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Signature of Arctic surface ozone depletion events in the isotope anomaly ($\Delta^{17}\text{O}$) of atmospheric nitrate

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depletion and $\Delta^{17}\text{O}$ in
atmospheric nitrate**

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Pronounced signature of arctic surface ozone depletion events after polar sunrise on $\Delta^{17}\text{O}$ in atmospheric nitrate

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Abstract

We report in this paper the first measurements of the isotopic anomaly of oxygen in Arctic atmospheric inorganic nitrate. Data and samples were collected at Alert, Nunavut, Canada (82°30' N, 62°19' W) in spring 2004. Focusing on the polar sunrise period, characterized by the occurrence of severe boundary layer ozone depletion events (ODEs), our data show a significant correlation between the evolution of atmospheric ozone (O₃) mixing ratios and $\Delta^{17}\text{O}$ in nitrate ($\Delta^{17}\text{O}(\text{NO}_3^-)$). This relationship can be expressed as: $\Delta^{17}\text{O}(\text{NO}_3^-)/\text{‰} = 0.15 \text{ O}_3 / (\text{nmol mol}^{-1}) + 28.6$, with $R^2 = 0.70$ ($n = 12$), for $\Delta^{17}\text{O}(\text{NO}_3^-)$ ranging between 29 and 34‰. To quantitatively interpret this relationship, we derive from mechanisms at play in the arctic boundary layer isotopic mass-balance equations, which depend on the concentrations of reactive species and their isotopic characteristics. Changes in the relative importance of O₃, RO₂ and BrO in the oxidation of NO_x during ODEs, and the large isotopic anomalies that O₃ and BrO carry, are the driving force for the high variability in the measured $\Delta^{17}\text{O}(\text{NO}_3^-)$. BrONO₂ hydrolysis is found to be the major source of nitrate in the arctic boundary layer, in agreement with recent modeling studies. In addition, the isotopic fingerprint of the activity of ozone in a relatively stable compound appears somewhat promising in the perspective of using the isotopic composition of nitrate embedded in polar ice-cores as a paleo-indicator of the atmospheric ozone level that may yield an indirect proxy for the oxidative power of past atmospheres.

1 Introduction

Stable isotope studies have been used for a long time to constrain fluxes and processes taking place at the surface of the Earth. Mass-dependent processes such as kinetics or thermodynamic equilibria lead to a quasi-linear relationship between oxygen isotope ratios in oxygen bearing compounds: $\delta^{17}\text{O} \approx 0.52 \delta^{18}\text{O}$, with the isotopic content reported as enrichments with respect to a standard reference:

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$\delta/\text{‰} = (R_{\text{sample}}/R_{\text{SMOW}} - 1) \times 1000$ where R is the $^{17}\text{O}/^{16}\text{O}$ or $^{18}\text{O}/^{16}\text{O}$ ratio in the sample or the Standard Mean Ocean Water (SMOW) taken as a reference (Thiemens, 1999). Due to a mass-independent formation process experimentally discovered by Thiemens and Heidenreich (1983), the oxygen isotopic composition in atmospheric O₃ does not fit the terrestrial fractionation line produced by mass-dependent processes (Mauersberger et al., 2001). This anomaly, termed by several authors as the Mass Independent Fractionation (MIF) contribution, is quantified as a deviation from the mass-dependent fractionation line often using the following linear expression: $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$. Tropospheric O₃ exhibits large $\Delta^{17}\text{O}$ values (up to 35‰ as measured by Krankowsky et al., 1995, and Johnston and Thiemens, 1997, and calculated by Lyons, 2001) and there is considerable evidence that this anomaly is transmitted through chemical reactions in the atmosphere to other oxygen bearing compounds (Thiemens, 1999). Michalski et al. (2003) showed that atmospheric models could reproduce the temporal evolution of the anomaly measured in particulate nitrate oxygen in a polluted marine boundary layer. Here we present the coupled evolution of $\Delta^{17}\text{O}(\text{NO}_3^-)$ and O₃ at Alert, Nunavut (82°30' N, 62°19' W) during the polar sunrise period in springtime 2004. At Alert, like everywhere else in the coastal Arctic, surface O₃ is subject to severe depletion events (ODE) in springtime (Bottenheim et al., 1986), during which the ozone mixing ratio can decrease from around 40 parts-per-billion in volume (nmol mol^{-1}), its mean background level, to values as low as 1 nmol mol^{-1} and below, and remain at this level for several days (Bottenheim et al., 2002). Ozone depletion is due to catalytic cycles involving ocean-originating halogen oxides and radicals such as BrO (Hönninger and Platt, 2002) but the understanding of the processes governing the release of such compounds from the surface is still a subject of debate (Dominé and Shepson, 2002).

To the best of our knowledge, our measurements are the first measurements of $\Delta^{17}\text{O}$ in atmospheric nitrate in coastal arctic, which therefore enhances the global representation of this variable. Permanent sunshine, sea-ice proximity and the associated halogen chemistry responsible for ODEs make the interpretation of our results a chal-

lenge for existing theories about isotopic anomalies in atmospheric nitrate and about ODE-related chemical mechanisms. Our analysis demonstrates the power of this isotopic tool to assess the magnitude of the reaction pathways leading to the formation of nitrate in various environments.

2 Experimental

2.1 Measurement site and sample collection

Measurements and sample collection were performed at the Global Atmospheric Watch (GAW) observatory and at the Special Studies Trailer (SST) which are located on a plateau, 190 m above sea level and 6 km to the South-South West of Canadian Forces Station Alert, the main base at the coast of Northern Ellesmere Island.

Surface O₃ was measured at the SST site with a UV absorption instrument (model TEI 49-C, Thermo Environmental Instruments, Inc., Franklin MA, USA), calibrated against standards traceable to the National Institute of Standards and Technology (NIST). This instrument was terminated on 4 May. In order to analyze ozone measurements during the entire period of isotopic measurements, the gap between 4 and 18 May is filled by using the raw (uncalibrated) O₃ GAW dataset, and recalibrating using a linear regression against the SST ozone dataset over the overlapping period of measurements. The time resolution for ozone measurements is 30 min.

Samples were collected between 29 March 2004 and 18 May 2004, on cellulose acetate filters (Whatman 41) on a semi-weekly basis using a high volume aerosol sampler operated by Environment Canada since 1980 (see e.g. Sirois and Barrie, 1999, for details on sampling procedures). Each of the 14 samples was collected over a period of 3 or 4 days.

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2.2 Aerosol chemical composition analysis

First, ionic species trapped on the filter were dissolved in 40 ml of ultra-pure water (Millipore). For each of the 14 aqueous samples, an aliquot (100 μ l) was taken out for the ion-chromatography analysis, and the rest of the sample was available for the isotopic analysis.

Inorganic anions (Cl^- , Br^- , NO_3^- and SO_4^{2-}) and cations (Na^+ , Ca^{2+} , Mg^{2+} , K^+ and NH_4^+) were measured using the ion-chromatography system described by Jaffrezo et al. (1998). Four field blanks were performed to assess the contribution of possible contaminations induced by the manipulation of filters and by the filters themselves, as Whatman 41 filters have been subject to questions regarding their initial loading in some trace elements (Watts et al., 1987). Field blank samples were obtained by loading clean filters in the sampler, keeping them there for 5 min and packing them exactly like the actual samples. The contamination was estimated by dividing the amount of species collected on the filter by the typical volume pumped through regular filters (ca. 10 000 m^3).

For the samples presented here, the blank contribution, integrating all possible sources of contaminations, represents less than 4% for all the measured cations. The contribution of contamination to the total measured NO_3^- , SO_4^{2-} and Br^- is less than 1%. Only Cl^- measurements are affected by a 10% blank effect. It must also be noted that the isotopic measurements undertaken here are not sensitive to non optimal aerosol collection efficiencies (though estimated by Sirois and Barrie, 1999, to be >95%, based on previous work by Watts et al., 1987). We therefore mainly use the chromatographic measurements to estimate the relative composition of the aerosol, although the absolute concentration may be affected by a 10% bias.

Existing literature on the collection of atmospheric inorganic nitrate by means of high volume sampling on a variety of media show that none is devoid of sampling artefact (e.g. Schaap et al., 2002). The use of cellulose acetate filter leads to the quantitative collection of both aerosol nitrate (p-NO_3^- , in the form of ammonium nitrate and

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nitric acid) and gaseous nitric acid (HNO_3), the sum of which being referred to as total inorganic nitrate (TIN, [Bottenheim et al., 1993](#)). However, it is worth keeping in mind that the measurements of $\Delta^{17}\text{O}(\text{NO}_3^-)$ based on filter collection are not sensitive to the chemical form of nitrate (either gaseous HNO_3 or particulate NO_3^-) because any fractionation occurring at the interface between the gas phase and the particulate phase obeys mass-dependent relationships, without affecting the $\Delta^{17}\text{O}$ value. In what follows, we present and discuss $\Delta^{17}\text{O}(\text{NO}_3^-)$ measurements, which represent the integrated isotopic anomaly of oxygen in TIN.

2.3 Isotopic analysis

The isotope analysis was performed using the method developed by [Michalski et al. \(2002\)](#). Chloride and sulphate were precipitated out of the samples, using BaCl_2 for SO_4^{2-} and subsequent removal of chloride using an Ag-form ion-exchange resin (AG 50W-X8 200-400 Mesh size, Bio-Rad, Hercules CA, USA). Nitrate was then isolated by Dionex ion chromatography and converted to silver nitrate using a ion exchange column (Dionex AMMS III, 4 mm) where the usual regenerant was replaced by Ag_2SO_4 (2.5 mmol.l^{-1}). The isotopic composition of oxygen in AgNO_3 was determined by thermal decomposition at 550°C in a vacuum line and analysis on a isotope ratio mass spectrometer (Dual Inlet IRMS, Finnigan MAT 253). All the analytical steps were simultaneously performed on nitrate standards (International Atomic Energy Agency USGS 34 and USGS 35, with $\Delta^{17}\text{O}=0\%$ for USGS 34 and 21.1% for USGS 35, [Böhlke et al., 2003](#)). Standards were only used for the correction of biases related to a blank effect represented by the mixing of $0.14 \mu\text{mol}$ of ambient O_2 ($\Delta^{17}\text{O}(\text{O}_2)=0$) with samples whose sizes range between 1 and $2 \mu\text{mol}$ of O_2 . A mass balance calculation derived by [Michalski et al. \(2002\)](#) allows for the correction of this effect on the $\Delta^{17}\text{O}$ values. Uncertainties on the $\Delta^{17}\text{O}(\text{NO}_3^-)$ values originate from the internal variability of the mass spectrometer (accounting for about $\pm 0.3\%$ for a detector voltage of 500 mV in average) and from the correction of the blank effect (accounting for about $\pm 1.0\%$). Both of

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these sources of uncertainty are correlated to the size of the O₂ samples. Because of a too low concentration of nitrate in two samples, the thermal decomposition yielded a too small amount of O₂ to be reliably analyzed. Therefore we present here the data obtained on 12 samples in terms of their isotopic composition.

From the $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values we calculated $\Delta^{17}\text{O}$ using the linear expression: $\Delta^{17}\text{O} = \delta^{17}\text{O} - \lambda \times \delta^{18}\text{O}$ with $\lambda = 0.52$, which is consistent with most articles dealing with oxygen isotopes in nitrate (e.g. [Thiemens, 1999](#); [Michalski et al., 2003](#); [Alexander et al., 2004](#)). We are aware that alternative expressions have been proposed for the mathematical expression of $\Delta^{17}\text{O}$ (see for instance [Thiemens, 1999](#); [Miller, 2002](#); [Kaiser et al., 2004](#)), the best of which being the non approximated and standard-independent expression proposed by [Miller \(2002\)](#):

$$\Delta^{17}\text{O} = \left(\frac{1 + \delta^{17}\text{O}}{1 + \delta^{18}\text{O}} - 1 \right) \quad \text{with} \quad \lambda' = 0.525 \quad (1)$$

This expression unambiguously defines $\Delta^{17}\text{O}$ as the deviation from the mass-dependent fractionation curve in term of a power law relationship between isotope ratios ([Miller, 2002](#)). Since we focus on nitrate, characterized by large and strongly variable heavy oxygen enrichments and anomalies, the use of this definition is not as crucial as for slightly anomalous species (e.g. N₂O), for which the historical linear definition ([Thiemens, 1999](#)) may be responsible for inaccuracies and interpretation errors, as pointed out by [Kaiser et al. \(2004\)](#). For instance, using the linear expression for our nitrate samples (see data in Table 1) results in an overestimation of $\Delta^{17}\text{O}$ of $(0.74 \pm 0.07)\text{‰}$ with respect to the non-linear expression ([Miller, 2002](#)), which lies within the range of the stated uncertainty (see above). In the case of nitrate, the choice of the expression for $\Delta^{17}\text{O}$ has therefore very little influence on the results.

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3 Results

We present the data acquired in Alert, Nunavut, between 29 March 2004 and 18 May 2004. They mainly consist of meteorological observations (temperature, wind speed and direction), ozone mixing ratios, aerosol inorganic composition and the triple isotopic composition of oxygen in inorganic nitrate.

3.1 Meteorology

During the course of the measurement campaign, sunlight was permanent. The mean daily temperature ranged between -30 and -10°C , gradually increasing over the measurement campaign. Cumulative precipitation (snow) was 22 mm during this period, with only one major (>8 mm) snowfall occurring on 12 April. Weather conditions were most of the time calm and clear.

3.2 Ozone

The ozone mixing ratio was highly variable during this period, and its time series features several drastic drops, commonly referred to as ozone depletion events (ODEs) that are ubiquitously observed in coastal polar regions (see also high resolution time series on Fig. 3) (Tarasick and Bottenheim, 2002). To quantify the link between the ozone mixing ratio and the composition of aerosols, the O_3 mixing ratio is averaged over each sampling period (i.e. 3–4 days).

3.3 Particulate bromide and BrO

The Fig. 1 shows the coupled evolution of the ozone mixing ratio and the particulate bromide load. Particulate bromide (Br^-) ranged between 2 and 20 ng m^{-3} , and therefore represents a negligible fraction of the anionic load. However, elevated Br^- contents ($>10 \text{ ng m}^{-3}$) were associated with ozone depleted air masses, which is consistent with the observations first made by Barrie et al. (1988) at Alert. Since particulate bromide

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mainly originates from wet deposition of active bromine species such as Br and BrO, a covariation of BrO and Br⁻ is expected. However, as evidenced by [Lehrer et al. \(1997\)](#) and [Evans et al. \(2003\)](#), inferring BrO mixing ratio from Br⁻ is only possible for limited period of times.

Unfortunately no continuous record of BrO is currently available for the spring 2004 period at Alert, but on some occurrences the mixing ratio of BrO could be derived from Multi-Axis Differential Optical Absorption Spectroscopy (MAX-DOAS) measurements carried out at Alert or in its vicinity. [Morin et al. \(2005\)](#) have shown that on 22–23 April 2004, BrO ranged between 1–3 pmol mol⁻¹ (“normal” ozone) and 10 pmol mol⁻¹ (strong ODE). This is inline with measurements presented by [Hönninger et al. \(2004\)](#), carried out in the vicinity of Alert in spring 2004. Overall, there seems to be evidence that, even during the strongest ODEs, BrO never reached values significantly above 10 pmol mol⁻¹ in spring 2004.

3.4 Origin of air masses

Following the approach of [Bottenheim et al. \(2006\)](#)¹ and previous trajectory studies, 6-days backtrajectories ([Stohl et al., 1995](#); [Stohl and Seibert, 1998](#); [Stohl, 1998](#)) starting at Alert during the sampling period (March–April 2004) are used to identify the origin and history of air masses. The meteorological data used for trajectory calculations originates from the European Centre for Medium Range Weather Forcasts (ECMWF). The spatial resolution is T106, which correspond to a latitude/longitude resolution of 1.125° × 1.125°, the temporal resolution is 6 h and 60 levels are available in the vertical direction. It is worth pointing out that trajectories for surface sites calculated from large-scale meteorological analyses are certainly far from being very accurate. Although their usefulness is limited for very specific and small-scale events, they can nonetheless provide relevant information on the gross features when large numbers of

¹Bottenheim, J. and Chan, E.: A Trajectory Study Into the Origin of Spring Time A, J. Geophys. Res., accepted, 2006.

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trajectories are considered. Each backtrajectory represented in Fig. 2 is a mean of all the backtrajectories starting from Alert at 500 m altitude every 6 h during the collection period (about 3–4 days) of each sample. They provide an indication of the mean origin and history of air masses contributing to a given aerosol sample. Backtrajectories starting at 1 km altitude (not shown here) were also considered but the overall features were similar. Each mean trajectory (corresponding to an aerosol sample) is color-coded in Fig. 2 according to its particulate bromide content, which is indicative of the activity of the heterogeneous bromine chemistry responsible for ODEs.

The conclusions that can be drawn from the analysis of the Fig. 2 are in-line with other studies discussing the origin of ozone depleted air masses (e.g. Hopper et al., 1998; Morin et al., 2005; Bottenheim et al., 2006¹, and references therein). In most cases, drastic changes in the ozone mixing ratios observed at Alert at polar sunrise can be related to the movement of air masses. During the course of our measurement campaign, most air masses depleted in ozone were advected at low altitude above the Arctic Ocean before reaching the coastal sites.

3.5 Inorganic chemical composition of the aerosols

Our main focus being the analysis of the isotopic composition in TIN, we only present here a summary of our measurements of inorganic chemical composition of aerosols. Extensive reviews of the composition of inorganic aerosols observed at Alert can be found elsewhere (e.g. Sirois and Barrie, 1999).

The relative composition of aerosol in terms of inorganic anions was found to be rather invariant with time during April and May, but the total amount varied greatly. $\text{NO}_3^- + \text{SO}_4^{2-} + \text{Cl}^-$ ranges between 145 and 1900 ng m^{-3} , in which Cl^- , NO_3^- and SO_4^{2-} represent $(7 \pm 6)\%$, $(23 \pm 8)\%$ and $(69 \pm 8)\%$ of the molar composition respectively. As the chloride composition is affected by the strongest blank effect, and that halide chemistry is involved in ozone depletion, we prefer to use Na^+ for the estimation of the marine contribution to the aerosol loading. Using a molar sea salt ratio of 0.0603 (Holland, 1978), the calculated non-sea salt sulphate component (nss-SO_4^{2-}) is found to account

for more than 99% of the sulphate concentration. Aerosols collected during this study represent a mixture of sulphuric acid droplets and sea salt particles, on which inorganic nitrate is adsorbed (Sirois and Barrie, 1999).

We see no noticeable correlation between the concentration of inorganic nitrate and the origin of air masses (data not shown). Based on nitrate concentrations only, it is virtually impossible to estimate the different sources of particulate nitrate, as alkyl nitrates, peroxyalkyl nitrates (PANs) and other organic nitrates dominate the budget of nitrate in the Arctic. Thus, the variability in particulate nitrate concentrations does not provide any insight in the budget of nitrate (Sirois and Barrie, 1999).

3.6 Isotopic composition of oxygen in atmospheric inorganic nitrate

We report elevated ^{18}O enrichments, with $\delta^{18}\text{O}$ values ranging from 78 to 92‰. $\Delta^{17}\text{O}(\text{NO}_3^-)$ ranges between 29 and 34‰ (see Table 1). The large temporal variability of $\Delta^{17}\text{O}(\text{NO}_3^-)$ during this period is shown in Fig. 3. High isotopic enrichments and anomalies are to be expected in atmospheric nitrate: in terms of range, our measurements are consistent with previous measurements of $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$, such as those carried out by Michalski et al. (2003) (La Jolla, California: $\delta^{18}\text{O}(\text{NO}_3^-)=50\text{--}89\text{‰}$ and $\Delta^{17}\text{O}(\text{NO}_3^-)=20\text{--}31\text{‰}$ during a year-round sampling campaign). High $\delta^{18}\text{O}(\text{NO}_3^-)$ values were also reported in snow at high latitudes in the northern hemisphere. For example, Hastings et al. (2004) reported $\delta^{18}\text{O}(\text{NO}_3^-)$ values ranging between 65 and 80‰ in samples collected at Summit, Greenland. Heaton et al. (2004) also found high $\delta^{18}\text{O}(\text{NO}_3^-)$ values (60–85‰) in samples collected at Ny Ålesund, Svalbard. Finally, Alexander et al. (2004) measured $\Delta^{17}\text{O}(\text{NO}_3^-)$ in the Site A ice core in Greenland, with values ranging between 27 and 29‰.

In polluted boundary layer conditions, Michalski et al. (2003) have measured $\Delta^{17}\text{O}(\text{NO}_3^-)=23\text{--}25\text{‰}$ in March–May. Our measurements for the same period of the year are much higher and highly variable, with variations as large as 5‰ from one sample to the other. Most of these variations are associated to the occurrence of

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ODEs, during which $\Delta^{17}\text{O}(\text{NO}_3^-)$ drops to values as low as 29‰. A linear regression between $\Delta^{17}\text{O}(\text{NO}_3^-)$ and the average ozone mixing ratio over the collection period of each aerosol sample gives: $\Delta^{17}\text{O}(\text{NO}_3^-)/\text{‰} = 0.15 \text{ O}_3/(\text{nmol mol}^{-1}) + 28.6$, with $R^2=0.70$ ($n=12$), showing that a strong link exists between these two variables (see Fig. 4).

4 Discussion

In this section, we first review the current knowledge regarding the origin of the isotopic anomaly in atmospheric nitrate and adapt it to the conditions experienced in the arctic springtime.

Based on this analysis, we then derive from known chemical mechanisms a relationship between $\Delta^{17}\text{O}$ in inorganic nitrate and the relative magnitude of the processes involved in its formation. We test this relationship using measured or estimated variables during the course of the measurement campaign, using a simple Monte-Carlo approach.

4.1 Overview of the present theory about the origin of $\Delta^{17}\text{O}$ to atmospheric nitrate

Based on field measurements in coastal California and modeling, the large $\Delta^{17}\text{O}$ measured in atmospheric nitrate has been convincingly attributed by Michalski et al. (2003) to a transfer of the ozone oxygen isotope anomaly to atmospheric nitrate. In these conditions, it is well established that oxygen anomalies observed in stable compounds such as particulate nitrate are due to chemical interactions between their precursors (NO_x) and ozone. Our observations somewhat support this theory by bringing to light a co-evolution between the O_3 mixing ratio and the isotopic composition of oxygen in aerosol nitrate during ODEs, showing that O_3 mixing ratio and nitrate isotopes are intimately coupled. However, in the arctic lower troposphere in springtime BrO plays an important role and interacts greatly with ozone and NO_x (Platt and Hönninger, 2003).

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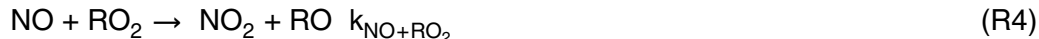
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The traditional view on $\Delta^{17}\text{O}(\text{NO}_3^-)$ has been extensively described in [Michalski et al. \(2003\)](#) and we briefly summarize the main aspects here. The origin of the isotopic anomaly of oxygen in nitrate can be accounted for considering a two-steps chemical oxidation mechanism for nitrogen oxides:

- NO_x are primarily recycled through the following photochemical cycle ([Finlayson-Pitts and Pitts, 2000](#)):



5 where RO_2 represents all peroxy and alkyl-peroxy radicals. Without taking into account BrO chemistry, at steady state, the anomaly in NO_2 only depends on the ratio between the rate of oxidation of NO by O_3 and RO_2 ([Röckmann et al., 2001](#); [Michalski et al., 2003](#)).

- NO_2 is converted into atmospheric HNO_3 and particulate NO_3^- through one of the following main reaction pathways ([Finlayson-Pitts and Pitts, 2000](#)):



10 Each of these reaction pathways ([R5](#), [R6](#) followed by [R7](#), and [R6](#) followed by [R8](#)) involves NO_2 , and also O_3 for the pathways ([R6+R8](#)) and ([R6+R7](#)), and therefore

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accounts for the transfer of anomalous oxygen to HNO_3 in different proportions. It is possible to calculate the resulting $\Delta^{17}\text{O}(\text{HNO}_3)$ for each channel (see Michalski et al., 2003, for details).

The first step acts upon time scales of minutes (lifetime of NO_2 with respect to photolysis) and the second one acts upon time scales of hours to days. It is therefore possible to fully decouple them when modeling the origin of the oxygen anomaly in particulate nitrate (Michalski et al., 2003).

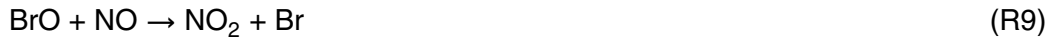
4.2 Bromine oxides and ozone depletion events

It is now well established that bromine is the key element in the processes responsible for tropospheric ozone depletion in the Arctic (Bottenheim et al., 2002). Bromine originates from sea-salt, but the exact location where bromide is activated into the radical form, which destroys ozone, is still a matter of debate (Dominé and Shepson, 2002). Sea-salt aerosols (Fan and Jacob, 1992), but also the seasonal snowpack (Tang and McConnell, 1996; Sander et al., 1997; Michalowski et al., 2000) should be the predominant sources of bromine in the atmosphere.

The catalytic cycles of Br/BrO in both the gas phase and the condensed phase are responsible for the so-called “bromine explosion” (Wennberg, 1999) which results in a fast and efficient removal of ozone from the arctic boundary layer. In these conditions, significantly high levels of BrO were measured (Hönninger and Platt, 2002), with peak values as high as 30 pmol mol^{-1} during a strong ODE near Alert in spring 2000.

Since BrO is a strong oxidant, it intervenes in both steps leading to nitrate formation:

- Oxidation of NO:



- Formation of nitrate through the hydrolysis of bromine nitrate (BrONO_2) in both

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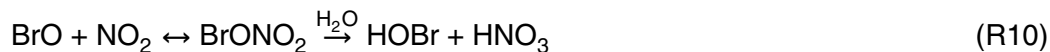
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gaseous phase and on wetted surfaces:



In what follows, we neglect Cl chemistry, since Br is by far the most active halogen during ODEs (Hönniger and Platt, 2002). However, taking into account these species would be crucial for stratospheric studies where chlorine chemistry dominates over bromine chemistry.

4.3 Oxidation of NO in the Arctic

We now examine the competition between the three major NO oxidants identified in the arctic troposphere in springtime (O_3 , RO_2 and BrO), in terms of kinetics and the subsequent influence on the isotopic composition of oxygen in NO_2 .

4.3.1 Reaction (R3): $\text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2(k_{\text{O}_3+\text{NO}})$

According to the analysis of Röckmann et al. (2001) and Michalski et al. (2003), in “normal” conditions (i.e. not influenced by bromine induced ozone depleting chemistry) this is the reaction responsible for the transmission of anomalous oxygen from ozone to NO_2 . Therefore the rate of transfer for $\Delta^{17}\text{O}$ between O_3 and NO_2 is one of the most critical parameter for our analysis. Since little is known regarding both the chemical mechanism for this reaction and the intramolecular isotope distribution in ozone, contradictory parameterizations have been published so far in various modeling studies: for some authors (see e.g. Lyons, 2001; Röckmann et al., 2001), only the terminal atom of ozone reacts with NO to yield NO_2 , although there is mechanistic evidence that the central atom of ozone also reacts with NO (van den Ende et al., 1982). In addition, the intramolecular distribution of oxygen isotopes in ozone is very likely to differ greatly from a stochastically expected distribution: this is the case for ^{18}O (Janssen, 2005), and in lack of experimental data regarding the intramolecular distribution of ^{17}O in ozone

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we assume that ¹⁷O behaves in a similar manner (Lyons, 2001). The combination of these two sources of uncertainties has made it impossible to consistently account for the transfer of anomaly resulting from Reaction (R3). Since it may be difficult to separate these two effects (even in controlled experiments), we introduce an integrated Δ¹⁷O transfer coefficient (τ) for this reaction, such that at photochemical steady-state, when only considering Reaction (R3) and the subsequent photolysis of NO₂:

$$\Delta^{17}\text{O}(\text{NO}_2) = \tau \times \Delta^{17}\text{O}(\text{O}_3) \quad (2)$$

Assuming that the overall transmission of anomalous oxygen from ozone to NO₂ proceeds as if the bulk composition of ozone was more or less equally transferred by each of its atoms, which is equivalent to τ=1, the parameterization of Michalski et al. (2003) has proven so far to be the most realistic in terms of comparison between modeled and measured Δ¹⁷O(NO₃⁻). Using an atmospheric chamber, Savarino et al. (2006)² are investigating this reaction to experimentally derive a measurement of τ in controlled conditions. So far none of these measurements contradict the simplified approach of Michalski et al. (2003). In addition, in no case the Δ¹⁷O of the O-atom transferred to the resulting NO₂ is measured higher than the initial bulk ozone oxygen anomaly. Given the fact that the terminal atoms in ozone are more anomalously enriched in heavy atoms (Janssen, 2005), this is an additional evidence that the alternative hypothesis made by Lyons (2001) is not correctly describing the transfer of Δ¹⁷O from ozone to NO₂. For the analysis of the results presented here, we take τ=0.9–1, which lies within the range derived from Savarino's experiments so far, and is the most consistent with the existing literature.

4.3.2 Reactions (R4): RO₂ + NO → NO₂ + RO(k_{RO₂+NO})

In this reaction, R represents H or any organic radical. As peroxy radicals are derived from atmospheric O₂, they do not bear a significant isotopic anomaly, so we take

²Savarino, J., unpublished results, in preparation, Atmos. Chem. Phys. Discuss., 2006

$\Delta^{17}\text{O}(\text{RO}_2)=0\text{‰}$ (Savarino and Thiemens, 1999; Röckmann et al., 2001).

4.3.3 Evaluation of $\Delta^{17}\text{O}(\text{BrO})$

In the arctic troposphere after polar sunrise, BrO is mostly produced by reaction with ozone, and plays an important role in the ozone destruction catalytic cycle (Platt and Hönniger, 2003):



Similarly to the $\text{NO}+\text{O}_3$ reaction and the associated photochemical cycle, which is conceptually similar to some extent to the bromine oxide ozone destruction catalytic cycle, it is expected a steady state isotopic equilibrium between BrO and O_3 to be reached within a few minutes. Since the position of O atoms in the ozone molecule determines their load of isotopic anomaly (Janssen, 2005), the steady state $\Delta^{17}\text{O}(\text{BrO})$ value is expected to depend both on the branching ratio between central/terminal O atom transfer to BrO and the intramolecular isotopic composition of ozone. Theoretical considerations based on kinetic measurements (Toohey et al., 1988) and molecular crossed beam studies (Zhang et al., 1997) show that $\text{Br} + \text{O}_3$ is a direct reaction, and that the Br atom most likely attacks a terminal ozone atom. Lyons (2001) calculated that terminal atoms in ozone carry an anomaly between 70 and 80‰. More recent work by Janssen (2005) shows that the intramolecular distribution of heavy isotopes in ozone is temperature dependent, favouring higher enrichments for terminal atoms at higher temperature, so the calculation by Lyons (2001) should be seen as an upper limit. An experimental confirmation of this prediction is strongly needed, but this calculation seems to indicate that BrO could feature the highest isotopic anomaly in a chemically active molecule in the troposphere. Given the increasing influence given to BrO in

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chemical mechanisms implemented in atmospheric models (e.g. Platt and Hönniger, 2003; von Glasow et al., 2004; Lary, 2005), this potentially unique isotopic signature could represent a tool of choice to test these hypothesis.

4.3.4 Reaction (R9): $\text{BrO} + \text{NO} \rightarrow \text{NO}_2 + \text{Br}(k_{\text{BrO}+\text{NO}})$

5 Since BrO is present in the arctic boundary layer after polar sunrise (Hausmann and Platt, 1994; Hönniger and Platt, 2002), NO oxidation by BrO must be taken into account for the assessment of the origin of the oxygen isotopic anomaly in NO_2 . When comparing the kinetic rates of oxidation of NO by BrO and O_3 (Atkinson et al., March 2005 version) in the context of the arctic boundary layer with temperatures ranging
10 between 233 and 273 K, one realizes that 1 pmol mol^{-1} BrO has the same power as $2\text{--}4 \text{ nmol mol}^{-1}$ O_3 in oxidising NO. In addition, as pointed out previously, the high isotopic anomaly in BrO makes it even more active as a source of anomalous O atom in NO_2 .

4.3.5 Derivation of the equation for the anomaly in NO_2

15 We calculate steady-state abundance ratios for a given NO_2 isotopologue using the kinetic equations derived from the photochemical cycling of NO_x and ozone, disturbed by peroxy radicals and bromine oxides. We neglect species containing more than one heavy O atom (^{17}O or ^{18}O) because of their extremely low abundances. In addition, in the kinetic equations for NO and NO_2 , NO_x sink terms such as the formation of HNO_3 are negligible compared to the NO– NO_2 interconversion terms. Indeed, the NO and NO_2 chemical lifetime (about a min) is much shorter than NO_x lifetime (about a day).

In what follows, Q denotes ^{17}O or ^{18}O , and O represents ^{16}O . We additionally assume that kinetic rates (k values) and photolysis frequencies (J values) are the same for all O-isotopologues of a given species. For brevity, we note $[\text{RO}_2]^\dagger = k_{\text{NO}+\text{RO}_2}[\text{RO}_2]$,
25 $[\text{ROQ}]^\dagger = k_{\text{NO}+\text{RO}_2}[\text{ROQ}]$, $[\text{BrO}]^\dagger = k_{\text{NO}+\text{BrO}}[\text{BrO}]$, $[\text{BrQ}]^\dagger = k_{\text{NO}+\text{BrO}}[\text{BrQ}]$, $[\text{O}_3]^\dagger = k_{\text{NO}+\text{O}_3}[\text{O}_3]$ and $[\text{O}_2\text{Q}]^\dagger = k_{\text{NO}+\text{O}_3}[\text{O}_2\text{Q}]$, where $[\text{X}]$ denotes the sum of atmospheric concentrations

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of the isotopomers of a given species X.

$$\frac{d}{dt}[\text{NQ}] = \frac{1}{2}J[\text{NOQ}] - [\text{NQ}] \times ([\text{O}_3]^\dagger + [\text{BrO}]^\dagger + [\text{RO}_2]^\dagger + [\text{O}_2\text{Q}]^\dagger + [\text{BrQ}]^\dagger + [\text{ROQ}]^\dagger) \quad (3)$$

$$\frac{d}{dt}[\text{NO}] = \frac{1}{2}J[\text{NOQ}] + J[\text{NOO}] - [\text{NO}] \times ([\text{O}_3]^\dagger + [\text{BrO}]^\dagger + [\text{RO}_2]^\dagger + [\text{O}_2\text{Q}]^\dagger + [\text{BrQ}]^\dagger + [\text{ROQ}]^\dagger) \quad (4)$$

$$\frac{d}{dt}[\text{NOQ}] = -J[\text{NOQ}] + [\text{NQ}] \times ([\text{O}_3]^\dagger + [\text{RO}_2]^\dagger + [\text{BrO}]^\dagger) + [\text{NO}] \times \left(\frac{\tau}{3}[\text{O}_2\text{Q}]^\dagger + [\text{BrQ}]^\dagger + \frac{1}{2}[\text{ROQ}]^\dagger\right) \quad (5)$$

$$\frac{d}{dt}[\text{NOO}] = -J[\text{NOO}] + [\text{NO}] \times ([\text{O}_3]^\dagger + [\text{RO}_2]^\dagger + [\text{BrO}]^\dagger) + [\text{NO}] \times \left(\frac{3-\tau}{3}[\text{O}_2\text{Q}]^\dagger + \frac{1}{2}[\text{ROQ}]^\dagger\right) \quad (6)$$

Assuming steady-state and adding Eqs. (4) and (6) yields:

$$[\text{NO}] = \frac{1}{2} \frac{J[\text{NOQ}]}{\frac{\tau}{3}[\text{O}_2\text{Q}]^\dagger + \frac{1}{2}[\text{ROQ}]^\dagger + [\text{BrQ}]^\dagger} \quad (7)$$

Substituting [NO] in Eq. (6) yields, after rearranging:

$$\frac{1}{2} \frac{[\text{NOQ}]}{[\text{NOO}]} = \frac{\frac{\tau}{3}[\text{O}_2\text{Q}]^\dagger + \frac{1}{2}[\text{ROQ}]^\dagger + [\text{BrQ}]^\dagger}{[\text{O}_3]^\dagger + [\text{RO}_2]^\dagger + [\text{BrO}]^\dagger + \frac{3-\tau}{3}[\text{O}_2\text{Q}]^\dagger + \frac{1}{2}[\text{ROQ}]^\dagger} \quad (8)$$

Since $\frac{[\text{O}_2\text{Q}]^\dagger}{[\text{O}_3]^\dagger} \ll 1$ and $\frac{[\text{ROQ}]^\dagger}{[\text{RO}_2]^\dagger} \ll 1$, this further simplifies to:

$$\frac{1}{2} \frac{[\text{NOQ}]}{[\text{NOO}]} = \frac{\frac{\tau}{3}[\text{O}_2\text{Q}]^\dagger + \frac{1}{2}[\text{ROQ}]^\dagger + [\text{BrQ}]^\dagger}{[\text{O}_3]^\dagger + [\text{RO}_2]^\dagger + [\text{BrO}]^\dagger} \quad (9)$$

The conversion of molecular fractions into atomic ratios is performed using the following equations (Janssen, 2005):

$$\left(\frac{[Q]}{[O]}\right)_{O_3} = \frac{[O_2Q]}{3 \times [O_3]} \quad (10)$$

$$\left(\frac{[Q]}{[O]}\right)_{NO_2} = \frac{[NOQ]}{2 \times [NOO]} \quad (11)$$

$$\left(\frac{[Q]}{[O]}\right)_{BrO} = \frac{[BrQ]}{[BrO]} \quad (12)$$

$$\left(\frac{[Q]}{[O]}\right)_{RO_2} = \frac{[ROQ]}{2 \times [RO_2]} \quad (13)$$

Substituting (10), (11), (12) and (13) in Eq. (9) gives:

$$\begin{aligned} \left(\frac{[Q]}{[O]}\right)_{NO_2} = & \frac{1}{[O_3]^\dagger + [RO_2]^\dagger + [BrO]^\dagger} \times \left(\tau \left(\frac{[Q]}{[O]}\right)_{O_3} [O_3]^\dagger \right. \\ & \left. + \left(\frac{[Q]}{[O]}\right)_{RO_2} [RO_2]^\dagger + \left(\frac{[Q]}{[O]}\right)_{BrO} [BrO]^\dagger \right) \end{aligned}$$

Finally, combining this equation and the linear definition of $\Delta^{17}O$ ($\Delta^{17}O = \delta^{17}O - \lambda \times \delta^{18}O$) gives:

$$\begin{aligned} \Delta^{17}O(NO_2) + 1 - \lambda = & \frac{1}{[O_3]^\dagger + [RO_2]^\dagger + [BrO]^\dagger} \times \\ & (\tau [O_3]^\dagger \times (\Delta^{17}O(O_3) + 1 - \lambda) \\ & + [RO_2]^\dagger \times (\Delta^{17}O(RO_2) + 1 - \lambda) \\ & + [BrO]^\dagger \times (\Delta^{17}O(BrO) + 1 - \lambda)) \end{aligned}$$

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This further reduces to:

$$\Delta^{17}\text{O}(\text{NO}_2) = \frac{\tau[\text{O}_3]^\dagger \Delta^{17}\text{O}(\text{O}_3) + [\text{BrO}]^\dagger \Delta^{17}\text{O}(\text{BrO})}{[\text{O}_3]^\dagger + [\text{RO}_2]^\dagger + [\text{BrO}]^\dagger} + \frac{(1 - \lambda)(\tau - 1)[\text{O}_3]^\dagger}{[\text{O}_3]^\dagger + [\text{RO}_2]^\dagger + [\text{BrO}]^\dagger}$$

5 The latter term is equal to zero when $\tau=1$, and ranges between 2–3‰ in the conditions presented here (see data in Table 1) and $\tau>0.95$. However it must be noted that if τ was to vary significantly from 1, this would alter Eq. (5) and require a specific analytical treatment. For the development of this expression we neglect the deviations which would result from τ values differing from 1, given the analytical uncertainties and the
 10 lack of knowledge regarding the transmission of anomaly from O_3 to NO_2 . Additionally, as discussed above, $\Delta^{17}\text{O}(\text{RO}_2)\simeq 0$. We therefore rewrite an approximated form for this equation:

$$\Delta^{17}\text{O}(\text{NO}_2) = \frac{\tau[\text{O}_3]^\dagger \Delta^{17}\text{O}(\text{O}_3) + [\text{BrO}]^\dagger \Delta^{17}\text{O}(\text{BrO})}{[\text{O}_3]^\dagger + [\text{RO}_2]^\dagger + [\text{BrO}]^\dagger} \quad (14)$$

15 In the extreme case where peroxy radicals disturbance of the photochemical cycling between NO_x and ozone is negligible and BrO does not play a significant role, we find indeed that at photochemical equilibrium $\Delta^{17}\text{O}(\text{NO}_2)=\tau \Delta^{17}\text{O}(\text{O}_3)$, with $\tau\simeq 0.9-1$. In addition, this equation is compatible with the formalism adopted by Michalski et al. (2003), which did not include BrO. A generalisation of this approach is possible: noting
 20 X_i a population of oxygen bearing NO oxidants, with τ_i their $\Delta^{17}\text{O}$ transfer coefficient (function of the intramolecular distribution of oxygen isotopes in X_i and of the mecha-

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nism of the reaction $X_i + \text{NO}$ and $[X_i]^\dagger = k_{\text{NO}+X_i} \cdot [X_i]$, one finds:

$$\Delta^{17}\text{O}(\text{NO}_2) = \frac{\sum_i \tau_i \times [X_i]^\dagger \times \Delta^{17}\text{O}(X_i)}{\sum_i [X_i]^\dagger} \quad (15)$$

4.4 Nitrate formation

As discussed before, because sunlight was permanent at the sampling site and in the Arctic basin during the whole measurement campaign, any processes involving nighttime radicals such as NO_3 is considered insignificant (the lifetime of NO_3 with respect to photolysis is only a few seconds). As a result, the pathways (R6+R8), and (R6+R7) can be discounted.

In these conditions, two processes arise to account for the formation of significant levels of inorganic nitrate in the lower troposphere: NO_2 either reacts with OH to form gas-phase nitric acid, or reacts with BrO to form BrONO_2 . Bromine nitrate subsequently undergoes hydrolysis on ice surfaces and yields particulate nitrate (Hanson et al., 1996), or sustains nitric acid formation through a gas-phase equilibrium with HOBr and HNO_3 (Sander et al., 1999). The role of BrONO_2 has been investigated since the early stages of the research effort on ODEs and is an important Br recycling mechanism (Fan and Jacob, 1992). However, its concomitant impact on nitrate formation has not drawn a similar attention until recent years. In a modeling effort dealing mainly with gas-phase mechanisms, Calvert and Lindberg (2003) showed that BrONO_2 would be the most abundant N-containing species in the arctic boundary layer. For Lary (2005), up to 35% of HNO_3 in the free troposphere could be formed through the BrONO_2 hydrolysis.

Based on temperature dependent kinetic rates (Atkinson et al., March 2005 version) and heterogeneous loss rates from Ridley and Orlando (2003) and Michalowski et al. (2000), we compared the speed of formation of nitrate through BrONO_2 hydrolysis and reaction of NO_2 with OH. We find that with only 1 pmol mol^{-1} BrO and 10^6 cm^{-3} OH, 40% of inorganic nitrate is produced through the BrONO_2 hydrolysis channel. This

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proportion dramatically increases to over 80% in conditions more representative of the arctic boundary layer in spring time, with 2–5 pmol mol⁻¹ BrO (Hönninger and Platt, 2002) and 5–10 × 10⁵ cm⁻³ OH (Evans et al., 2003).

4.4.1 Implications on $\Delta^{17}\text{O}(\text{NO}_3^-)$ values

- 5 For the gas phase OH + NO₂ reaction, it is clear that in the resulting nitrate two O atoms carry an isotopic signature corresponding to the parent NO₂, and one with the isotopic signature of OH (Michalski et al., 2003), so that

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

10 [Dubey et al. \(1997\)](#) have measured the kinetic rate for the isotopic exchange of ¹⁸O between OH and gaseous H₂O at various temperatures. Such an equilibrium is mass-dependent, therefore one expects the exchange rate of ¹⁷O, and hence the equilibration of $\Delta^{17}\text{O}$ between these two oxygen-bearing species to follow the same temperature dependency. In all meteorological conditions found in the Arctic basin, the equilibration between H₂O and OH is always the fastest process, compared to other
15 sink reactions for OH. Consequently, as $\Delta^{17}\text{O}(\text{tropospheric H}_2\text{O})$ is zero (tropospheric H₂O lies on the terrestrial fractionation line), $\Delta^{17}\text{O}(\text{OH})$ is taken to be zero. Therefore in nitrate produced through this channel,

$$\Delta^{17}\text{O}(\text{NO}_3^-) = 2/3\Delta^{17}\text{O}(\text{NO}_2) \quad (16)$$

20 For the reaction involving BrONO₂, it is necessary to address the origin of the third atom in the resulting nitrate, since it could carry the isotopic signature of BrO or that of water depending on the hydrolysis mechanism. By means of independent techniques, [Gane et al. \(2001\)](#) and [McNamara and Hillier \(2001\)](#) reached the conclusion that in the hydrolysis process the O atom initially bound to Br would bind the N atom in NO₂ to form nitrate, incorporating the isotopic signature of BrO. Thus in nitrate produced

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through this channel:

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

Finally, combining these two competing mechanisms and the numerical expression for $\Delta^{17}\text{O}(\text{NO}_2)$ yields:

$$\Delta^{17}\text{O}(\text{NO}_3^-) = \frac{r}{3}\Delta^{17}\text{O}(\text{BrO}) + \frac{2}{3} \frac{\tau[\text{O}_3]^\dagger \Delta^{17}\text{O}(\text{O}_3) + [\text{BrO}]^\dagger \Delta^{17}\text{O}(\text{BrO})}{[\text{O}_3]^\dagger + [\text{RO}_2]^\dagger + [\text{BrO}]^\dagger}$$

with r the proportion of nitrate produced through BrONO_2 hydrolysis.

This relationship allows for the calculation of $\Delta^{17}\text{O}(\text{NO}_3^-)$ produced in conditions influenced by the local chemical composition of the lower atmosphere. Long range transport does not have any influence on the isotopic budget of nitrate: NO_y are mainly transported as PAN and locally decompose to yield NO_2 . In turn, it quickly conforms to the isotopic composition of ambient NO_2 . If particulate nitrate was to be transported to the Arctic, it is likely that it would undergo dry or wet deposition on the sea surface or onto the seasonal snowpack. NO_x subsequently emitted from the snowpack (Ridley et al., 2000; Beine et al., 2002) would also quickly gain a local isotopic signature. Finally, if particulate nitrate was to be transported as it to the Arctic without any modification of its isotopic composition, this would not explain the large anomalies we measured because air masses originating from the south would most probably carry an isotopic signature comparable to the values reported by Michalski et al. (2003), i.e. between 23 and 25‰ for this time of the year. We consequently assume that all of the inorganic nitrate we analyzed carries a local signature, and that our measurements only cannot address the question of the origin of nitrate in the Arctic.

4.5 Estimation of variables of Eq. (18) and implications

To quantitatively interpret isotope data on inorganic nitrate during ODEs, we derived from existing chemical reactions a relationship between $\Delta^{17}\text{O}(\text{NO}_3^-)$ and variables that

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are likely to describe the isotope kinetics in the arctic lower troposphere (see Eq. 18). We now inspect the terms in this equation and propose a set of parameters which consistently account for the observed co-evolution of $\Delta^{17}\text{O}(\text{NO}_3^-)$ and the mixing ratio of ozone during ODEs.

5 Except for $\Delta^{17}\text{O}(\text{NO}_3^-)$, the only measured variable in this equation is the mixing ratio of ozone. Other variables are estimated as follows:

4.5.1 $\Delta^{17}\text{O}(\text{O}_3)$

We use the widely accepted tropospheric value for $\Delta^{17}\text{O}(\text{O}_3)$ of 35‰ (Thiemens, 1999; Röckmann et al., 2001; Lyons, 2001; Michalski et al., 2003, 2005; McCabe et al., 2006).

10 However, no systematic measurement of $\Delta^{17}\text{O}(\text{O}_3)$ in the troposphere has ever been undertaken. To the best of our knowledge, only two studies (Johnston and Thiemens, 1997; Krankowsky et al., 1995) attempted to describe this variable in the troposphere based on field measurements. Johnston and Thiemens (1997) show highly variable measurements, with $\Delta^{17}\text{O}(\text{O}_3)$ ranging between 22 and 35‰ depending on the environmental conditions at the sampling site, and especially the NO_x load of the atmosphere. According to these authors, “the greater the degree of photochemistry, the more mass-dependently fractionated the ozone” i.e. the lower the $\Delta^{17}\text{O}(\text{O}_3)$, because it is controlled by the balance between ozone formation (mass-independent) and its decomposition (mass-dependent). Lyons (2001) modeled the vertical distribution of $\Delta^{17}\text{O}(\text{O}_3)$ in a standard atmosphere, using approximated kinetic data and the pressure-temperature dependencies described by Morton et al. (1990), and showed that at the surface $\Delta^{17}\text{O}(\text{O}_3)=35$ ‰. We are aware that in the Arctic this value may not be valid, but until a systematic study of the variability of $\Delta^{17}\text{O}(\text{O}_3)$ in the troposphere has been achieved we use the most trusted value as a starting point.

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4.5.2 [RO₂][†]

To the best of our knowledge no surface peroxy radical measurements have ever been undertaken at Alert in early spring and very little RO_x–HO_x data is available in the arctic boundary layer during ODEs. Nonetheless, we calculate the evolution of RO₂ ratio during ODEs based on the field data acquired in the arctic boundary layer during the campaign TOPSE 2000 (Tropospheric Ozone Production about the Spring Equinox experiment, see [Atlas et al., 2003](#)). [Evans et al. \(2003\)](#) summarized the boundary layer data acquired during TOPSE by binning mean measurements of species according to the ozone levels. According to [Cantrell et al. \(2003\)](#), the [HO₂]/[RO₂] ratio was found to be more or less constant (0.75) during this whole campaign so that [HO₂]=0.75 [RO₂]. The dominant alkyl-peroxy radical is CH₃O₂ ([Cantrell et al., 2003](#)), so for the purpose of this study we take [CH₃O₂]=0.25 [RO₂]. In what follows, we therefore calculate $k_{\text{RO}_2+\text{NO}} = 0.75k_{\text{HO}_2+\text{NO}} + 0.25k_{\text{CH}_3\text{O}_2+\text{NO}}$ so that RO₂ is treated as a virtual species integrating the combined kinetic rates of its two main components according to their relative abundances.

[Evans et al. \(2003\)](#) showed that during ODEs, when the ozone mixing ratios drops from about 40 nmol mol⁻¹ to 5 nmol mol⁻¹ on average (consistent with our averaging approach), RO₂ concentrations decrease from (2.2±1.2) 10⁸ cm⁻³ to (1.3±0.6) 10⁸ cm⁻³, corresponding roughly to a factor 2 division. At the same time, during ODEs, CH₂O was found to drop by about a factor 4. This is consistent with the simplified RO₂ chemical budget described in [Evans et al. \(2003\)](#) where the main source of RO₂ is the photolysis of species such as CH₂O, and the main sink is the self reaction RO₂+RO₂ (mainly HO₂+HO₂). Thus, at steady state, the RO₂ concentrations are expected to be proportional to the square root of the concentration of CH₂O, which appears to be mostly the case during TOPSE 2000. CH₂O mainly originates from the snowpack ([Sumner and Shepson, 1999](#)) and its drop during ODEs seems to be driven by reactions with halogen atoms, according to model studies ([Evans et al., 2003](#)). Overall, during ODEs, RO₂ concentrations drop by a factor much lower than the reduction factor

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of ozone concentrations (ca. factor 2 vs. factor 10).

The data presented by [Evans et al. \(2003\)](#) are grouped in four ozone mixing ratio bins ($<1 \text{ nmol mol}^{-1}$, $1 \text{ to } 10 \text{ nmol mol}^{-1}$, $10 \text{ to } 30 \text{ nmol mol}^{-1}$, and $>30 \text{ nmol mol}^{-1}$). Since in no case the average ozone mixing ratio during the sampling time of an aerosol sample was lower than 5 nmol mol^{-1} , we do not consider here the bin corresponding to the lowermost ozone mixing ratio. From these data, we observe that RO_2 and O_3 are positively correlated. From these data, to estimate the concentration of RO_2 as a function of the ozone mixing ratio at Alert during our measurement campaign, we applied the following relationship: $\text{RO}_2/10^8 \text{ cm}^{-3} = (0.09 \text{ O}_3/\text{nmol mol}^{-1} + 1.31)^{1/2}$, and calculated the corresponding $[\text{RO}_2]^\dagger$ accordingly, using kinetic rates from [Atkinson et al. \(March 2005 version\)](#).

4.5.3 $[\text{BrO}]^\dagger$

In springtime 2004, some BrO measurements were carried out at Alert: [Morin et al. \(2005\)](#) show that on the frozen ocean a few km off the coast north of Alert, in ODE conditions instantaneous BrO levels did not exceed 10 pmol mol^{-1} , and that in normal conditions BrO was in the $1\text{--}3 \text{ pmol mol}^{-1}$ range. This is quite similar to the observations made in spring 2003 by [Hönninger and Bottenheim \(2003\)](#) at Alert. In addition, the detailed study carried out by [Hönninger and Platt \(2002\)](#) shows that BrO reaches significant levels (above 5 pmol mol^{-1}) only when ozone drops below 5 nmol mol^{-1} : in no case this situation happened during the entire course of an aerosol sampling period, since the minimum averaged ozone mixing ratio is $5.2 \text{ nmol mol}^{-1}$.

To check the consistency of our approach and its predictive capacity, we implemented a simple Monte-Carlo method to calculate the following remaining variables: r , τ , $\Delta^{17}\text{O}(\text{BrO})$ and $[\text{BrO}]^\dagger$. We assume that they are constant during the measurement campaign, the idea being to derive mean values for $\Delta^{17}\text{O}(\text{BrO})$ and $[\text{BrO}]^\dagger$ that would be representative of ODE conditions. In these simulations, r was allowed to vary

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between 0 and 1, τ between 0.9 and 1, $\Delta^{17}\text{O}(\text{BrO})$ between 20 and 80‰, and $[\text{BrO}]^\dagger$ corresponding to a 1–10 pmol mol⁻¹ BrO range. For each variable, 10 values linearly distributed in the stated interval were considered, and the chosen values correspond to a minimization of the quantity:

$$\sum_{i=1}^{12} \left(\Delta^{17}\text{O}(\text{NO}_3^-)_{\text{measured},i} - \Delta^{17}\text{O}(\text{NO}_3^-)_{\text{calculated},i} \right)^2$$

for the $i = 1 \dots 12$ data points analyzed for this study, and $\Delta^{17}\text{O}(\text{NO}_3^-)_{\text{calculated},i}$ using Eq. (18) and the variables described above.

With this method, we find $r=0.9$, $\tau=1$, $[\text{BrO}]^\dagger$ corresponding to a 1.9 pmol mol⁻¹ BrO mixing ratio and $\Delta^{17}\text{O}(\text{BrO})=44\text{‰}$. The r value is in excellent agreement with the previously mentioned kinetics calculations showing that in the conditions of the arctic boundary layer in springtime most of the nitrate should be produced through the $\text{BrO} + \text{NO}_2$ reaction, followed by the hydrolysis of BrONO_2 . $\tau=1$ is fully consistent with current knowledge regarding the $\text{NO} + \text{O}_3$ reaction (see above). $\Delta^{17}\text{O}(\text{BrO})=44\text{‰}$ is a confirmation that BrO features a high isotopic anomaly, which is in-line with chemical mechanisms and isotopic transfer issues discussed above: BrO is more anomalously enriched in ¹⁷O than the bulk of its parent molecule, namely ozone. In the case of $[\text{BrO}]^\dagger$, the value we obtain (1.9 pmol mol⁻¹ BrO mixing ratio) is perfectly in-line with the data presented by [Hönninger and Platt \(2002\)](#) and [Morin et al. \(2005\)](#) for situations where the ozone mixing ratio remains over 5 nmol mol⁻¹ (which, as discussed previously, was on average the case for all the situations experienced during the measurement campaign).

Figure 6 shows a direct comparison of the measured and calculated $\Delta^{17}\text{O}(\text{NO}_3^-)$ values, using Eq. (18) and variables as determined above. The overall variability in $\Delta^{17}\text{O}(\text{NO}_3^-)$ is well reproduced by our simulated values, as well as the range of variation. Our analysis would be greatly improved if continuous BrO measurements were available during the course of this measurement campaign, however even if we do not

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account for the BrO variability we consistently account for its presence in the arctic boundary layer. Nevertheless, our simplified approach allows for a semi-quantitative understanding of the correlation between $\Delta^{17}\text{O}(\text{NO}_3^-)$ and average ozone mixing ratio: on measured values, we obtain a slope of 0.15 between the linear regression of $\Delta^{17}\text{O}(\text{NO}_3^-)$ with ozone mixing ratio (see above), and on simulated data the slope is 0.10, with very comparable regression coefficient ($R^2=0.70$ for measured values, and $R^2=0.74$ for simulated data). This shows that the broad picture is well captured by our interpretation, even if improvements are highly desirable for a better quantification of the processes at play.

5 Conclusions

Using present knowledge regarding the transmission of the ozone oxygen isotopic anomaly to particulate nitrate through photochemical reactions between NO_x and ozone, and the mechanisms responsible for the conversion of NO_2 to inorganic nitrate in the polar atmosphere after polar sunrise, we demonstrated in this paper that its isotopic composition records a footprint of the tropospheric ozone depletion events which occur in this environment, based on atmospheric inorganic nitrate samples collected at Alert during 7 weeks in spring 2004. Including Arctic-specific processes in the analytical scheme first proposed by Michalski et al. (2003), we show that most of the nitrate is produced through hydrolysis of BrONO_2 after the $\text{BrO} + \text{NO}_2$ reaction. This complements the widely accepted crucial role of this process in recycling BrO and acting to destroy ozone in the arctic boundary layer in springtime (Fan and Jacob, 1992). We also showed that, in the conditions experienced during our measurement campaign, the expected increase in BrO mixing ratio during strong depletion events did not happen significantly, since the correlation between $\Delta^{17}\text{O}(\text{NO}_3^-)$ and the mixing ratio of ozone during the sampling interval was not changed at low ozone mixing ratio.

This extended theoretical framework predicts that, in situations of sustained strong ODE during the whole sampling interval of a filter sample (i.e. $\text{O}_3 < 5 \text{ nmol mol}^{-1}$), the

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accompanying high BrO levels could result in higher $\Delta^{17}\text{O}(\text{NO}_3^-)$ values, since elevated BrO levels would then efficiently transfer their anomaly to NO_2 , hence to nitrate. Indeed, we found evidence for such a situation in samples collected at Barrow, Alaska in March 2005 (Morin et al., 2006³), where the linear correlation between $\Delta^{17}\text{O}(\text{NO}_3^-)$ and the ozone mixing ratio reversed for low ozone mixing ratios.

In addition to the analysis of this specific situation, we generalized the isotopic mass-balance approach proposed by Michalski et al. (2003) to a situation where more than one anomalous oxygen bearing NO oxidant acts in the system. Our formalism is compatible with previous studies and it demonstrates the urgent need for better characterizations of $\Delta^{17}\text{O}$ values for active species (namely, tropospheric ozone and BrO in various environments) and anomaly transfer coefficients (τ values) for reactions with NO.

Finally, our results can be interpreted in term of the reaction of the atmospheric reactor to a change in its oxidative power: during ODEs, the ozone mole fraction drops are associated with a strong decrease in the oxidative power of the atmosphere, as O_3 is a prominent oxidant of the atmosphere and chemically linked to HO_x chemistry. It has been suggested, in light of the first findings on the origin of the oxygen anomaly in nitrate, that the oxygen isotopic content of nitrate recorded in polar ice cores could be used as a proxy for past oxidative power, crucially needed to take into account chemical feedbacks on the Earth climate. More work is required to test this idea on a broader dataset, and to use these empirical observations to develop a model that would account for these links in a predictable manner. In addition, post-depositional effects within the firn and in the ice have to be studied carefully in order to assess past $\Delta^{17}\text{O}(\text{NO}_3^-)$ values in the atmosphere, and obtain an estimate for the past oxidant activity, since they may in some cases induce the strongest signal in the isotopic record (see the recent studies by Blunier et al., 2005 and McCabe et al., 2005).

³Morin, S., Savarino, J., Bekki, S., et al.: Surface Ozone Depletion Events and Oxygen Isotopes in Atmospheric Inorganic Nitrate: Insights from two Field Campaigns in the High Arctic, in preparation, 2006.

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Table 1. Summary of the data used in this study. Date ON represents the time (UTC) when the sample started to be collected. Less than 5 min separate each sampling period (data not shown), so the end of sampling correspond to the beginning of the next sample. All data represent averages over each sampling period. $\Delta^{17}\text{O}(\text{NO}_3^-)_{\text{calc.}}$ is calculated using Eq. (18) and the stated $[\text{O}_3]^\dagger$ and $[\text{RO}_2]^\dagger$. Additional variables are estimated (see text for details), such as: $[\text{BrO}]^\dagger = 1.2 \cdot 10^{-3} \text{ cm}^{-3} \text{ s}^{-1}$ (corresponding to $1.9 \text{ pmol mol}^{-1} \text{ BrO}$), $\tau=1$, $r=0.9$ and $\Delta^{17}\text{O}(\text{BrO})=44\%$. $\Delta^{17}\text{O}(\text{NO}_3^-)_{\text{meas.}}$ measurements carry an uncertainty between 0.6 and 1.2‰. $\delta^{18}\text{O}(\text{NO}_3^-)$ measurements carry an uncertainty of 4‰, due to the analytical procedure used for this study, which is not optimized for $\delta^{18}\text{O}(\text{NO}_3^-)$ measurements.

Date ON UTC (in 2004)	Temp. K	NO ₃ ⁻ ng m ⁻³	O ₃ (1σ) nmol mol ⁻¹	[O ₃] [†] cm ⁻³ s ⁻¹	[RO ₂] [†] cm ⁻³ s ⁻¹	Δ ¹⁷ O(NO ₃ ⁻) _{meas.} ‰	Δ ¹⁷ O(NO ₃ ⁻) _{calc.} ‰	δ ¹⁸ O(NO ₃ ⁻) ‰
29 March 18:26	243	52	10.4 (10.3)	1.7 10 ⁻³	1.6 10 ⁻³	28.9	29.8	90
1 April 18:26	243	106	16.7 (16.4)	2.7 10 ⁻³	1.8 10 ⁻³	30.7	30.5	83
5 April 19:48	243	120	12.3 (9.1)	2.0 10 ⁻³	1.6 10 ⁻³	31.8	30.1	85
8 April 18:44	243	150	31.1 (8.5)	5.0 10 ⁻³	2.2 10 ⁻³	32.2	31.3	85
12 April 19:40	253	151	17.4 (9.0)	3.4 10 ⁻³	1.7 10 ⁻³	32.2	31.4	89
16 April 15:55	253	136	19.7 (9.0)	3.9 10 ⁻³	1.8 10 ⁻³	32.8	31.5	88
19 April 20:04	253	132	33.5 (9.4)	6.6 10 ⁻³	2.2 10 ⁻³	33.7	32.2	88
22 April 17:30	258	142	30.7 (14.2)	6.7 10 ⁻³	2.0 10 ⁻³	32.8	32.5	87
26 April 19:16	253	32	9.4 (6.3)	1.8 10 ⁻³	1.5 10 ⁻³	28.8	30.5	82
30 April 17:58	253	155	16.4 (8.6)	3.2 10 ⁻³	1.7 10 ⁻³	31.2	31.3	84
3 May 19:58	253	110	5.2 (1.9)	1.0 10 ⁻³	1.4 10 ⁻³	29.2	29.6	78
7 May 15:19	253	49	17.8 (8.6)	3.5 10 ⁻³	1.7 10 ⁻³			
10 May 21:18	258	105	24.7 (7.8)	5.4 10 ⁻³	1.9 10 ⁻³	32.6	32.2	92
14 May 17:00	263	42	32.8 (7.6)	7.9 10 ⁻³	2.0 10 ⁻³			

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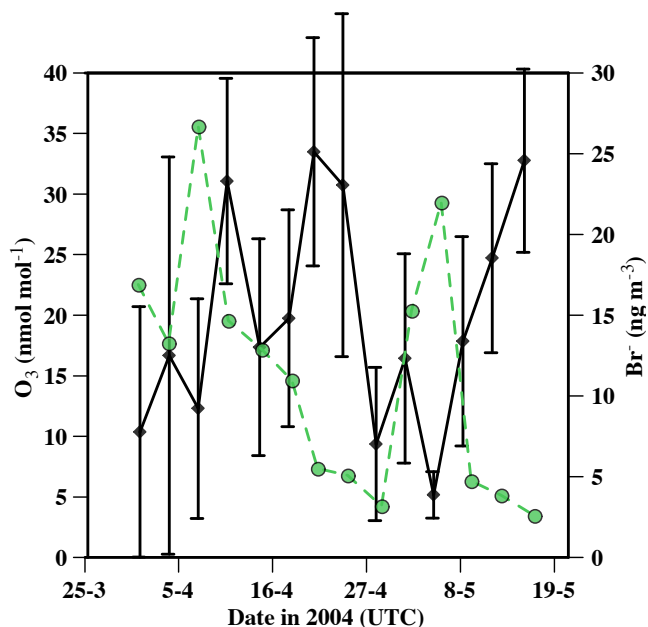


Fig. 1. Time series of the ozone mixing ratio (diamonds, black line) and particulate bromide concentration (circles, green dashed line). The error bars associated to the ozone mixing ratio represent its variability (1σ) within each averaging period. The concentration of particulate bromide carries an uncertainty of about 10%, not shown for clarity.

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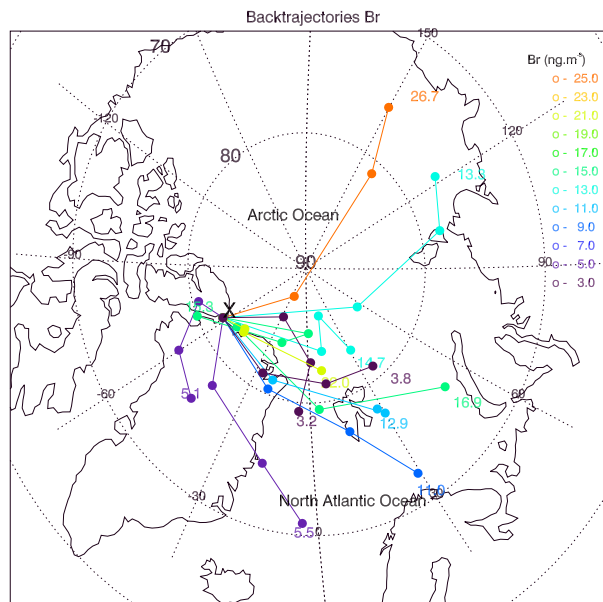


Fig. 2. Mean 6-days backtrajectories of air masses arriving at Alert during the sampling period (March–April 2004). Each backtrajectory is a mean of all the backtrajectories starting from Alert every 6 h during the collection period (about 3–4 days) of each aerosol sample (for a total of 12 samples). This provides an indication of the origin and history of air masses contributing to a given aerosol sample. The filled circles represent the position of the air masses every 2 days. The circles and lines are color-coded according to the particle bromide concentration measured in each sample (in ng m^{-3}). Note that most samples with enhanced bromide concentration are associated with trajectories originating from the siberian side of the Arctic basin or to rather motionless air masses, sitting over the Arctic Ocean. Such areas are believed to be key locations for the bromine heterogeneous chemistry involved in Arctic surface ozone depletion events.

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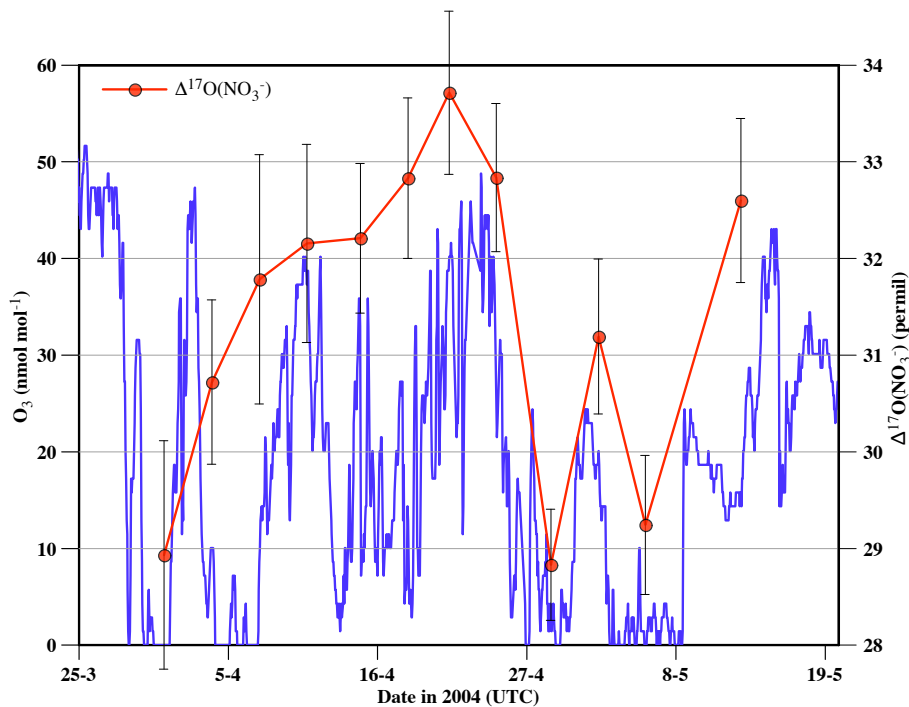


Fig. 3. Coupled evolution of surface O₃ mixing ratio (plain line) and $\Delta^{17}\text{O}(\text{NO}_3^-)$ (•). Error bars represent the uncertainty due to the mass-spectrometer internal standard error and the correction of the blank effect.

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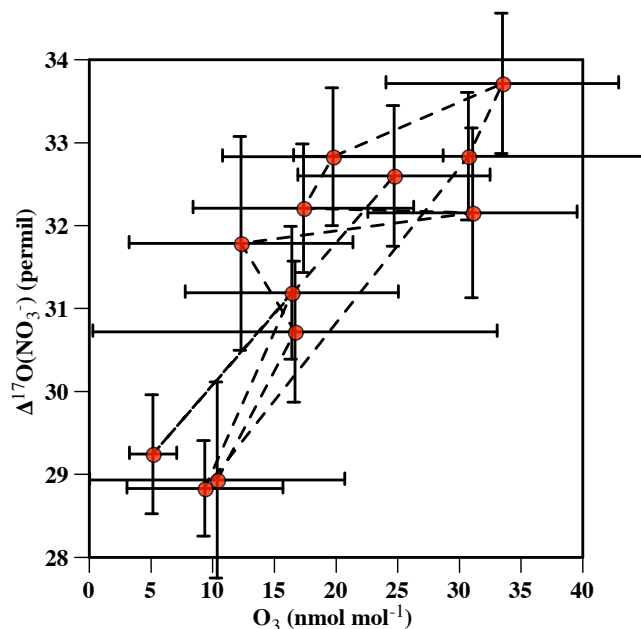


Fig. 4. Correlation plot of $\Delta^{17}\text{O}(\text{NO}_3^-)$ vs. O_3 . Ozone measurements are averaged over the collection period of each aerosol sample, horizontal error bars refer to the standard deviation. The linear regression is: $\Delta^{17}\text{O}(\text{NO}_3^-)/\text{‰} = 0.15 \text{ O}_3 / (\text{nmol mol}^{-1}) + 28.6$, with $R^2 = 0.70$ ($n = 12$).

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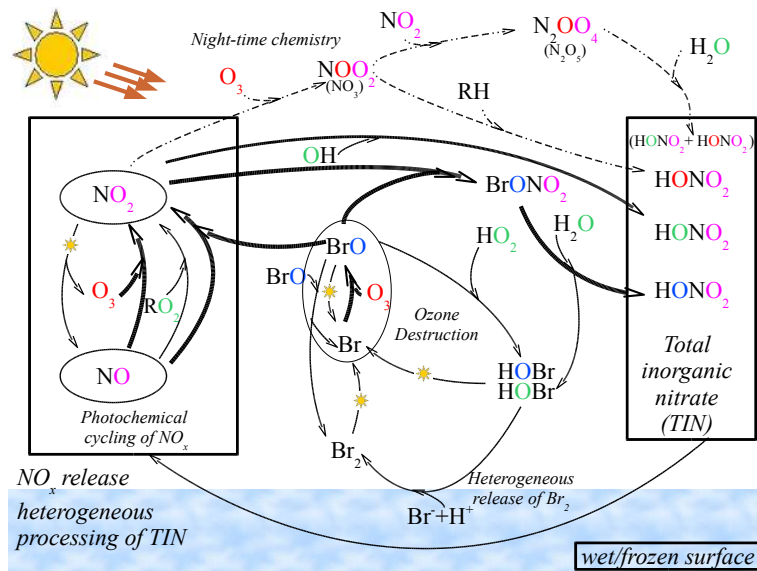


Fig. 5. Chemical cycling of nitrogen oxides (NO_x) and total inorganic nitrate (TIN) in the context of ODEs in the arctic spring at Alert. Oxygen atoms are color coded according to their isotopic anomaly, determined by the reaction between parent molecules (see text for details). The night-time chemistry channels are mentioned for completeness regarding the theoretical framework about Δ¹⁷O(NO₃⁻) (2 dots 3 dashes-arrows). Note that these channels are suppressed in the case of this study, since sunlight was permanent during the sampling campaign. Major reactions involved in anomalous oxygen transfer (for day-light reactions only) are highlighted using thicker arrow. Simplified processes for the release and the cycling of BrO are included in this figure (modified after Hönninger and Bottenheim, 2003). We neglect Cl-bearing species for clarity. Homogeneous and heterogeneous reactions are not specified in this scheme, since some may proceed both pathways (e.g. BrONO₂ + H₂O → HONO₂ + HOBr). This has no implication on the isotopic budget presented here since gas-to-particle conversions obey mass-dependent relationships. Only significant reaction products are kept in this figure.

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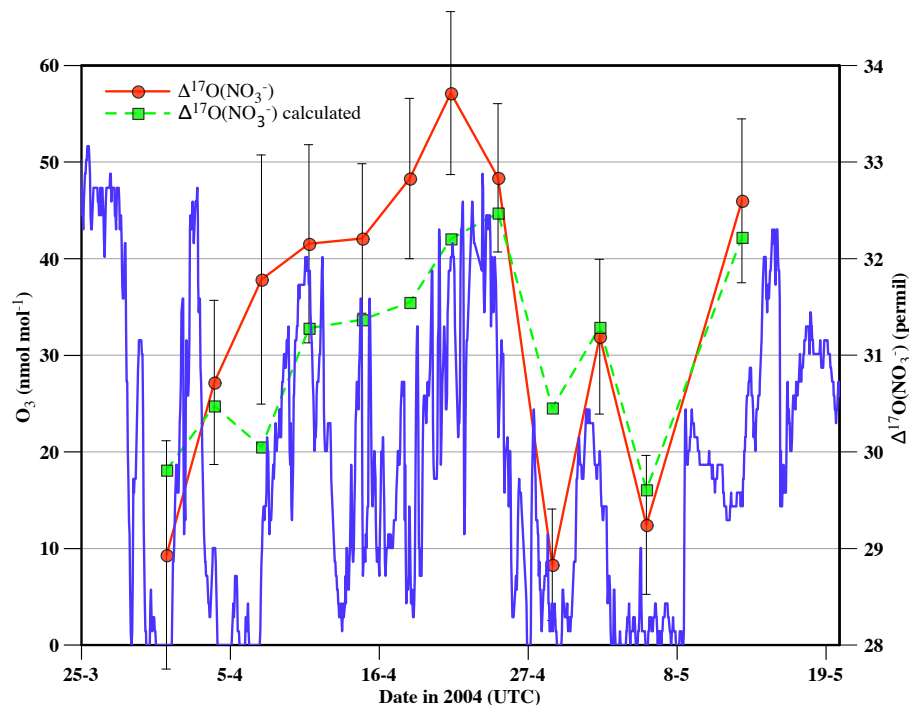


Fig. 6. Coupled evolution of surface O₃ mixing ratio (plain line), measured $\Delta^{17}\text{O}(\text{NO}_3^-)$ (•) and calculated $\Delta^{17}\text{O}(\text{NO}_3^-)$ (squares). Errors bars on measured values represent the uncertainty due to the mass-spectrometer internal standard error and the correction of the blank effect. The calculated isotopic anomalies are based on the analysis summarized in Eq. (18) and variables measured or estimated (see text for details).

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