thiemens, 1999). In the present study, we use the non-approximated and reference-independent expression proposed by Miller (2002) and Kaiser et al. (2006a, 2004), and the exponent from

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Barkan and Luz (2005), rounded in accordance with our analytical precision:

$$\Delta^{17}\text{O} = \frac{1 + \delta^{17}\text{O}}{(1 + \delta^{18}\text{O})^\lambda} - 1 \text{ with } \lambda = 0.528 \quad (2)$$

3 Results

We present data from 27 collection periods at DDU, covering the period from 6 January 5 to 22 December 2001. In parallel to our collection, an aerosol monitoring program (AMP) has been in operation since 1991, measuring the ionic composition of the aerosol continuously with year-round daily observations. Measurements of meteorological data, lidar aerosol and ozone concentrations, solar flux at ground level and vertical profiles of temperature, ozone, solar flux, wind direction and wind speed are 10 performed regularly. These datasets were used whenever appropriate.

3.1 Data treatments

The analysis showed that blank levels were at most 10% and 6% of the wintertime and summertime concentration respectively, with 4% on average. For each filter sample, the blank was subtracted using an isotopic mass balance, based on the blank concentration and its isotopic composition.

Jourdain and Legrand (2002) and Rankin and Wolff (2003) have used size-segregated analysis of nitrate particles in coastal Antarctica. Both studies seem to indicate that p-NO_3^- is formed locally by the interaction of HNO_3 with sea-salt particles or eventually with NH_3 in summer at DDU, the latter being emitted by the dense penguin population (Legrand et al., 1998). Size mass distribution of particle nitrate shows a quasi mono-modal mode centered at $1\text{ }\mu\text{m}$ (Jourdain and Legrand, 2002). The results from the BF and SF show significant differences, but a similar seasonal cycle (Fig. S1 in supplemental materials – <http://www.atmos-chem-phys-discuss.net/>

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6/8817/2006/acpd-6-8817-2006-supplement.pdf). As we are mostly interested in the variations throughout the year, it is therefore justified to merge both datasets into one, weighting the isotopic composition of the BF and SF filters by the corresponding filter loadings. Further analysis of other collections archived in our laboratory will be used at
5 a later stage to investigate the differences between the isotopic composition of nitrate retained by the BF and SF filters, respectively.

3.2 Atmospheric concentration of inorganic nitrate aerosols

Atmospheric nitrate concentrations were calculated from the aerosol filter loading and the air volume pumped through the filter, assuming a constant flow rate throughout the
10 year. For most samples, the field operators did not record the ending date of sampling, in which case we assume that the collection was running until the starting date of the following sample. The concentration data obtained from the HVAS could therefore be up to a factor of two higher for isolated samples but, because the seasonal pattern of the atmospheric concentration varies by a factor of 16, this potential error has a
15 negligible impact on the interpretation of the seasonal variation and does not affect the calculation of the weighted average δ values. For the same reasons, temperature and pressure correction of the sample volume was neglected.

Figure 1a shows a comparison between the HVAS nitrate concentration time series and the one obtained by the AMP (M. Legrand and S. Preunkert, personal communication, 2006) for the year 2001. Data of the AMP have been averaged over each
20 HVAS collection period in order to facilitate the comparison. We observe no significant difference between the two time series despite very different sampling conditions (Table 1). Atmospheric concentrations of particulate nitrate show a strong seasonal cycle: From January to March (period 1), concentrations decrease steadily and reach a background concentration level ($\approx 12 \text{ ng m}^{-3}$) during the winter (period 2). From mid
25 July to September (period 3), concentrations increase to a peak of $\approx 50 \text{ ng m}^{-3}$. This moderate concentration increase at this time of the year is a significant and general observation observed around Antarctica (Wagenbach et al., 1998). Finally, October to



December (period 4) is characterized by the occurrence of a major concentration peak, with concentrations reaching $\approx 170 \text{ ng m}^{-3}$. The observed seasonal pattern of p- NO_3^- concentration in 2001 at DDU is in line with any other year analyzed so far (Rankin and Wolff, 2003; Wagenbach et al., 1998). However, DDU is known to be a place with high atmospheric ammonia and sea-salt concentrations (Jourdain and Legrand, 2002; Legrand et al., 1998; Wagenbach et al., 1998), leading to an alkaline bulk aerosol year-round. Recent measurements (Jourdain and Legrand, 2002) using denuder techniques revealed that partitioning between gaseous HNO_3 and particulate nitrate is close to 1:1. Such a high gaseous fraction may interfere with the alkaline bulk aerosols deposited on the filter, generating erroneously high p- NO_3^- measurements. Until direct isotopic measurement is performed on gaseous HNO_3 , the impact of such a compound on the isotopic composition of the bulk nitrate collected on filter media will remain unknown. Such a remark is also valid for other nitrogen oxide gases such as PAN, NO_x , N_2O_5 , HONO, HO_2NO_2 , CH_3ONO_2 (NO_y family), even if in this list only CH_3ONO_2 , PAN, NO_x and HNO_3 seem to be concentrated enough (Jacobi et al., 2000; Jones et al., 1999) to have the potential to interfere with the sampled aerosol. At this stage no evaluation can be made on such interferences, and the atmospheric community is restricted to the interpretation of what it is recovered on the filters (Schaap et al., 2002; Wagenbach et al., 1998).

20 3.3 Isotopic measurements and reproducibility

Table 2 provides the measured values of the concentration, $\delta^{15}\text{N}$, $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$. Standard deviation is estimated based on replicate measurements of a subset of samples (i.e. 0.2‰ for $\delta^{15}\text{N}$, 0.5‰ for $\delta^{18}\text{O}$ (denitrifier method; Casciotti et al., 2002), 0.3‰ for $\delta^{18}\text{O}$ and 0.9‰ for $\Delta^{17}\text{O}$ (N_2O decomposition method, Kaiser et al., 2006b¹)). As a general observation, the isotopic ratios show strong seasonal patterns, in line with the concentration and represent the most extremes values ever reported for nitrate.

Nitrate aerosol $\delta^{15}\text{N}$ values range from -46.7 to +10.8‰, with its minimum during late springtime. This seasonal pattern is identical to the one previously reported by

Wagenbach et al. (1998) at Neumayer (Fig. 1b). To the best of our knowledge, the low $\delta^{15}\text{N}$ nitrate values observed during the late spring concentration peak have only been documented in Antarctic environments (i.e. sediment, snow, air) (Michalski et al., 2005; Wada et al., 1981; Wagenbach et al., 1998).

Our $\delta^{18}\text{O}$ measurements also show an extended range of values, spanning from about 62 to 110‰ with relatively good agreement between the two analytical methods (direct N_2O , Casciotti et al., 2002, and gold decomposition of N_2O , Kaiser et al., 2006b¹) used in the present study (Fig. 1c). Like $\delta^{15}\text{N}$, this upper limit represents the highest ^{18}O enrichment ever reported for nitrate in natural environments (Hastings et al., 2003, 2005, 2004; Heaton et al., 2004; Kendall, 1998; Michalski et al., 2005, 2004a, b, 2003; Morin et al., 2006). Fewer studies exist on $\Delta^{17}\text{O}$ due to the difficulty of measuring the less abundant ^{17}O isotope. $\Delta^{17}\text{O}$ values span from 16.2 to 41.0‰ (Table 2 and Fig. 1d). Again, this is the largest range ever observed (Alexander et al., 2004; Michalski et al., 2005, 2004a, b, 2003; Morin et al., 2006), only matched by recent measurements of atmospheric nitrate at the South Pole (McCabe et al., 2006²). These graphs show that the four periods established from the concentration measurements re-appear in the isotope profiles. In Table 3, we give the principal characteristics for each period. Figure 2 summarizes the above presentation. In this figure, $\Delta^{17}\text{O}$ is plotted against $\delta^{15}\text{N}$ along with the nitrate atmospheric concentration. The four periods established from the time-series are clearly visible. Each period bears its own concentration, nitrogen and oxygen isotopic characteristics in a seasonal cycle that follow a cycle-type evolution in this plot.

As expected, there is a strong correlation between nitrate $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ (Fig. 3), showing that $\delta^{18}\text{O}$ is essentially the result of the isotopic identity of the O atoms being transferred from ozone and that fractionations during these transfers are of only marginal importance.

²McCabe, J. R., Thiemens, M. H., and Savarino, J.: Discovery of a proxy of the Ozone hole variability in South Pole Antarctic snow: The role of nitrate oxygen isotopes, Geophys. Res. Lett., submitted, 2006.

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4 Discussion

Due to the remoteness of the Antarctic continent, three sources of nitrate are deemed most important: stratospheric input, continental background (biomass burning, lightning) sources (Wolff, 1995) and possibly the ocean (Jones et al., 1999). The only real effort to interpret the seasonal pattern of p-NO₃⁻ in Antarctic atmosphere was given by Wagenbach et al. (1998), who based their interpretation on cosmogenic/radioactive tracers (³H, ⁷Be, ¹⁰Be, ²¹⁰Pb), spatio-temporal variability of concentrations and nitrogen isotopes. With the notable exception of the late spring peak, they conclude that concentration time series can be accounted for by a combination of stratosphere/troposphere exchange and tropospheric background sources. Wagenbach et al. (1998) also evaluated the possible role of snowpack reemission during the late spring months, but they dismissed this source based upon both flux estimates and lack of knowledge of the exact loss mechanism responsible for the reemission. The unexplained late spring concentration peak is presumed to be a consequence of Polar Stratospheric Cloud (PSC) subsidence. This proposition is based on the extreme ¹⁵N depletion of the nitrate ($\delta^{15}\text{N} = -50\text{\textperthousand}$) at this time of the year, backed by an estimation of HNO₃ downward flux from this source. As we will see, this interpretation is inconsistent with our best understanding of the N isotope systematic of N₂O destruction, the dominant source of NO_x in the stratosphere, the specific timing of stratospheric inputs to the Antarctic troposphere, as well as snow post-depositional effects.

4.1 The stratospheric source for nitrogen oxides

4.1.1 Mass flux

Winter denitrification of the Antarctic stratosphere is well established (Fahey et al., 1990; Santee et al., 1995; Van Allen et al., 1995). As daylight wanes, gas-phase HNO₃ accrues in the Antarctic stratosphere, mainly via reaction of nitrogen pentoxide (N₂O₅) with H₂O on preexisting aerosols. At the end of winter, when stratospheric

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temperatures drop below 195 K (von Savigny et al., 2005), ClONO₂ decomposition (hydrolysis or reaction with HCl) becomes a significant source of gaseous nitric acid (Sander et al., 2003; S. Bekki, personal communication, 2006). When its vapor pressure reaches the threshold for formation of PSC clouds, gaseous HNO₃ condenses to the solid phase. Based upon satellite observations, Muscari et al. (2003) calculated for the entire 1995 polar vortex, which encompasses approximately the entirety of Antarctica (von Savigny et al., 2005), a drop in the NO_y column corresponding to a total loss of $\Delta N = (6.3 \pm 2.6) \times 10^7$ kg. Assuming that this nitrogen is entirely in the form of HNO₃ and completely lost into the troposphere (Muscari et al., 2003; Santee et al., 2004), such an injection corresponds to an increase of the HNO₃ burden of $(28.4 \pm 11.7) \times 10^7$ kg. Assuming that this injection occurs continuously during 90 days (cf. ³H data from Wagenbach et al., 1998) between August and October into the entire Antarctic troposphere (area 16 million km², tropospheric column of 10 000 m), we calculate a constant input above background of about 20 ng m⁻³ d⁻¹ during late springtime. Assuming a lifetime of about a week for the nitrate, we find an additional steady state atmospheric concentration of about 140 ng m⁻³. Assuming that this contribution is partitioned equally between gaseous nitrate and particulate nitrate, as observed for extant nitrate load, an additional contribution of about 70 ng m⁻³ can be expected, a reasonable value in comparison with the observed late winter concentration increase of 38 ng m⁻³ and the crude character of this calculation.

A similar conclusion was reached by Wagenbach et al. (1998) using independent data. It is therefore conceivable to consider PSCs as a possible source of the late spring concentration peak. In support of this hypothesis, Wagenbach et al. (1998) invoked the highly depleted ¹⁵N of the late spring nitrate peak, similar to our present observations. Since such low $\delta^{15}\text{N}$ values had not been reported anywhere else on the planet, Wagenbach et al. (1998) interpreted this anomalous $\delta^{15}\text{N}$ value as evidence of a PSC signature. However, this interpretation is rendered implausible by recent findings on stratospheric N₂O isotope chemistry and its consequences for the isotopic composition of upper atmospheric NO_y, as explained in the following.

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4.1.2 Nitrogen isotopes in stratospheric NO_x and nitrate

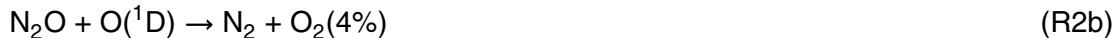
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N₂O is destroyed in the stratosphere mainly by photolysis in the atmospheric UV “window region” between 185 and 220 nm. This reaction accounts for 90% of its loss (Minschwaner et al., 1993) (Reaction R1). Chemical reactions with electronically excited oxygen atoms, O(¹D), are an additional stratospheric N₂O sink. This last reaction shows two exit channels, one “re-active” producing NO (Reaction R2a), the other “inert” leading to the formation of N₂ and O₂ (Reaction R2b) (Cantrell et al., 1994; Sander et al., 2000).



Precursors of lower stratospheric HNO₃ are NO_x produced by the reaction N₂O+O(¹D) and NO_x produced following N₂ photo-ionization and photo-dissociation in the thermosphere, mesosphere and upper stratosphere (Brasseur and Solomon, 1986; de Zafra and Smyshlyaev, 2001; Funke et al., 2005; Orsolini et al., 2005; Stiller et al., 2005). According to these authors, NO_x sources above the stratopause represent just a few per cent of the amount produced by in situ N₂O oxidation (Santee et al., 2004).

Neglecting this upper atmosphere contribution, the nitrogen isotope composition of stratospheric NO_x can be estimated from the degree of N₂O destruction in the stratosphere and the isotopic fractionation associated with the reaction N₂O+O(¹D) (Kaiser et al., 2002a; Toyoda et al., 2004). After mathematical calculation and integration, one obtains (see Appendix A for details):

$$\overline{\delta^{15}\text{N}(\text{NO})} = \left(1 + {}^{15}\varepsilon_{\text{R2a}}\right) \frac{1 + \delta^{15}\text{N}(\text{N}_2\text{O})_0}{1 + {}^{15}\varepsilon_{\text{sinks}}} \frac{1 - f^{1 + {}^{15}\varepsilon_{\text{sinks}}}}{1 - f} - 1 \quad (3)$$

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In this analytical expression, the first term in brackets describes the fractionation due to Reaction (R2a) while the second term expresses the fractionation of N₂O by all its sink processes. Because PSCs can be formed up to an altitude of 25 km above DDU (Santacesaria et al., 2001) and slowly subside from this altitude, we use

5 the averaged fractionation constant observed for Antarctica by Toyoda et al. (2004):

$\varepsilon_{\text{sinks}}^{15} = -31\text{\textperthousand}$. For f, we use the value of (0.15 ± 0.06) , corresponding to a mixing ratio of N₂O of (50 ± 20) nmol mol⁻¹ (altitude ≈ 25 km) (Toyoda et al., 2004), and initial stratospheric $\delta^{15}\text{N}(\text{N}_2\text{O})_0$ of $(6.7 \pm 0.1)\text{\textperthousand}$ with $\mu(\text{N}_2\text{O})_0 = (320 \pm 1)$ nmol mol⁻¹ (Kaiser et al., 2003a; Röckmann and Levin, 2005). This calculation yields an average stratospheric

10 $\delta^{15}\text{N}(\text{NO}) = (19 \pm 3)\text{\textperthousand}$ with the uncertainty based on the largest variable parameter: f

$(\pm 40\%)$. $\delta^{15}\text{N}(\text{NO})$ is actually a lower limit, because it does not take into account the

influence of transport processes such as mixing or diffusion.

Considering that more than 90% of NO_y is eliminated from the stratosphere during the denitrification process (Fahey et al., 1990; Muscari et al., 2003), it is expected that $\delta^{15}\text{N}(\text{p-NO}_3^-) \approx \delta^{15}\text{N}(\text{HNO}_3) \approx \delta^{15}\text{N}(\text{NO}) = (19 \pm 3)\text{\textperthousand}$. This result excludes the stratosphere as the source of heavily depleted ¹⁵N nitrate in late spring (Fig. 1c), a result already suggested by Heaton et al. (2004) based on a similar reasoning.

4.1.3 Oxygen isotopes in stratospheric nitrate

Michalski et al. (2003) developed the first theoretical framework for understanding of the triple oxygen isotopic composition of atmospheric nitrate. The theory is based on the oxygen isotopic anomaly transfer of the oxygen isotope anomaly of O₃ to NO_x and subsequently to HNO₃. The first step relies on the oxygen isotope transfer during photostationary equilibrium between NO_x and O₃. Lyons (2001), using an atmospheric chemistry model to investigate the propagation of this oxygen isotopic anomaly up to the mesospheric oxygen-bearing species, have predicted the isotope anomaly of stratospheric NO_x. Recently, Zahn et al. (2006) improved and updated the isotopic anomaly transfer scheme between O₃ and NO_x. However, in both models, the authors

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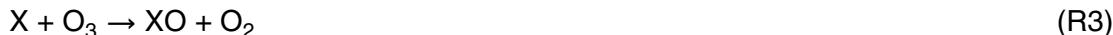
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assume that NO reacts only with the terminal atom of O₃, a hypothesis contradicted by experimental observations (van den Ende et al., 1982; Viswanathan and Raff, 1983) and recently discussed in Morin et al. (2006) for its isotopic implications. In a set of laboratory experiments (manuscript in preparation), we have observed the macroscopic anomaly transfer of $\Delta^{17}\text{O}(\text{NO}_2) \approx 0.8 \Delta^{17}\text{O}(\text{O}_3)$. No data are currently available for the isotopic composition of stratospheric Antarctic ozone. A re-evaluation of the most recent isotope measurements for stratospheric ozone from the Northern Hemisphere with a three isotope exponent of 0.528 gives a range from 25.0 to 38.9‰ (Krankowsky et al., 2000; Lämmenzahl et al., 2002; Mauersberger et al., 2001). Combining these observations with our experimental $\Delta^{17}\text{O}$ transfer rate, $\Delta^{17}\text{O}(\text{NO}_2)$ is expected to vary in the range of 20.0 to 31.1‰.

Two oxidation pathways lead to the formation of nitric acid in the dark polar winter stratosphere (Fig. 4). The first involves the heterogeneous hydrolysis of N₂O₅, i.e. pathway (2) listed in the Introduction. Oxygen atoms mass balance shows that this route leads to $\Delta^{17}\text{O}(\text{HNO}_3) = 5/6 \Delta^{17}\text{O}(\text{NO}_2)$ (Michalski et al., 2003), thus in the range of 16.6 to 25.9‰. The other reaction pathway involves ClONO₂ and BrONO₂ (Hanson and Ravishankara, 1991; Sander et al., 2003) when vortex temperature falls below 195 K in winter (pathway (4) in the Introduction):



where X=Cl or Br. Morin et al. (2006) showed that, in this case, because halogen radicals abstract directly a terminal oxygen atom in ozone during Reaction (R3) (Toohey et al., 1988; Zhang et al., 1997) and that these atoms are more enriched in heavy isotopes than the bulk ozone molecule (Janssen, 2005), $\Delta^{17}\text{O}(\text{XO}) = \Delta^{17}\text{O}(\text{O}_3)_{\text{terminal}} = (30.0 - 46.7)\text{‰}$, assuming Janssen's approach and identical enrichment for ¹⁷O ozone iso-

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topologues. Thus, we have for the nitric acid made off XONO_2 (Morin et al., 2006)

$$\Delta^{17}\text{O}(\text{HNO}_3) = 1/3\Delta^{17}\text{O}(\text{XO}) + 2/3\Delta^{17}\text{O}(\text{NO}_2) \quad (4)$$

which gives a range of 23.3 to 36.3‰. Thus, it appears that very high oxygen isotopic anomalies of inorganic nitrate (up to 41‰), a unique characteristic of Antarctic nitrate (McCabe et al., 2006²; Michalski et al., 2005), cannot be explained by the current knowledge, even if we take into account the halogen chemistry. Yet, it should be borne in mind that the ozone isotopic dataset used here may not be representative of Antarctic stratospheric ozone due to the unique chemistry and photolysis conditions prevailing in the vortex. Furthermore, the anomaly of the terminal oxygen atoms in O_3 may actually be higher (Tuzson, 2005). The bottom line, however, is that stratospheric chemistry is the only clear candidate to explain such high $\Delta^{17}\text{O}(\text{NO}_3^-)$ (Fig. 4).

4.1.4 Relevance of atmospheric transport dynamics

Santacesaria et al. (2001) provided a detailed statistical analysis of PSC occurrence above DDU. From their observations, after the end of July, PSC clouds are often observed within 1 km of the tropopause. A weak tropopause barrier generally characterizes this time of the year (Fig. 5) (see also König-Langlo et al., 1998) and injection of stratospheric material into the troposphere is facilitated at the end of July.

Tritium (${}^3\text{H}$) contained in water is a reasonable tracer of stratospheric water. ${}^3\text{H}$ is mainly produced in the lower stratosphere by cosmic ray and exhibits a much higher abundance in stratospheric water vapor than tropospheric water (Ehhalt et al., 2002). At Halley Bay station (Antarctica), ${}^3\text{H}$ in precipitation peaks during period 3 (July–October) (Wagenbach et al., 1998). On the other hand, the maximum of p- NO_3^- , attributed by Wagenbach et al. (1998) to PSC subsidence, peaks in late spring (period 4). In the Antarctic, unlike the Arctic, denitrification is accompanied by a simultaneous de-hydration of the stratosphere in late winter (Fahey et al., 1990; Santee et al., 1995). If both ${}^3\text{H}_2\text{O}$ and the late spring p- NO_3^- peaks are presumed to be stratospheric in origin,

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their maxima should be simultaneous. For two species that are injected into the troposphere in a gaseous form, the observed time lag is difficult to reconcile with a common (stratospheric) source for both species, a failing already mentioned by Wagenbach et al. (1998).

5 4.2 Tropospheric nitrate

4.2.1 Nitrogen Isotopes

In other parts of the world, $\delta^{15}\text{N}$ ranges between –20 to +20‰ in particulate nitrate (Burns and Kendall, 2002; Campbell et al., 2002; Fogel and Paerl, 1993; Freyer, 1978, 1991; Freyer et al., 1996; Hastings et al., 2003; Heaton, 1987; Hoering, 1957; Koba et al., 1997; Moore, 1977; Pichlmayer et al., 1998; Russel et al., 1998), nitrate in Arctic snow or ice (Hastings et al., 2005, 2004; Heaton et al., 2004), alpine ice (Freyer et al., 1996), and NO_x (Heaton, 1990; Moore, 1977). With the notable exception of the period 4, DDU $\delta^{15}\text{N}$ values are in this typical range. There is probably information in variations within this range but the N isotope systematic of the atmospheric N cycle of 15 Antarctica are not yet well enough known to make use of the more subtle variations.

4.2.2 Oxygen isotopic anomaly

Usual tropospheric chemistry has a lower efficiency mechanism to transfer O_3 oxygen atoms to the nitrate product. Moreover, tropospheric ozone shows a tendency to a lower isotopic anomaly than stratospheric ozone (Irion et al., 1996; Johnston and Thiemens, 1997; Krankowsky et al., 1995; Lämmertzahl et al., 2002; Mauersberger et al., 2001). For these reasons, tropospheric-produced nitrate is expected to have lower isotopic anomalies than stratospheric-produced nitrate (Fig. 4). Recently, Morin et al. (2006) suggested that a high anomaly is also possible in the troposphere. Indeed, in the springtime Arctic boundary layer, characterized by significant levels of BrO , BrONO_2 hydrolysis can become a major route of HNO_3 formation. As in the case 25

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of stratospheric chemistry, such oxidation pathways involving halogen chemistry can enhance the oxygen isotopic anomaly transfer from precursors to products. However, satellite-derived tropospheric BrO maps (Richter et al., 2002) show that the DDU area never experiences significant BrO blooms. The DMSO/DMS ratio at DDU does show an anomalous increase which may be related to the fast oxidation of DMS to DMSO by BrO (von Glasow and Crutzen, 2004), but only in August (M. Legrand, personal communication, 2006). In addition, air masses reaching DDU mainly originate from the interior of the continent (König-Langlo et al., 1998) and are not exposed to marine BrO-enriched conditions for a long period. Such halogen chemistry seems therefore to be marginal, but needs further investigation. During nighttime formation of HNO_3 , more oxygen atoms of ozone are incorporated. Based on Michalski's observations, $\Delta^{17}\text{O}$ ranges from 28 to 30‰ and 22 to 25‰ in the troposphere for wintertime and summertime, respectively (Michalski et al., 2003) (see Fig. 4 for the complete scheme). Comparing these tropospheric ranges with our $\Delta^{17}\text{O}$ seasonal cycle, it appears that with the notable exception of period 3, all other periods are compatible with tropospheric-produced nitrate.

4.3 Snowpack emissions

In their study, Wagenbach et al. (1998) considered snowpack emissions as a source of atmospheric nitrate but because of incomplete data at the time, they did not consider this source to be significant. Since their work, a better understanding of the fate of nitrate in snow has been achieved. At high accumulation sites ($>30\text{ cm}$ of snow a^{-1}), nitrate and its isotopic signature are rather well conserved (Hastings et al., 2004; Röthlisberger et al., 2000, 2002). On the other hand, at low accumulation sites like Dome C (snow accumulation $\approx 10\text{ cm a}^{-1}$), photolysis and reemission of nitrate dominate, leading to a sharp decrease in concentrations, accompanied by emission of NO_x and NO_y . Such process was also observed during the ISCAT 2000 project at South Pole (Dibb et al., 2004).

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4.3.1 Mass flux

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al., 1998), we calculated a source emission of $\Delta N = (1.2 \pm 1.0) \times 10^7$ kg of NO_y using a surface snow density of 0.3 g cm^{-3} . Such an estimation has to be compared with $\Delta N = (6.3 \pm 2.6) \times 10^7$ kg for the PSC source calculated by Muscari et al. (2003) or NO_x snow emission of $\Delta N = 0.76 \times 10^7$ kg estimated by Jones et al. (2001). Because snow is a surface emission source and summers are characterized by temperature inversion in the Antarctic boundary layer (Fig. 5), this source can easily accommodate the late spring concentration peak observed at DDU. If such a quantity is emitted in 90 days (late springtime/yearly summertime), into a 1000 m tropospheric column, a concentration of $\Delta[\text{HNO}_3] \approx 38 \text{ ng m}^{-3} \text{ d}^{-1}$ during this period is added to the background situation over the entire Antarctic (16 million km^2), assuming a total conversion of NO_y to nitric acid and neglecting any meridional transport. Such increase is similar to the one calculated for the PSC source. Using a nitrate lifetime of seven days and a 1:1 partitioning between gaseous and particulate nitrate, we would expect an increase of the particulate nitrate concentration of 133 ng m^{-3} , in good agreement with the observed increase of 120 ng m^{-3} .

4.3.2 Nitrogen isotopes of snowpack emissions

Recently Blunier et al. (2005) performed a survey of the $^{15}\text{N}/^{14}\text{N}$ of nitrate in DC snow. They observed a sharp increase in $\delta^{15}\text{N}$, concomitant with the depletion of nitrate concentration. In the first 15 cm of snow, the $\delta^{15}\text{N}(\text{NO}_3^-)$ rises dramatically from +10 to +200‰, deducing an apparent net isotope effect of $\varepsilon_{\text{snow}} = -54\text{‰}$ for the post depositional processes acting on nitrate.

Blunier et al.'s data indicate that NO_x and nitric acid emitted by the snow in the central plateau of Antarctica should be depleted in ^{15}N isotope. Applying an isotopic Rayleigh-type fractionation for Dome C snowpack with $\varepsilon_{\text{snow}} = -53.9\text{‰}$ (Blunier et al., 2005), the

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average $\delta^{15}\text{N}(\text{HNO}_3)_{\text{emitted}}$ is

$$\overline{\delta^{15}\text{N}(\text{HNO}_3)}_{\text{emitted}} = \left(1 + \delta^{15}\text{N}_0\right) \frac{1 - f^{15}\varepsilon_{\text{snow}} + 1}{1 - f} - 1 \quad (5)$$

with f , the mass fraction of the residual nitrate remaining in the snow and $\delta^{15}\text{N}_0$, the nitrogen isotopic composition of surface snow nitrate. Taking f as 0.7 ± 0.2 (i.e., 30% lost of nitrate occur during the late spring/early summer months, see Sect. 4.3.1.), and $\delta^{15}\text{N}_0 \approx 12\text{\textperthousand}$ (Blunier et al., 2005), one finds average $\delta^{15}\text{N}$ of HNO_3 emitted in the order of $-34 \pm 6\text{\textperthousand}$, a value very close to the isotopic composition of the late spring nitrate peak at DDU but inaccessible for stratospheric nitrate. All published atmospheric nitrate ^{15}N so far never displayed such low $\delta^{15}\text{N}$ values (Heaton et al., 2004, and references therein), with the notable exception of Antarctica. We are unaware of a physical or chemical process in the atmosphere capable of generating such ^{15}N -depleted nitrate.

4.3.3 Oxygen isotopes of snowpack emissions

McCabe et al. (2006)² gave the first comprehensive oxygen isotopic survey of Antarctic nitrate. The comparison between seasonal composition in aerosol, surface snow and snow pit at South Pole indicates that the isotopic composition of atmospheric nitrate is transferred to the surface snow (McCabe et al., 2006²). The annual average $\Delta^{17}\text{O}(\text{NO}_3^-) = 28.8\text{\textperthousand}$ in 2003, as preserved by firn snow, compared well with the annual average, $29.3\text{\textperthousand}$, obtained with monthly surface snow sample of the year 2004. Such observation coupled with laboratory experiments (McCabe et al., 2005) suggest a good preservation of the $\Delta^{17}\text{O}(\text{NO}_3^-)$ in snow. Flux model study (Wolff et al., 2002) indicate that photolysis and thermodynamically-controlled (e.g. diffusion) processes are quantitatively equivalent in snow. It can be deduced therefore that flux emission of NO_y from the snow will be essentially in the form of NO_x and HNO_3 in equal proportion. The NO_x will lead to a summer tropospheric-type oxygen isotopic signature of nitrate, i.e. $\Delta^{17}\text{O}(\text{NO}_3^-)_{\text{tropo summer}} \approx 26\text{\textperthousand}$ (McCabe et al., 2006²), during transport

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from inland to the coast, whereas reemitted HNO_3 should keep its mean annual isotopic anomaly in snow, i.e. $\Delta^{17}\text{O}(\text{NO}_3^-)_{\text{snow}} \approx 29\text{\textperthousand}$, giving an average $\Delta^{17}\text{O} \approx 27.5\text{\textperthousand}$ for the reemitted HNO_3 reaching the coast. Such values compare well with the average December $\Delta^{17}\text{O}(\text{NO}_3^-)$ of nitrate aerosols observed at DDU (28\text{\textperthousand}, Fig. 1d). Oxygen isotopic anomaly of reemitted nitrate is therefore not in contradiction with the idea of the snow being the main source of late spring nitrate peak.

König-Langlo et al. (1998) have discussed in details the meteorology of DDU. Year-round, ground level air mass flows are characterized by katabatic winds where large quantities of cold and dry air are drained from the central plateau of Antarctica. Vertical profiles of meridional winds show that such flows take place up to an altitude of approximately 2 km and are well organized throughout the year. A similar shear in the wind field structure is observed for the zonal winds, with ground level flows governed by easterly wind drift, switching to westerly above 2 km height. This particularity of DDU area strongly limits direct advects of oceanic air masses and further suggests that the Antarctic plateau is the main source of air reaching DDU station.

4.4 Seasonal variations

Summarizing all the information developed in the latter sections, we obtain the following main observations:

- stratospheric PSC nitrate should possess an isotopic composition of $\delta^{15}\text{N}(\text{NO}_y)_{\text{strato}} > (19 \pm 3)\text{\textperthousand}$ and $\Delta^{17}\text{O}(\text{NO}_y)_{\text{strato}} = (23\text{--}36)\text{\textperthousand}$,
- the isotopic composition of tropospheric nitrate is best constrained by $\delta^{15}\text{N}(\text{HNO}_3) = (-20 \text{ to } +20)\text{\textperthousand}$ and $\Delta^{17}\text{O}$ from 28 to 30\text{\textperthousand} and 22 to 25\text{\textperthousand} for wintertime and summertime, respectively,
- snow-emitted nitrate (including nitrate formed by conversion of its snow-emitted precursors such as NO_x) is expected to possess $\delta^{15}\text{N}(\text{NO}_3^-)_{\text{emitted}} \approx -34 \pm 6\text{\textperthousand}$ and $\Delta^{17}\text{O}(\text{NO}_3^-)_{\text{emitted}} \approx 27.5\text{\textperthousand}$

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- nitrate source fluxes from snow and PSCs are both compatible with late spring nitrate concentration peaks
- air mass meteorology at DDU is dominated all year-round by inland drift
- subsidence and penetration of PSC into the troposphere occur during the wintertime/springtime transition when the tropopause barrier is weak and the lower stratosphere very cold

5 4.4.1 Periods 1 and 2

From January to July, corresponding to our period 1 and 2, Wagenbach et al. (1998),
10 using radionuclide tracers, estimated the relative contribution of tropospheric and stratospheric sources to be roughly 1:1, with some variability from month to month. At this time of the year, the stratospheric input is the result of air mass intrusions. We are unable to prove or disprove such estimation. The nitrogen isotopic signature of tropospheric nitrate overlaps the stratospheric range (Heaton et al., 2004; Moore, 1974), it is therefore impossible from our dataset to distinguish the exact influence of these
15 two reservoirs. We cannot draw firm conclusions about the slow increase in $\delta^{15}\text{N}$ from –20 to 10‰ between January and end of August. We note however that during this period, the average temperature drops from 0 to –15°C and kinetic isotopic effects associated with inter coupling of NO_y species and decline of photochemistry might be an explanation for this trend in $\delta^{15}\text{N}$ values.

20 The oxygen isotopic anomaly indicates two different regimes, with $\Delta^{17}\text{O}$ ranging between 20–25‰ and 27–30‰ for summer and fall, respectively. Figure 6 exhibits the oxygen isotopic anomaly versus the erythemal UV doses (MED) received at ground level in 2001 in this coastal Antarctic site. Erythemal UV doses are used here as an indicator of sunlight intensity. As sunlight wanes, $\Delta^{17}\text{O}(\text{NO}_3^-)$ increases. $\Delta^{17}\text{O}$ ranges
25 observed during period 1 and 2 (lower line in Fig. 6) are in good agreement with the ones reported by Michalski et al. (2003) for summer and winter, respectively. We therefore suggest that the oxygen isotopic anomaly of nitrate from January (high MED) to

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July (low MED) is the result of tropospheric NO_x chemistry, as modeled by Michalski et al. (2003) and suggested by Hastings et al. (2003, 2004), and such results could be a powerful technique to constrain oxidant fields in this part of the world. This indicates that the winter source of nitrate is most presumably local oxidation of background NO_x, probably generated by organic nitrates.

4.4.2 Period 3

This period is characterized by a small but significant enhancement of particulate nitrate concentration. Such an increase is in phase with ³H activity of the snow found in the coastal site of Halley Bay, a marker for stratospheric water. Oxygen isotopic anomalies of nitrate peak at this time of the year and are best explained by stratospheric-produced nitrate, taking the upper limit of prognosticated oxygen isotopic signature for this reservoir. At this stage, however there are too many unknowns to go beyond these qualitative arguments, especially in absence of measurements of the isotopic composition of ozone in the Antarctic vortex.

Because of the overlap between nitrogen isotopic composition of stratospheric and tropospheric-produced nitrate, ¹⁵N signatures of the period 3 do not bring new information but at least are compatible with a stratospheric origin.

Flux calculations performed previously do not contradict this suggestion. We estimated the additional concentration per day to be around 30 ng m⁻³. Such a value at first glance seems to overestimate the observed increase of late winter atmospheric concentration relatively to the period 4 concentration increased. However, it should be borne in mind that part of this stratospheric nitrate will be stored temporarily and/or permanently in snow. Measurements suggest that the Antarctic plateau receives 2.4–5.7 kg N km⁻² a⁻¹ from denitrification (Muscari et al., 2003) among which 2.1 kg N km⁻² a⁻¹ are buried as nitrate, based on ice core analysis (Legrand and Kirchner, 1990). Meteorology of PSC above DDU further supports the hypothesis of a stratospheric source for the late winter concentration peak.

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4.4.3 Period 4

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Considering arguments developed above, we propose that the late spring nitrate peak is not the result of PSC sedimentation. The striking feature of the $\delta^{15}\text{N}$ profile are the negative values observed during period 4 (Fig. 1b). Such low values are in remarkable contrast with the tropospheric range and call for a distinctive process peculiar to Antarctica since no other parts of the world show such depletion (Heaton et al., 2004). Estimation of the nitrogen isotopic composition of reemitted NO_y from the snow strongly suggests that snow emission is responsible for the late spring concentration peak. We are not aware of any other source capable of producing such low $\delta^{15}\text{N}$ isotopic ratios, especially in the atmosphere.

Oxygen isotopic anomalies during this period is compatible with snow emissions if one assumes an equal mixture of snow-emitted HNO_3 and snow-emitted NO_x , the former having the mean annual oxygen isotopic signature of inland snow, the latter acquiring a tropospheric signature during transport from inland to the coast. This suggestion offers a possible explanation for the offset observed in Fig. 6, with summertime nitrate still possessing a fraction with a stratospheric-type oxygen isotopic composition.

Inland drift of air masses is symptomatic of the DDU wind field. Our estimate of NO_y fluxes from the snow support our conclusion, based on concentration profiles observed at different low accumulation sites.

20 5 Summary and conclusions

Year-round aerosol collections of inorganic particulate nitrate have been analyzed for their isotopic content. This study constitutes the first comprehensive isotopic survey of atmospheric nitrate in coastal Antarctica. Using the bacterial denitrifier technique, the $\delta^{18}\text{O}$, $\Delta^{17}\text{O}$ and $\delta^{15}\text{N}$ have been precisely measured on small samples. Size segregated analysis show no fundamental seasonal variation differences between particle size fractions below and above $1\ \mu\text{m}$, even if some significant disparities exist punc-

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tually. In the absence of multiple year analysis, we ignored these disparities and we have preferred to treat the mass and isotopic weighted average signal. Applying current knowledge on the origin of the ozone oxygen isotopic anomaly ($\Delta^{17}\text{O}$) and the ^{15}N fractionation constants in the stratosphere and snow, we have established the main isotopic characteristics of tropospheric, stratospheric, and snow reservoirs of nitrate. A comparison between our isotopic dataset and the isotopic signature of these sources suggests the following scenario:

1. The precise source of background concentrations of atmospheric nitrate is not identifiable. However, the $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ of background atmospheric nitrate are compatible with nitrate formed predominantly in the local troposphere, with isotopic variations being explained by sunlight-driven changes in the mechanism of NO_x oxidation to HNO_3 .
2. Evaluation of the stratospheric isotopic composition of nitrate revealed that the secondary peak around August–September is most likely associated with polar stratospheric cloud sedimentation.
3. Snow reemissions of NO_x and nitric acid from the interior of the Antarctic continent seem to be the principal cause of the major late spring peak. Only this source has all the characteristics necessary to generate atmospheric nitrate that is highly depleted in ^{15}N .
- 20 Our new scenario, backed by mass balance calculations, reconciles the observed simultaneity between tritium and nitrate. Furthermore, it confirms the potentially higher oxygen isotopic anomaly of the stratosphere over the troposphere. However, only measurements of the stratospheric ozone isotopic composition inside the polar vortex will definitely permit accurate quantification and influence of the denitrification process in Antarctic boundary layer.

In summary, the dynamic of atmospheric inorganic nitrate in coastal Antarctic boundary layer can be described by a stable tropospheric background source with the stratosphere injecting large amounts of nitrate via polar stratospheric clouds denitrification

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in late winter, with the majority of it captured and trapped in the snow until the thermodynamical conditions of spring/summer times allow its release from this buffered reservoir. Such a scenario could be further tested as follows: Late winter in the Antarctic plateau should be characterized by a high concentration of gaseous nitric acid. Data to test this prediction are not currently available. We want to emphasize that particulate nitrate measurements will not be a suitable measurement to reveal such seasonal features in inland sites. Nitric acid has a high affinity to alkaline aerosols, therefore revealing more the seasonal cycle of aerosols than the nitric acid concentration variability. We expect other tropospheric trace gases to be also influenced by snowpack emissions in summer on coastal sites, a phenomenon already observed for formaldehyde (HCOOH) and hydrogen peroxide (H_2O_2) (Frey et al., 2005; Riedel et al., 2005).

Appendix A

Estimation of nitrogen isotopic composition of polar stratospheric nitrate

The $^{15}\text{N}/^{14}\text{N}$ ratio of stratospheric N_2O can be described empirically by a Rayleigh fractionation equation (Kaiser et al., 2002a, 2006a; Rahn and Wahlen, 1997; Toyoda et al., 2004):

$$\ln \frac{\delta^{15}\text{N}(\text{N}_2\text{O}) + 1}{\delta^{15}\text{N}(\text{N}_2\text{O})_0 + 1} = {}^{15}\varepsilon_{\text{sinks}} \ln \frac{\mu(\text{N}_2\text{O})}{\mu(\text{N}_2\text{O})_0} \quad (\text{A1})$$

where δ and $\mu(\text{N}_2\text{O})$ are the isotopologue ratio and mixing ratios of N_2O , respectively, with the subscript “0” referring to the initial value before decomposition (i.e. in the troposphere). $\varepsilon_{\text{sinks}}$ ³ is the apparent fractionation constant between N_2O and the overall

³The definition of fractionation constant we adopted here is the one commonly used in geochemistry, i.e. the definition using the ratio of the heavy isotope over the light isotope (ε). For publications using the reverse ratio (ε'), we use the relation $\varepsilon = -\varepsilon' / (\varepsilon' + 1)$ to recalculate the fractionation constant according to our definition.

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destruction processes, which is related to the overall rate constant of the decomposition reaction involving heavy (k_h) and light (k_l) N_2O isotopologues and binds the isotopic composition of N_2O and the products:

$$^{15}\varepsilon_{\text{sinks}} = \frac{k_h}{k_l} - 1 = \frac{\delta^{15}\text{N}(\text{products}) - \delta^{15}\text{N}(\text{N}_2\text{O})}{1 + \delta^{15}\text{N}(\text{N}_2\text{O})} \quad (\text{A2})$$

- 5 Isotopic fractionation of N_2O during photo-dissociation and oxidation-reduction have been studied intensively (Johnston et al., 1995; Kaiser et al., 2002b, 2003b; Miller and Yung, 2000; Rahn and Wahlen, 1997; Röckmann et al., 2000; Zhang et al., 2000), and these studies yielded a high quality dataset to estimate the ^{15}N composition of the N_2O decomposition products.
- 10 For Reaction (R1), the process controlling the N_2O concentration, but exerting no impact on stratospheric NO isotopic composition, laboratory experiments give a range of $^{15}\varepsilon_{\text{R1}}$ between $-48.5\text{\textperthousand}$ and $-34.8\text{\textperthousand}$ at 233 K (Kaiser et al., 2002b; Röckmann et al., 2001; Toyoda et al., 2004), a relatively high fractionation constant for an irreversible process. Kaiser et al. (2002a) showed that the isotopic fractionation constant for (R2)
- 15 reactions is $^{15}\varepsilon_{\text{R2}} = k(^{15}\text{N}^{14}\text{NO})/k(^{14}\text{N}_2\text{O}) - 1 = -5.5\text{\textperthousand}$, and is insensitive to temperature and pressure. Reaction (R2a) is the main source of NO_y in the stratosphere and explains the correlation observed between NO_y and N_2O concentration in the stratosphere (Muscari et al., 2003). Therefore, only this branch (R2a) needs to be considered here to estimate the $^{15}\text{N}/^{14}\text{N}$ of stratospheric NO_y . Kaiser et al. (2002a) have
- 20 estimated, based on transition state theory, the isotopic fractionation constant of the (R2a) exit channels. This reaction is characterized by a $^{15}\varepsilon_{\text{R2a}}$ of $-8.1\text{\textperthousand}$. Rearranging equation Eq. (A2), and applying it to Reaction (R2a) gives:

$$\delta^{15}\text{N}(\text{NO}) = \delta^{15}\text{N}(\text{N}_2\text{O}) \left(1 + ^{15}\varepsilon_{\text{R2a}} \right) + ^{15}\varepsilon_{\text{R2a}} \approx \delta^{15}\text{N}(\text{N}_2\text{O}) + ^{15}\varepsilon_{\text{R2a}} \quad (\text{A3})$$

- Since $|^{15}\varepsilon_{\text{R2a}}|$ is small compared to $|^{15}\varepsilon_{\text{R1}}|$ and since Reaction (R2a) represents only 25 6 to 9% of the total N_2O sinks (Fahey et al., 1990; Muscari et al., 2003), $\delta^{15}\text{N}(\text{N}_2\text{O})$

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in the stratosphere is mainly controlled by Reaction (R1) and not by Reaction (R2a). From Eq. (A3), it appears that the isotopic composition of NO in the stratosphere closely parallels N₂O nitrogen isotopic profile for all $\delta^{15}\text{N}(\text{N}_2\text{O})$ observed but shifted by –8.1‰. Combining Eq. (A1) and Eq. (A3), the analytic expression of $\delta^{15}\text{N}(\text{NO})$ as a function of fractionation constants and N₂O concentration is obtained:

$$\frac{\delta^{15}\text{N}(\text{NO}) + 1}{\delta^{15}\text{N}(\text{N}_2\text{O})_0 + 1} = \left(1 + {}^{15}\varepsilon_{\text{R2a}}\right) \left(\frac{\mu(\text{N}_2\text{O})}{\mu(\text{N}_2\text{O})_0}\right)^{{}^{15}\varepsilon_{\text{sinks}}} \quad (\text{A4})$$

Defining $f = \mu(\text{N}_2\text{O})/\mu(\text{N}_2\text{O})_0$, the average isotopic composition of NO produced by Reaction (R2a) at any given f (i.e. altitude or N₂O mixing ratio) is obtained by integrating Eq. (A4):

$$\overline{\frac{\delta^{15}\text{N}(\text{NO}) + 1}{\delta^{15}\text{N}(\text{N}_2\text{O})_0 + 1}} = \left(1 + {}^{15}\varepsilon_{\text{R2a}}\right) \frac{\int_1^f f^{{}^{15}\varepsilon_{\text{sinks}}} df}{\int_1^f df} \quad (\text{A5})$$

10

after integration and rearrangement, we finally have:

$$\overline{\delta^{15}\text{N}(\text{NO})} = \left(1 + {}^{15}\varepsilon_{\text{R2a}}\right) \frac{1 + \delta^{15}\text{N}(\text{N}_2\text{O})_0}{1 + {}^{15}\varepsilon_{\text{sinks}}} \frac{1 - f^{1+{}^{15}\varepsilon_{\text{sinks}}}}{1 - f} - 1 \quad (\text{A6})$$

15

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- Alexander, B., Savarino, J., Kreutz, K., and Thiemens, M. H.: Impact of preindustrial biomass-burning emissions on the oxidative pathways of tropospheric sulfur and nitrogen, *J. Geophys. Res.*, 109, D08303, doi:10.1029/2003JD004218, 2004.
- 5 Barkan, E. and Luz, B.: High-precision measurements of $^{17}\text{O}/^{16}\text{O}$ and $^{18}\text{O}/^{16}\text{O}$ ratios in H_2O , *Rapid Communications in Mass Spectrometry*, 19, 3737–3742, 2005.
- Beine, H. J., Honrath, R. E., Domine, F., Simpson, W. R., and Fuentes, J. D.: NO_x during background and ozone depletion periods at Alert: Fluxes above the snow surface, *J. Geophys. Res.*, 107(D21), 4584, doi:10.1029/2002JD002082, 2002.
- 10 Bigeleisen, J.: The effects of isotopic substitutions on the rates of chemical reactions, *J. Phys. Chem.*, 56, 823–828, 1952.
- Blunier, T., Floch, G. L., Jacobi, H.-W., and Quansah, E.: Isotopic view on nitrate loss in Antarctica surface snow, *Geophys. Res. Lett.*, 32, L13501, doi:10.1029/2005GL023011, 2005.
- Brand, W. A.: High precision isotope ratio monitoring techniques in mass spectrometry, *J. Mass Spectrometry*, 225–235, 1996.
- 15 Brasseur, G. and Solomon, S.: Aeronomy of the middle atmosphere, 452 pp, Reidel, D., Norwell, MA, 1986.
- Brenninkmeijer, C. A. M., Janssen, C., Kaiser, J., Röckmann, T., Rhee, T. S., and Assonov, S.: Isotope effects in the chemistry of atmospheric trace compounds, *Chem. Rev.*, 103(12), 5125–5161, 2003.
- 20 Burkhardt, J. F., Hutterli, M., Bales, R. C., and McConnell, J. R.: Seasonal accumulation timing and preservation of nitrate in firn at Summit, Greenland, *J. Geophys. Res.*, 109, D19302, doi:10.1029/2004JD004658, 2004.
- Burns, D. A. and Kendall, C.: Analysis of delta N-15 and delta O-18 to differentiate NO_3^- sources in runoff at two watersheds in the Catskill Mountains of New York, *Water Resour. Res.*, 38(5), 2002.
- 25 Campbell, D. H., Kendall, C., Chang, C. C. Y., Silva, S. R., and Tonnessen, K. A.: Pathways for nitrate release from an alpine watershed: Determination using delta N-15 and delta O-18, *Water Resour. Res.*, 38(5), doi:10.1029/2001WR001578, 2002.
- 30 Cantrell, C. A., Shetter, R. E., and Calvert, J. G.: Branching ratios for the $\text{O}({}^1\text{D}) + \text{N}_2\text{O}$ reaction, *J. Geophys. Res.*, 99(D2), 3739–3743, 1994.
- Casciotti, K. L., Sigman, D. M., Galanter Hastings, M., Böhlke, J. K., and Hilkert, A.: Measure-

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- ment of the Oxygen Isotopic Composition of Nitrate in Seawater and Freshwater Using the Denitrifier Method, *Anal. Chem.*, 74, 4905–4912, 2002.
- Cotter, E. S. N., Jones, A. E., Wolff, E. W., and Bauguitte, S. J. B.: What controls photochemical NO and NO₂ production from Antarctic snow? Laboratory investigation assessing the wavelength and temperature dependence, *J. Geophys. Res.*, 108(D4), 4147, doi:10.1029/2002JD002602, 2003.
- Davis, D., Chen, G., Buhr, M., Crawford, J., Lenschow, D., Lefer, B., Shetter, R., Eisele, F., Mauldin, L., and Hogan, A.: South Pole NOx chemistry: an assessment of factors controlling variability and absolute levels, *Atmos. Environ.*, 38(32), 5375–5388, 2004a.
- Davis, D. D., Eisele, F., Chen, G., Crawford, J., Huey, G., Tanner, D., Slusher, D., Mauldin, L., Oncley, S., Lenschow, D., Semmer, S., Shetter, R., Lefer, B., Arimoto, R., Hogan, A., Grube, P., Lazzara, M., Bandy, A., Thornton, D., Berresheim, H., Bingemer, H., Hutterli, M., McConnell, J., Bales, R., Dibb, J., Buhr, M., Park, J., McMurry, P., Swanson, A., Meinardi, S., and Blake, D.: An overview of ISCAT 2000, *Atmos. Environ.*, 5363–5373, 2004b.
- de Zafra, R. and Smyshlyaev, S. P.: On the formation of HNO₃ in the Antarctic mid to upper stratosphere in winter, *J. Geophys. Res.*, 106(D19), 23 115–23 125, 2001.
- Dibb, J. E., Huey, L. G., Slusher, D. L., and Tanner, D. J.: Soluble reactive nitrogen oxides at South Pole during ISCAT 2000, *Atmos. Environ.*, 38(32), 5399–5409, 2004.
- Dibb, J. E. and Whitlow, S.: Recent climate anomale and their impact on snow chemistry at South Pole, 1987–1994, *Geophys. Res. Lett.*, 23(10), 1115–1118, 1996.
- Domine, F. and Shepson, P. B.: Air-snow interactions and atmospheric chemistry, *Science*, 297(5586), 1506–1510, 2002.
- Dreschhoff, G. and Zeller, E. J.: Ultra-high resolution nitrate in polar ice as indicator of past solar activity, *Solar Physics*, 177(1–2), 365–374, 1998.
- Dreschhoff, G. A. M. and Zeller, E. J.: Evidence of Individual Solar Proton Events in Antarctic Snow, *Solar Physics*, 127(2), 333–346, 1990.
- Ehhalt, D. H., Rohrer, F., Schaufler, S., and Pollock, W.: Tritiated water vapor in the stratosphere: Vertical profiles and residence time, *J. Geophys. Res.*, 107(D24), 4757, doi:10.1029/2001JD001343, 2002.
- Fahey, D. W., Kelly, K. K., Kawa, S. R., and Tuck, A. F.: Observations of denitrification and dehydration in the winter polar atmosphere, *Nature*, 344, 321–324, 1990.
- Farquhar, J., Savarino, J., Jackson, T. L., and Thiemens, M. H.: Evidence of atmospheric sulfur in the Martian regolith from sulfur isotopes in meteorites, *Nature*, 404, 50–52, 2000.

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- Finlayson-Pitts, B. J. and Pitts, J. N.: Chemistry of the upper and lower atmosphere: Theory, experiments and applications, 969 pp, Academic Press, San Diego, CA, 2000.
- Fogel, M. L. and Paerl, H. W.: Isotopic Tracers of Nitrogen from Atmospheric Deposition to Coastal Waters, *Chemical Geology*, 107(3–4), 233–236, 1993.
- 5 Frey, M. M., Stewart, R. W., McConnell, J. R., and Bales, R. C.: Atmospheric hydroperoxides in West Antarctica: Links to stratospheric ozone and atmospheric oxidation capacity, *J. Geophys. Res.*, 110(D23), D23301, doi:10.1029/2005JD006110, 2005.
- Freyer, H. D.: Seasonal trends of NH_4^+ and NO_3^- nitrogen isotope composition in rain at Jülich, Germany, *Tellus*, 30, 83–92, 1978.
- 10 Freyer, H. D.: Seasonal variation of $^{15}\text{N}/^{14}\text{N}$ ratios in atmospheric nitrate species, *Tellus*, 43B, 30–44, 1991.
- Freyer, H. D., Kobel, K., Delmas, R. J., Kley, D., and Legrand, M. R.: First results of N-15/N-14 ratios in nitrate from alpine and polar ice cores, *Tellus Series B-Chemical and Physical Meteorology*, 48(1), 93–105, 1996.
- 15 Funke, B., Lopez-Puertas, M., Gil-Lopez, S., von Clarmann, T., Stiller, G. P., Fischer, H., and Kellmann, S.: Downward transport of upper atmospheric NO_x into the polar stratosphere and lower mesosphere during the Antarctic 2003 and Arctic 2002/2003 winters, *J. Geophys. Res.*, 110, D24308, doi:10.1029/2005JD006463,, 2005.
- Hanson, D. R. and Ravishankara, A. R.: The Reaction Probabilities of ClONO_2 and N_2O_5 on 20 Polar Stratospheric Cloud Materials, *J. Geophys. Res.*, 96(D3), 5081–5090, 1991.
- Hastings, M. G., Sigman, D. M., and Lipschultz, F.: Isotopic evidence for source changes of nitrate in rain at Bermuda, *J. Geophys. Res.-Atmos.*, 108(D24), 4790, doi:10.1029/2003JD003789, 2003.
- 25 Hastings, M. G., Sigman, D. M., and Steig, E. J.: Glacial/interglacial changes in the isotopes of nitrate from the Greenland Ice Sheet Project 2 (GISP2) ice core, *Global Biogeochem. Cycles*, 19, GB4024, doi:10.1029/2005GB002502, 2005.
- Hastings, M. G., Steig, E. J., and Sigman, D. M.: Seasonal variations in N and O isotopes of nitrate in snow at Summit, Greenland: Implications for the study of nitrate in snow and ice cores, *J. Geophys. Res.-Atmos.*, 109, D20306, doi:10.1029/2004JD004991, 2004.
- 30 Heaton, T. H. E.: $^{15}\text{N}/^{14}\text{N}$ ratios of nitrate and ammonium in rain at Pretoria, South Africa, *Atmos. Environ.*, 21(4), 843–852, 1987.
- Heaton, T. H. E.: $^{15}\text{N}/^{14}\text{N}$ ratios of NO_x from vehicle engines and coal-fired power stations, *Tellus*, 42B, 304–307, 1990.

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- Heaton, T. H. E., Wynn, P., and Tye, A. M.: Low $^{15}\text{N}/^{14}\text{N}$ ratios for nitrate in snow in the High Arctic (79°N), *Atmos. Environ.*, 38(33), 5611–5621, 2004.
- Herron, M. M.: Impurity Sources of F-, Cl-, NO_3^- and SO_4^{2-} in Greenland and Antarctic Precipitation, *J. Geophys. Res.-Oceans and Atmospheres*, 87(NC4), 3052–3060, 1982.
- Hoering, T.: The isotopic composition of the ammonia and the nitrate ion in rain, *Geochim. Cosmochim. Acta*, 12, 97–102, 1957.
- Honrath, R. E., Guo, S., Peterson, M. C., Dziobak, M. P., Dibb, J. E., and Arsenault, M. A.: Photochemical production of gas phase NO_x from ice crystal NO_3 , *J. Geophys. Res.*, 105(D19), 24 183–24 190, 2000a.
- Honrath, R. E., Lu, Y., Peterson, M. C., Dibb, J. E., Arsenault, M. A., Cullen, N. J., and Steffen, K.: Vertical fluxes of NO_x , HONO, and HNO_3 above the snowpack at Summit, Greenland, *Atmos. Environ.*, 36(15–16), 2629–2640, 2002.
- Honrath, R. E., Peterson, M. C., Dziobak, M. P., Dibb, J. E., Arsenault, M. A., and Green, S. A.: Release of NOx from sunlight-irradiated midlatitude snow, *Geophys. Res. Lett.*, 27(15), 2237–2240, 2000b.
- Honrath, R. E., Peterson, M. C., Guo, S., Dibb, J. E., Shepson, P. B., and Campbell, B.: Evidence of NOx production within or upon ice particles in the Greenland snowpack, *Geophys. Res. Lett.*, 26(6), 695–698, 1999.
- Irion, F. W., Gunson, M. R., Rinsland, C. P., Yung, Y. L., Abrams, M. C., Chang, A. Y., and Goldman, A.: Heavy ozone enrichments from ATMOS infrared solar spectra, *Geophys. Res. Lett.*, 23(17), 2377–2380, 1996.
- Jackman, C. H., Douglass, A. R., Rood, R. B., McPeters, R. D., and Meade, P. E.: Effect of Solar Proton Events on the Middle Atmosphere During the Past 2 Solar-Cycles as Computed Using a 2-Dimensional Model, *J. Geophys. Res.*, 95(D6), 7417–7428, 1990.
- Jacobi, H. W., Weller, R., Jones, A. E., Anderson, P. S., and Schrems, O.: Peroxyacetyl nitrate (PAN) concentrations in the Antarctic troposphere measured during the photochemical experiment at Neumayer (PEAN'99), *Atmos. Environ.*, 34(29–30), 5235–5247, 2000.
- Janssen, C.: Intramolecular isotope distribution in heavy ozone ((OOO) $^{16}\text{O}^{18}\text{O}^{16}\text{O}$ and (OOO) $^{16}\text{O}^{16}\text{O}^{18}\text{O}$), *J. Geophys. Res.*, 110, D08308, doi:10.1029/2004JD005479, 2005.
- Johnston, J. C., Cliff, S. S., and Thiemens, M. H.: Measurement of multioxgen isotopic (Delta-O-18 and Delta-O-17) fractionation factors in the stratospheric sink reactions of nitrous-oxide, *J. Geophys. Res.*, 100(D8), 16 801–16 804, 1995.
- Johnston, J. C. and Thiemens, M. H.: The isotopic composition of tropospheric ozone in three

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- environments, *J. Geophys. Res.*, 102(D21), 25 395–25 404, 1997.
- 5 Jones, A. E., Weller, R., Anderson, P. S., Jacobi, H. W., Wolff, E. W., Schrems, O., and Miller, H.: Measurements of NO_x emissions from the Antarctic snowpack, *Geophys. Res. Lett.*, 28(8), 1499–1502, 2001.
- 10 Jones, A. E., Weller, R., Minikin, A., Wolff, E. W., Sturges, W. T., McIntyre, H. P., Leonard, S. R., Schrems, O., and Bauguitte, S.: Oxidized nitrogen chemistry and speciation in the Antarctic troposphere, *J. Geophys. Res.*, 104(D17), 21 355–21 366, 1999.
- 15 Jones, A. E., Weller, R., Wolff, E. W., and Jacobi, H. W.: Speciation and rate of photochemical NO and NO₂ production in Antarctic snow, *Geophys. Res. Lett.*, 27(3), 345–348, 2000.
- 20 Jones, A. E. and Wolff, E. W.: An analysis of the oxidation potential of the South Pole boundary layer and the influence of stratospheric ozone depletion, *J. Geophys. Res.*, 108(D18), 4565, doi:10.1029/2003JD003379, 2003.
- Jourdain, B. and Legrand, M.: Year-round records of bulk and size-segregated aerosol composition and HCl and HNO₃ levels in the Dumont d'Urville (coastal Antarctica) atmosphere: Implications for sea-salt aerosol fractionation in the winter and summer, *J. Geophys. Res.*, 107(D22), 4645, doi:10.1029/2002JD002471, 2002.
- 25 Kaiser, J., Brenninkmeijer, C. A. M., and Röckmann, T.: Intramolecular ¹⁵N and ¹⁸O fractionation in the reaction of N₂O with O(¹D) and its implications for the stratospheric N₂O isotope signature, *J. Geophys. Res.*, 107, 4214, 10.1029/2001JD001506, 2002a.
- 30 Kaiser, J., Engel, A., Borchers, R., and Röckmann, T.: Probing stratospheric transport and chemistry with new balloon and aircraft observations of the meridional and vertical N₂O isotope distribution, *Atmos. Chem. Phys.*, 6, 4273–4324, 2006a.
- Kaiser, J., Röckmann, T., and Brenninkmeijer, C. A. M.: Complete and accurate mass spectrometric isotope analysis of tropospheric nitrous oxide, *J. Geophys. Res.-Atmos.*, 108(D15), 4476, doi:10.1029/2003JD003613, 2003a.
- Kaiser, J., Röckmann, T., and Brenninkmeijer, C. A. M.: Contribution of mass-dependent fractionation to the oxygen isotope anomaly of atmospheric nitrous oxide, *J. Geophys. Res.-Atmos.*, 109, D03305, doi:10.1029/2003JD004088, 2004.
- Kaiser, J., Röckmann, T., and Brenninkmeijer, C. A. M.: Temperature dependence of isotope fractionation in N₂O photolysis, *Phys. Chem. Chem. Phys.*, 4, 4420–4430, 2002b.
- Kaiser, J., Röckmann, T., Brenninkmeijer, C. A. M., and Crutzen, P. J.: Wavelength dependence of isotope fractionation in N O photolysis, *Atmos. Chem. Phys.*, 3, 303–313, 2003b.
- Kendall, C.: Tracing Nitrogen Sources and Cycling in Catchments, in: *Tracers in Catchment*

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Hydrology, edited by: Kendall, C. and McDonnell, J. J., p 519–576, Elsevier Science, Amsterdam, 1998.

Koba, K., Tokuchi, N., Wada, E., Nakajima, T., and Iwatsubo, G.: Intermittent denitrification: The application of a N-15 natural abundance method to a forested ecosystem, *Geochim. Cosmochim. Acta*, 61(23), 5043–5050, 1997.

König-Langlo, G., King, J. C., and Pettre, P.: Climatology of the three coastal Antarctic stations Dumont d'Urville, Neumayer, and Halley, *J. Geophys. Res.*, 103(D9), 10 935–10 946, 1998.

Krankowsky, D., Bartecki, F., Klees, G. G., Mauersberger, K., Schellenbach, K., and Stehr, J.: Measurement of heavy isotope enrichment in tropospheric ozone, *Geophys. Res. Lett.*, 22(13), 1713–1716, 1995.

Krankowsky, D., Lämmenzahl, P., and Mauersberger, E.: Isotopic measurements of stratospheric ozone, *Geophys. Res. Lett.*, 27(17), 2593–2595, 2000.

Laird, C. M., Zeller, E. J., Armstrong, T. P., and Parker, B. C.: Solar-Activity and Nitrate Deposition in South-Pole Snow, *Geophys. Res. Lett.*, 9(10), 1195–1198, 1982.

Lämmenzahl, P., Röckmann, T., Brenninkmeijer, C. A. M., Krankowsky, D., and Mauersberger, K.: Oxygen isotope composition of stratospheric carbon dioxide, *Geophys. Res. Lett.*, 29(12), 1582, doi:10.1029/2001GL014343, 2002.

Legrand, M., Ducroz, F., Wagenbach, D., Mulvaney, R., and Hall, J.: Ammonium in coastal Antarctic aerosol and snow: Role of polar ocean and penguin emissions, *J. Geophys. Res.*, 103(D9), 11 043–11 056, 1998.

Legrand, M. R. and Delmas, R. J.: Relative contributions of tropospheric and stratospheric sources to nitrate in Antarctic snow, *Tellus, Series B: Chemical and Physical Meteorology*, 38B(3–4), 236–249, 1986.

Legrand, M. R. and Kirchner, S.: Origins and variations of nitrate in south polar precipitation, *J. Geophys. Res.*, 95(D4), 3493–3507, 1990.

Lyons, J. R.: Mass-independent fractionation of oxygen-containing radicals in the atmosphere, *Geophys. Res. Lett.*, 28(17), 3231–3234, 2001.

Mariotti, A.: Atmospheric Nitrogen Is a Reliable Standard for Natural N-15 Abundance Measurements, *Nature*, 303(5919), 685–687, 1983.

Mariotti, A.: Natural N-15 Abundance Measurements and Atmospheric Nitrogen Standard Calibration, *Nature*, 311(5983), 251–252, 1984.

Matsuhsia, Y., Goldsmith, J. R., and Clayton, R. N.: Mechanisms of Hydrothermal Crystallization of Quartz, *Geochim. Cosmochim. Acta*, 42, 173–182, 1978.

Isotopic constraints of atmospheric Antarctic nitrate

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- Mauersberger, K., Lämmenzahl, P., and Krankowsky, D.: Stratospheric ozone isotope enrichments – revisited, *Geophys. Res. Lett.*, 28(16), 3155–3158, 2001.
- Mayewski, P. A., Lyons, W. B., Spencer, M. J., Twickler, M. S., Buck, C. F., and Whitlow, S.: An Ice-Core Record of Atmospheric Response to Anthropogenic Sulphate and Nitrate, *Nature*, 346(6284), 554–556, 1990.
- McCabe, J. R., Boxe, C. S., Colussi, A. J., Hoffman, M. R., and Thiemens, M. H.: Oxygen isotopic fractionation in the photochemistry of nitrate in water and ice, *J. Geophys. Res.*, 110, D15310, doi:10.1029/2004JD005484, 2005.
- McCracken, K. G., Dreschhoff, G. A. M., Smart, D. F., and Shea, M. A.: Solar cosmic ray events for the period 1561–1994 2. The Gleissberg periodicity, *J. Geophys. Res.-Space Physics*, 106(A10), 21 599–21 609, 2001a.
- McCracken, K. G., Dreschhoff, G. A. M., Zeller, E. J., Smart, D. F., and Shea, M. A.: Solar cosmic ray events for the period 1561–1994 1. Identification in polar ice, 1561–1950, *J. Geophys. Res.-Space Physics*, 106(A10), 21 585–21 598, 2001b.
- Michalski, G., Bockheim, J. G., Kendall, C., and Thiemens, M.: Isotopic composition of Antarctic Dry Valley nitrate: Implications for NO_y sources and cycling in Antarctica, *Geophys. Res. Lett.*, 32(13), L13817, doi:10.1029/2004GL02212, 2005.
- Michalski, G., Böhlke, J. K., and Thiemens, M.: Long term atmospheric deposition as the source of nitrate and other salts in the Atacama Desert, Chile: New evidence from mass-independent oxygen isotopic compositions, *Geochim. Cosmochim. Acta*, 68(20), 4023–4038, 2004a.
- Michalski, G., Meixner, T., Fenn, M., Hernandez, L., Sirulnik, A., Allen, E., and Thiemens, M.: Tracing atmospheric nitrate deposition in a complex semiarid ecosystem using $\Delta^{17}\text{O}$, *Environ. Sci. Technol.*, 38(7), 2175–2181, 2004b.
- Michalski, G., Scott, Z., Kabiling, M., and Thiemens, M. H.: First measurements and modeling of $\Delta^{17}\text{O}$ in atmospheric nitrate, *Geophys. Res. Lett.*, 30(16), 1870, doi:10.1029/2003GL017015, 2003.
- Miller, C. E. and Yung, Y. L.: Photo-induced isotopic fractionation, *J. Geophys. Res.*, 105(D23), 29 039–29 051, 2000.
- Miller, M. F.: Isotopic fractionation and the quantification of O-17 anomalies in the oxygen three-isotope system: an appraisal and geochemical significance, *Geochim. Cosmochim. Acta*, 66(11), 1881–1889, 2002.
- Minschwaner, K., Salawitch, R. J., and McElroy, M. B.: Absorption of solar radiation by O₂:

Isotopic constraints of atmospheric Antarctic nitrate

J. Savarino et al.

- Implications for O₃ and lifetimes of N₂O, CFCl₃, and CF₂Cl₂, *J. Geophys. Res.*, 98(D6), 10 543–10 561, 1993.
- Monks, P. S.: Gas-phase radical chemistry in the troposphere, *Chem. Soc. Rev.*, 34(5), 376–395, 2005.
- Moore, H.: Isotopic Measurement of Atmospheric Nitrogen-Compounds, *Tellus*, 26(1–2), 169–174, 1974.
- Moore, H.: The isotopic composition of ammonia, nitrogen dioxide and nitrate in the atmosphere, *Atmos. Environ.*, 11, 1239–1243, 1977.
- Morin, S., Savarino, J., Bekki, S., Gong, S., and Bottenheim, J. W.: Pronounced Signature of Arctic Surface Ozone Depletion Events after Polar Sunrise on Δ¹⁷O in Atmospheric Nitrate, *Atmos. Chem. Phys.*, 6, 6255–6297, 2006.
- Mulvaney, R., Wagenbach, D., and Wolff, E. W.: Postdepositional change in snowpack nitrate from observation of year-round near-surface snow in coastal Antarctica, *J. Geophys. Res.*, 103(D9), 11 021–11 031, 1998.
- Muscat, G., de Zafra, R. L., and Smyshlyaev, S.: Evolution of the NO_y-N₂O correlation in the Antarctic stratosphere during 1993 and 1995, *J. Geophys. Res.-Atmos.*, 108(D14), 4428, doi:10.1029/2002JD002871, 2003.
- Nakamura, K., Nakawo, M., Ageta, Y., Goto-Azuma, K., and Kamiyama, K.: Post-depositional loss of nitrate in surface snow layers of the Antarctic ice sheet, *Bull. Glaciol. Res.*, 17, 11–16, 2000.
- Neubauer, J. and Heumann, K. G.: Determination of nitrate at the ng/g level in Antarctic snow samples with Ion chromatography and isotope-dilution mass-spectrometry, *Fresenius Zeitschrift Fur Analytische Chemie*, 170–173, 1988.
- Orsolini, Y. J., Manney, G. L., Santee, M. L., and Randall, C. E.: An upper stratospheric layer of enhanced HNO₃ following exceptional solar storms, *Geophys. Res. Lett.*, 32, L12S01, doi:10.1029/2004GL021588, 2005.
- Palmer, A. S., van Ommen, T. V., Curran, M. A. J., and Morgan, V.: Ice-core evidence for a small solar-source of atmospheric nitrate, *Geophys. Res. Lett.*, 28(10), 1953–1956, 2001.
- Pichlmayer, F., Schoner, W., Seibert, P., Stichler, W., and Wagenbach, D.: Stable isotope analysis for characterization of pollutants at high elevation alpine sites, *Atmos. Environ.*, 32(23), 4075–4085, 1998.
- Preunkert, S., Legrand, M., and Wagenbach, D.: Sulfate trends in a Col du Dome (French Alps) ice core: A record of anthropogenic sulfate levels in the European midtroposphere over the

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- twentieth century, *J. Geophys. Res.*, 106, 31 991–32 004, 2001.
- Rahn, T. and Wahlen, M.: Stable isotope enrichment in stratospheric nitrous oxide, *Science*, 278, 1776–1778, 1997.
- Rankin, A. M. and Wolff, E. W.: A year-long record of size-segregated aerosol composition at 5 Halley, Antarctica, *J. Geophys. Res.-Atmos.*, 108(D24), 4775, doi:10.1029/2003JD003993, 2003.
- Richter, A., Wittrock, F., Ladtsätter-Weissenmayer, A., and Burrows, J. P.: GOME measurements of stratospheric and tropospheric BrO, *Adv. Space Res.*, 29(11), 1667–1672, 2002.
- Riedel, K., Allan, W., Weller, R., and Schrems, O.: Discrepancies between formaldehyde measurements and methane oxidation model predictions in the Antarctic troposphere: An assessment of other possible formaldehyde sources, *J. Geophys. Res.*, 110(D15), D15308, doi:10.1029/2005JD005859, 2005.
- Röckmann, T., Brenninkmeijer, C. A. M., Wollenhaupt, M., Crowley, J. N., and Crutzen, P. J.: Measurement of the isotopic fractionation of $^{15}\text{N}^{14}\text{N}^{16}\text{O}$, $^{14}\text{N}^{15}\text{N}^{16}\text{O}$ and $^{14}\text{N}^{14}\text{N}^{18}\text{O}$ in the UV photolysis of nitrous oxide, *Geophys. Res. Lett.*, 27(9), 1399–1402, 2000.
- Röckmann, T., Kaiser, J., Brenninkmeijer, C. A. M., Crowley, J. N., Borchers, R., Brand, W. A., and Crutzen, P. J.: Isotopic enrichment of nitrous oxide ($^{15}\text{N}^{14}\text{NO}$), ($^{14}\text{N}^{15}\text{NO}$), ($^{14}\text{N}^{14}\text{N}^{18}\text{O}$) in the stratosphere and in the laboratory, *J. Geophys. Res.*, 106(D10), 10 403–10 410, 2001.
- Röckmann, T. and Levin, I.: High-precision determination of the changing isotopic composition of atmospheric N_2O from 1990 to 2002, *J. Geophys. Res.*, 110, D21304, doi:10.1029/2005JD006066, 2005.
- Röthlisberger, R., Hutterli, M. A., Sommer, S., Wolff, E. W., and Mulvaney, R.: Factors controlling nitrate in ice cores: Evidence from the Dome C deep ice core, *J. Geophys. Res.*, 105(D16), 20 565–20 572, 2000.
- Röthlisberger, R., Hutterli, M. A., Wolff, E. W., Mulvaney, R., Fischer, H., Bigler, M., Goto-Azuma, K., Hansson, M. E., Ruth, U., Siggaard-Andersen, M. L., and Steffensen, J. P.: Nitrate in Greenland and Antarctic ice cores: a detailed description of post-depositional processes, *Ann. Glaciol.*, 35, 209–216, 2002.
- Russel, K. M., Galloway, J. N., Macko, S. A., Moody, J. L., and Scudlark, J. R.: Sources of 30 nitrogen in wet deposition to the Chesapeake bay region, *Atmos. Environ.*, 32(14/15), 2453–2465, 1998.
- Sander, S. P., Friedl, R. R., DeMore, W. B., Ravishankara, A. R., Golden, D. M., Kolb, C. E., Kurylo, M. J., Hampson, R. F., Huie, R. E., Molina, M. J., and Moortgat, G. K.: Chemical

Isotopic constraints of atmospheric Antarctic nitrate

J. Savarino et al.

- kinetics and photochemical data for use in stratospheric modeling, supplement to evaluation 12: Update of key reactions, JPL Publication 00-003, Evaluation number 13, 2000.
- Sander, S. P., Ravishankara, A. R., Golden, D. M., Kolb, C. E., Kurylo, M. J., Molina, M. J., Finlayson-Pitts, B. J., and Moortgat, G. K.: Chemical kinetics and photochemical data for use in atmospheric studies, JPL Publication 02-25, Evaluation number 14, 2003.
- Santacesaria, V., MacKenzie, A. R., and Stefanutti, L.: A climatological study of polar stratospheric clouds (1989–1997) from LIDAR measurements over Dumont d'Urville (Antarctica), Tellus Series B-Chemical and Physical Meteorology, 53(3), 306–321, 2001.
- Santee, M. L., Manney, G. L., Livesey, N. J., and Read, W. G.: Three-dimensional structure and evolution of stratospheric HNO_3 based on UARS Microwave Limb Sounder measurements, J. Geophys. Res., 109, D15306, doi:10.1029/2004JD004578, 2004.
- Santee, M. L., Read, W. G., Waters, J. W., Froidevaux, L., Manney, G. L., Flower, D. A., Jarnot, R. F., Harwood, R. S., and Peckham, G. E.: Interhemispheric differences in polar stratospheric HNO_3 , H_2O , ClO , and O_3 , Science, 267(5199), 849–852, 1995.
- Schaap, M., Muller, K., and ten Brink, H. M.: Constructing the European aerosol nitrate concentration field from quality analysed data, Atmos. Environ., 36(8), 1323–1335, 2002.
- Shallcross, D. E., Biggs, P., CanosaMas, C. E., Clemitchshaw, K. C., Harrison, M. G., Alanon, M. R. L., Pyle, J. A., Vipond, A., and Wayne, R. P.: Rate constants for the reaction between OH and CH_3ONO_2 and $\text{C}_2\text{H}_5\text{ONO}_2$ over a range of pressure and temperature, J. Chemical Society-Faraday Transactions, 93(16), 2807–2811, 1997.
- Sigman, D. M., Casciotti, K. L., Andreani, M., Barford, C., Galanter, M., and Böhlke, J. K.: A bacterial method for the nitrogen isotopic analysis of nitrate in seawater and freshwater, Anal. Chem., 73, 4145–4153, 2001.
- Stiller, G. P., Tsidu, G. M., von Clarmann, T., Glatthor, N., Hopfner, M., Kellmann, S., Linden, A., Ruhnke, R., Fischer, H., Lopez-Puertas, M., Funke, B., and Gil-Lopez, S.: An enhanced HNO_3 second maximum in the Antarctic midwinter upper stratosphere 2003, J. Geophys. Res., 110, D20303, doi:10.1029/2005JD006011, 2005.
- Thiemens, M. H.: Mass-independent isotope effects in planetary atmospheres and the solar system, Science, 283, 341–345, 1999.
- Thiemens, M. H. and Heidenreich III, J. E.: The Mass-independent fractionation of oxygen: A novel isotope effect and its possible cosmochemical implications, Science, 219, 1073–1075, 1983.
- Thiemens, M. H., Savarino, J., Bao, H., and Farquhar, J.: Mass independent isotope composi-

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- tions in terrestrial and extraterrestrial solids and their applications, *Acc. Chem. Res.*, 34(8), 645–652, 2001.
- Toohey, D. W., Brune, W. H., and Anderson, J. G.: Rate-Constant for the Reaction $\text{Br}+\text{O}_3 \rightarrow \text{BrO}+\text{O}_2$ from 248-K to 418-K – Kinetics and Mechanism, *Int. J. Chem. Kinet.*, 20(2), 131–144, 1988.
- Toyoda, S., Yoshida, N., Urabe, T., Nakayama, Y., Suzuki, T., Tsuji, K., Shibuya, K., Aoki, S., Nakazawa, T., Ishidoya, S., Ishijima, K., Sugawara, S., Machida, T., Hashida, G., Morimoto, S., and Honda, H.: Temporal and latitudinal distributions of stratospheric N_2O isotopomers, *J. Geophys. Res.*, 109, D08308, doi:10.1029/2003JD004316, 2004.
- Tuzson, B.: Symmetry specific study of ozone isotopomer formation, PhD-Thesis, Ruprecht-Karls Universität, Heidelberg, 2005.
- Van Allen, R., Liu, X., and Murcay, F. K.: Seasonal variation of atmospheric nitric acid over the South Pole in 1992, *Geophys. Res. Lett.*, 22(1), 49–52, 1995.
- van den Ende, D., Stolte, S., Cross, J. B., Kwei, G. H., and Valentini, J. J.: Evidence for two different transition states in the reaction of $\text{NO}+\text{O}_3 \rightarrow \text{NO}_2+\text{O}_2$, *J. Chem. Phys.*, 77(4), 2206–2208, 1982.
- Viswanathan, R. and Raff, L. M.: Theoretical investigations of the reaction dynamic of polyatomic gas-phase systems: The O_3+NO reaction, *J. Phys. Chem.*, 87, 3251–3266, 1983.
- von Glasow, R. and Crutzen, P. J.: Model study of multiphase DMS oxidation with a focus on halogens, *Atmos. Chem. Phys.*, 4, 589–608, 2004.
- von Glasow, R., von Kuhlmann, R., Lawrence, M. G., Platt, U., and Crutzen, P. J.: Impact of reactive bromine chemistry in the troposphere, *Atmos. Chem. Phys.*, 4, 2481–2497, 2004.
- von Savigny, C., Ulasi, E. P., Eichmann, K. U., Bovensmann, H., and Burrows, J. P.: Detection and mapping of polar stratospheric clouds using limb scattering observations, *Atmos. Chem. Phys.*, 5, 3071–3079, 2005.
- Wada, E., Shibata, R., and Torii, T.: N-15 Abundance in Antarctica – Origin of Soil-Nitrogen and Ecological Implications, *Nature*, 292(5821), 327–329, 1981.
- Wagenbach, D., Legrand, M., Fischer, H., Pichlmayer, F., and Wolff, E. W.: Atmospheric near-surface nitrate at coastal Antarctic sites, *J. Geophys. Res.*, 103(D9), 11 007–11 020, 1998.
- Wagnon, P., Delmas, R. J., and Legrand, M.: Loss of volatile acid species from the upper firm layers at Vostok, Antarctica, *J. Geophys. Res.*, 104(D3), 3423–3431, 1999.
- Warneck, P.: Chemistry of the natural atmosphere, 927 pp., Academic Press, San Diego, 2000.

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- Wolff, E.: Nitrate in polar ice, in: *Ice core studies of global biogeochemical cycles*, edited by: Delmas, R., pp. 195–224, Springer-Verlag, New York, 1995.
- Wolff, E., Legrand, M., and Wagenbach, D.: Coastal Antarctic aerosol and snowfall chemistry, *J. Geophys. Res.*, 103(D), 10927–10934, 1998.
- 5 Wolff, E. W., Jones, A. E., Martin, T. J., and Grenfell, T. C.: Modelling photochemical NO_x production and nitrate loss in the upper snowpack of Antarctica, *Geophys. Res. Lett.*, 29(20), 1944, doi:10.1029/2002GL015823, 2002.
- Zahn, A., Franz, P., Bechtel, C., Grooß, J.-U., and Röckmann, T.: Modelling the budget of middle atmospheric water vapour isotopes, *Atmos. Chem. Phys.*, 6, 2073–2090, 2006.
- 10 Zeller, E. J. and Dreschhoff, G. A. M.: Anomalous Nitrate Concentrations in Polar Ice Cores – Do They Result from Solar Particle Injections into the Polar Atmosphere, *Geophys. Res. Lett.*, 22(18), 2521–2524, 1995.
- Zeller, E. J., Dreschhoff, G. A. M., and Laird, C. M.: Nitrate Flux on the Ross Ice Shelf, Antarctica and Its Relation to Solar Cosmic-Rays, *Geophys. Res. Lett.*, 13(12), 1264–1267, 1986.
- 15 Zeller, E. J. and Parker, B. C.: Nitrate Ion in Antarctic Firn as a Marker for Solar-Activity, *Geophys. Res. Lett.*, 8(8), 895–898, 1981.
- Zhang, H., Wennberg, P. O., Wu, V. H., and Blake, G. A.: Fractionation of (NNO)-N-14-N-15-O-16 and (NNO)-N-15-N-14-O-16 during photolysis at 213 nm, *Geophys. Res. Lett.*, 27(16), 2481–2484, 2000.
- 20 Zhang, J. S., Miau, T. T., and Lee, Y. T.: Crossed molecular beam study of the reaction Br+O₃, *J. Phys. Chem. A*, 101(37), 6922–6930, 1997.

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Table 1. Sampling and analytical methodologies for the aerosol collections used for the high-volume and low volume aerosol collector.

	Low-Vol	Hi-Vol
Collection interval	1–3 days	10–15 days
Location	At the rear of building “Labo 3”, 1.8 m above ground	20 m away from building “Labo 3”, 1 m above ground
Filter media	Ø47 mm, 0.4 µm PTFE	20.3×25.4 cm glass filter, mounted with four slotted 12.7×17.8 cm glass filter in series (impactor stages)
Pumping flow	0.01 m ³ min ⁻¹	Typically 1.2 m ³ min ⁻¹

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Table 2. Weighted average of the two size ranges for $\delta^{15}\text{N}$, $\delta^{18}\text{O}$, $\Delta^{17}\text{O}$, and atmospheric mass loading of nitrate as recorded at Dumont d'Urville in 2001. $\delta^{18}\text{O}$ values are the ones obtained by the N_2O decomposition method (Kaiser et al., 2006b¹). Standard deviations are 0.2, 0.9 and 0.5‰ for $\delta^{15}\text{N}$, $\delta^{18}\text{O}$, $\Delta^{17}\text{O}$, respectively (see text for details).

Dates ^a	Atmospheric concentration (ng m ⁻³)	$\delta^{15}\text{N}$ (‰)/air	$\delta^{18}\text{O}$ (‰)/SMOW	$\Delta^{17}\text{O}$ ^b (‰)
6 Jan 2001	41.8	-20.4	63.2	23.6
16 Jan 2001	13.6	-18.4	63.2	20.8
30 Jan 2001	26.5	-22.3	64.1	23.0
9 Feb 2001	21.7	-11.9	59.8	20.5
19 Feb 2001	17.3	-16.6	66.8	22.8
5 March 2001	10.1	-11.4	61.6	16.2
27 March 2001	11.3	-6.7	78.0	25.8
10 April 2001	17.7	-11.4	85.0	28.9
19 April 2001	11.5	-7.6	85.6	30.1
5 May 2001	16.2	0.5	86.3	30.6
16 May 2001	10.8	0.0	75.2	27.4
31 May 2001	9.5	0.5	71.0	26.2
18 June 2001	12.7	0.7	77.6	30.6
6 July 2001	22.9	5.0	70.2	27.4
19 July 2001	14.7	9.9	103.4	38.3
3 Aug 2001	57.0	6.4	97.9	34.8
7 Aug 2001	23.1	10.0	111.5	40.5
22 Aug 2001	50.8	10.8	111.0	41.0
12 Sep 2001	36.4	-0.1	100.8	36.5
27 Sep 2001	56.8	-12.3	98.1	36.7
9 Oct 2001	60.3	-21.1	91.2	35.7
23 Oct 2001	95.8	-28.9	84.9	31.3
2 Nov 2001	85.1	-46.9	74.9	27.7
16 Nov 2001	156.8	-36.0	72.6	30.4
28 Nov 2001	165.3	-29.3	74.3	28.5
14 Dec 2001	151.8	-28.9	72.3	27.5
22 Dec 2001	99.5	-38.2	70.7	27.0

^a Starting date of collection

^b Calculated using Eq. (2) (see text)

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Table 3. Principal statistics of the four periods defining the seasonal cycles of inorganic nitrate particles at DDU.

	Period 1 (Jan to March)	Period 2 (March to mid July)	Period 3 (mid-July to Sep)	Period 4 (Oct to Jan)
NO_3^- (ng g $^{-1}$)				
Max	41.8	22.9	57.0	165.3
Min	13.6	9.5	23.1	60.3
Mean±s.d.	24.2±11.0	13.7±4.2	44.8±14.8	116.4±41.1
$\delta^{15}\text{N}$ (‰)				
Max	-11.9	9.9	10.8	-21.1
Min	-22.3	-11.4	-12.3	-46.9
Mean±s.d.	-17.9±4.0	-2.0±7.0	3.0±9.5	-32.7±8.4
$\delta^{18}\text{O}$ (‰)				
Max	66.8	103.4	111.5	91.2
Min	59.8	61.6	97.9	70.7
Mean±s.d.	63.4±2.5	79.4 ±11.5	103.9±6.9	77.2±7.7
$\Delta^{17}\text{O}$ (‰)				
Max	23.6	38.3	41.0	35.7
Min	20.5	16.2	34.8	27.0
Mean±s.d.	22.1±1.4	28.2±5.5	37.9±2.7	29.8±3.1

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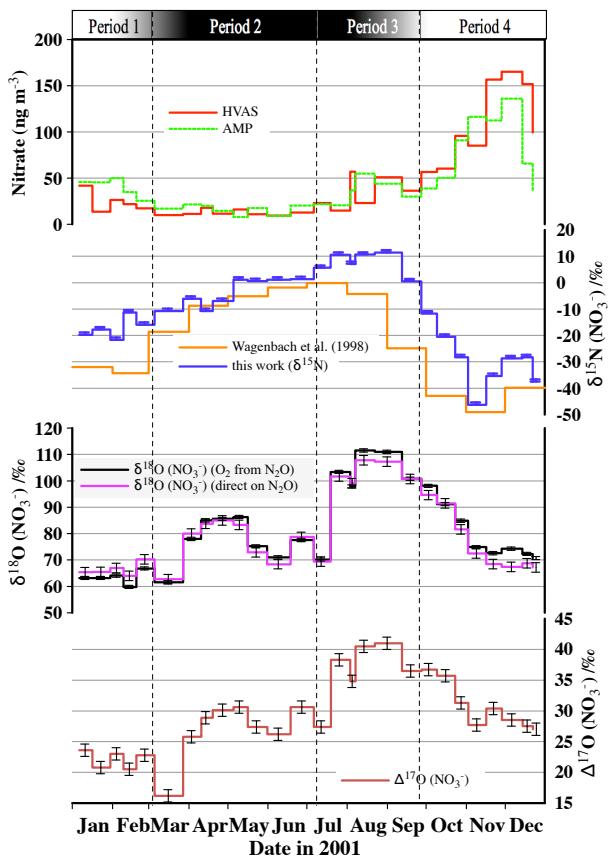


Fig. 1.

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Fig. 1. From the top to bottom: top banner symbolizes the nighttimes and daytimes of the year. **(a)** Particulate nitrate concentration as recorded by our HiVol aerosol sampler (red) and by the aerosol monitoring program (green). For the latter, data has been averaged according to the same time window than the HVAS collection time. Concentrations exhibit a strong seasonal variation with maximum observed in late spring (Nov–Dec). A significant secondary peak is observed in late winter (Aug–Sep) **(b)** $\delta^{15}\text{N}(\text{NO}_3^-)$ as observed by this study (blue) compared with the published data of Wagenbach et al. (1998). Both profiles are very similar and display strong negative $\delta^{15}\text{N}$ values in late spring. **(c)** Same as (b) but for $\delta^{18}\text{O}$. We have used two techniques to measure $\delta^{18}\text{O}(\text{NO}_3^-)$. The former uses the thermal decomposition of N_2O on gold (black line) and the analysis is performed on produced O_2 , the latter uses directly N_2O as the working gas (pink line). There is an excellent match between the two techniques. As for ^{15}N , $\delta^{18}\text{O}(\text{NO}_3^-)$ values vary seasonally with their maximum observed in late winter (ca. +110‰). A secondary peak is observed during polar sunset (April–June). **(d)** Same as (c) but for $\Delta^{17}\text{O}(\text{NO}_3^-)$. $\Delta^{17}\text{O}$ values exhibit the same feature than $\delta^{18}\text{O}$ with a maximum value of ca. +40‰ in late winter. This is one of the highest oxygen isotopic anomalies ever recorded for nitrate.

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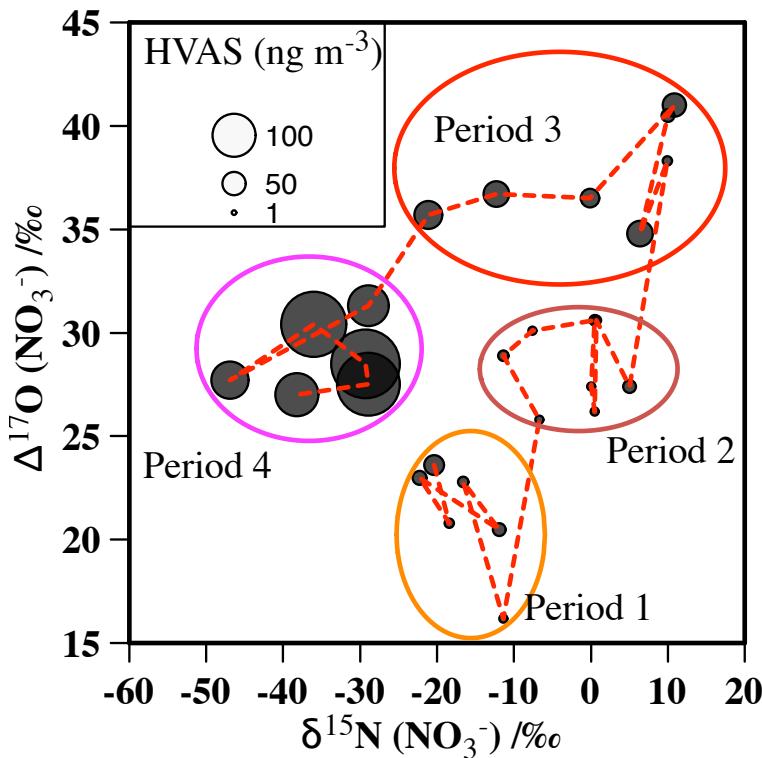


Fig. 2. Plot of $\Delta^{17}\text{O}$ vs. $\delta^{15}\text{N}(\text{NO}_3^-)$ at DDU over the course of year 2001, showing the seasonal variations in both N and O isotopic compositions. The size of the circles corresponds to the atmospheric particulate nitrate concentrations. The four periods discriminated from the concentration time series are highlighted in terms of their isotopic characteristics and show that distinct isotopic signatures are associated with each of them, hence justifying this separation into separate periods. Periods 1 and 2 are best explained by tropospheric isotopic chemistry. Period 3 corresponds to stratospheric nitrate injection while period 4 is explained by inland snow re-emissions.

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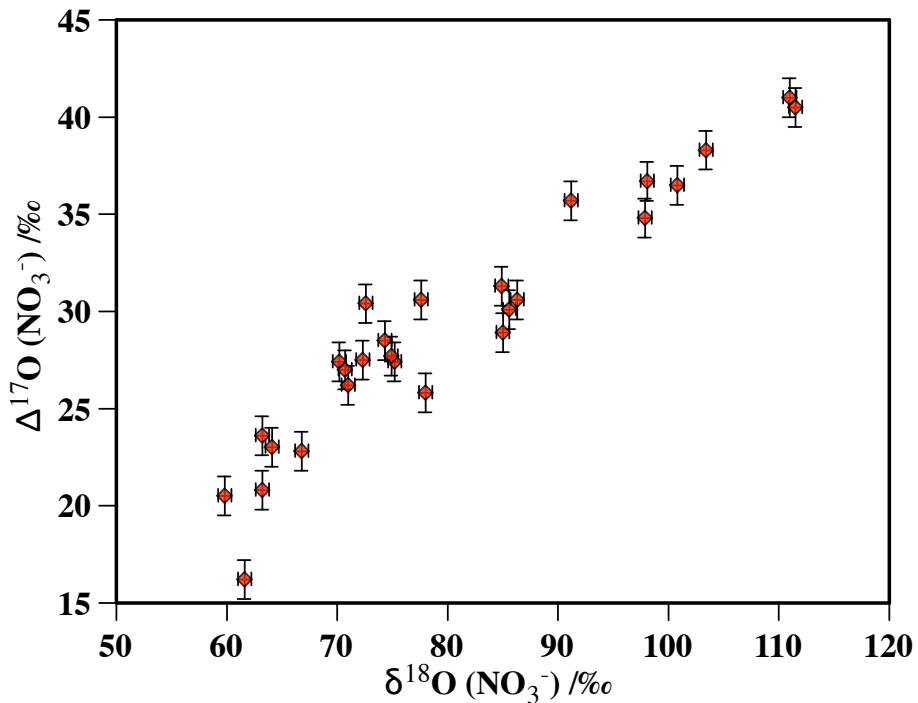
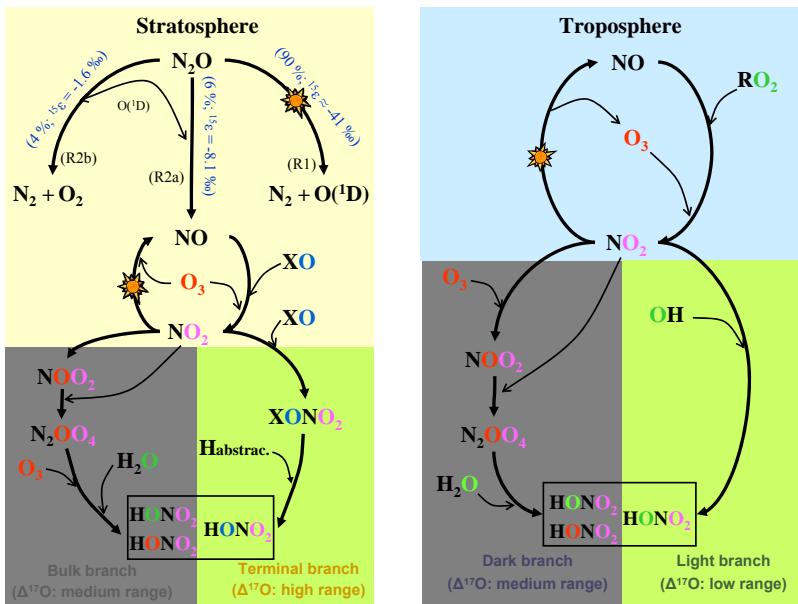


Fig. 3. Correlation between $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$. The good correlation between these two variables indicates that $\delta^{18}\text{O}$ is the result of ozone oxygen atom transfer and not by a secondary mass dependent fractionation process.

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**Fig. 4.**

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Fig. 4. Chemical cycling of nitrogen oxides (NO_x) in the stratosphere and troposphere. As described in the text, the $\delta^{15}\text{N}$ signature in of stratospheric NO is gained from the dissociation reactions of N_2O , the primary stratospheric NO_x source (top left). Then, NO enters the chemical interactions cycle with ozone and halogen oxides (bottom left) and the resulting NO_2 acquires an isotopic anomaly dependent on the reactivity of NO with respect to oxidant species (O_3 , XO). NO_2 is then converted in to nitric acid through different pathways, incorporating different amounts of O_3 -derived oxygen atoms, hence leading to varying isotopic anomalies. This scheme constitutes the high range of $\Delta^{17}\text{O}$ values. The tropospheric scheme is based on previous work of Michalski et al. (2003) where nitrate get its oxygen isotopic anomaly only from ozone interaction. Nighttime and daytime NO_x chemistry lead to medium and low ranges of $\Delta^{17}\text{O}$ values. Oxygen atoms are color coded according to their isotopic anomaly, determined by the reaction between parent molecules. Homogeneous and heterogeneous reactions are not specified in these schemes, since some may proceed both pathways (e.g. $\text{BrONO}_2 + \text{H}_2\text{O} \rightarrow \text{HONO}_2 + \text{HOBr}$). This has no major influence on the ^{17}O anomaly budget presented here since gas-to-particle conversions are expected to obey mass-dependent relationships. Only isotopically significant reaction products are shown in this figure.

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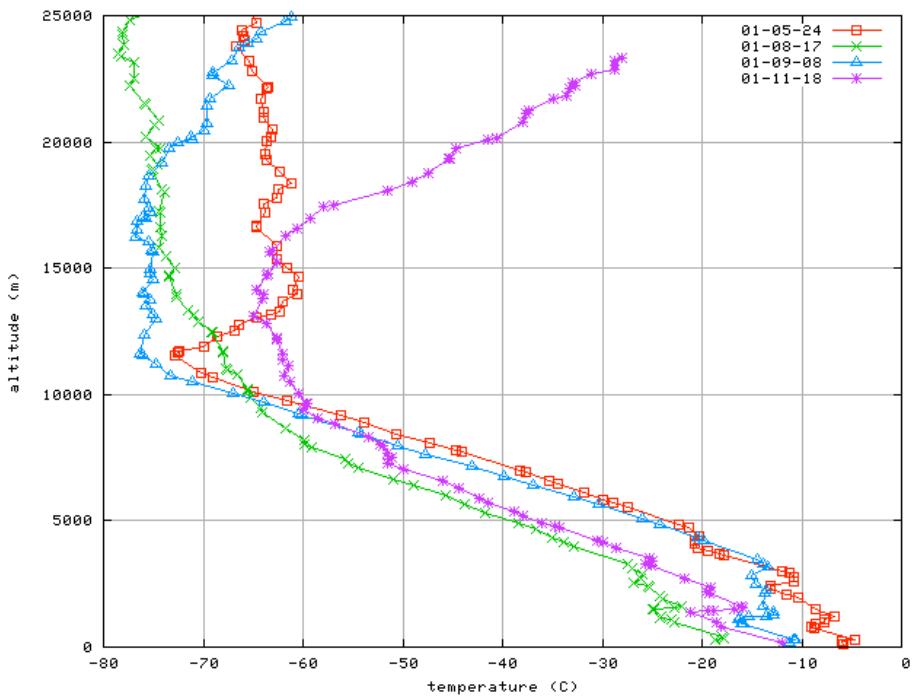


Fig. 5. Typical temperature profiles at four different periods of the year measured by balloon sounding above DDU in 2001. At ground level, there is a year-round inversion layer ($h \approx 1$ km) while during the late winter/early spring period, the tropopause barrier ($h \approx 11$ km) is weaker than the rest of the year (Data courtesy of Christine David, Service d'Aéronomie, Paris), favoring intrusion of stratospheric air masses into the troposphere.

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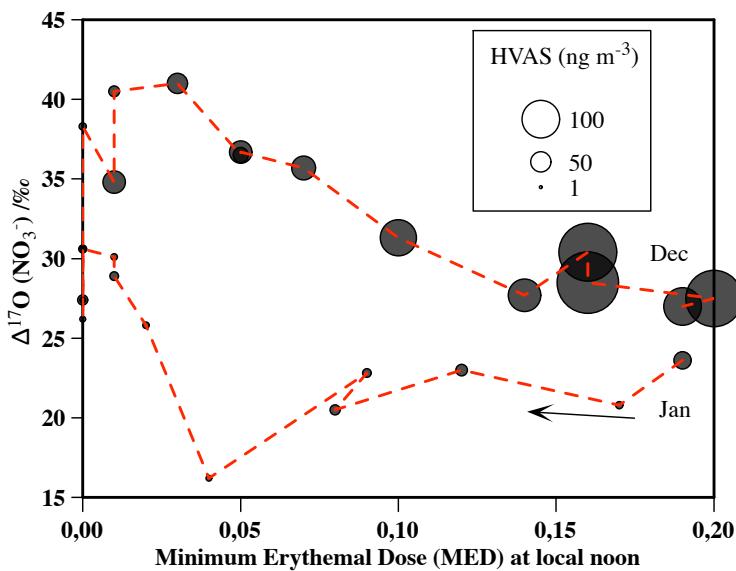


Fig. 6. Yearly cycle of $\Delta^{17}\text{O}(\text{NO}_3^-)$ as a function of local insolation (proportional to daily minimum erythema dose (MED)). The size of the circles refer to the concentration of atmospheric nitrate for each sample. Maximum MED correspond to summer conditions, while minimum MED (0) correspond to winter conditions. $\Delta^{17}\text{O}$ shows a tendency to higher values in winter and lower values in summer, consistently with the developments by Michalski et al. (2003) and the details given in the text. Late winter values (increasing MED) are shifted to higher $\Delta^{17}\text{O}$ values because of the influence of the stratosphere: the denitrification occurring in mid-winter leads to a sudden increase by ca. 8% in $\Delta^{17}\text{O}$ values, with a little concurrent concentration increase (period 3, see text for details). The large concentration peak (largest circles in the figure) is still isotopically influenced by the stratospheric source of nitrate to a lower extent, due to snowpack processing and tropospheric oxidation mechanisms for re-emitted NO_x (period 4, see text for details).

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