

Major influence of BrO on the NO_x and nitrate budgets in the Arctic spring, inferred from Δ¹⁷O(NO₃⁻) measurements during ozone depletion events

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Environmental context. Ozone depletion events (ODEs) in the Arctic lower atmosphere drive profound changes in the chemistry of nitrogen oxides (NO_x) because of the presence of bromine oxide (BrO). These are investigated using the isotopic composition of atmospheric nitrate (NO₃⁻), which is a ubiquitous species formed through the oxidation of nitrogen oxides. Since BrO is speculated to play a key role in the atmospheric chemistry of marine regions and in the free troposphere, our studies contribute to the improvement of the scientific knowledge on this new topic in atmospheric chemistry.

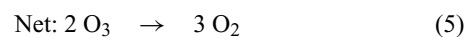
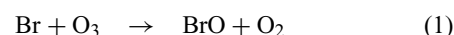
Abstract. The triple oxygen isotopic composition of atmospheric inorganic nitrate was measured in samples collected in the Arctic in springtime at Alert, Nunavut and Barrow, Alaska. The isotope anomaly of nitrate (Δ¹⁷O = δ¹⁷O - 0.52δ¹⁸O) was used to probe the influence of ozone (O₃), bromine oxide (BrO), and peroxy radicals (RO₂) in the oxidation of NO to NO₂, and to identify the dominant pathway that leads to the production of atmospheric nitrate. Isotopic measurements confirm that the hydrolysis of bromine nitrate (BrONO₂) is a major source of nitrate in the context of ozone depletion events (ODEs), when brominated compounds primarily originating from sea salt catalytically destroy boundary layer ozone. They also show a case when BrO is the main oxidant of NO into NO₂.

Additional keywords: atmospheric chemistry, halogen compounds, isotopes, nitrates, ozone depletion events.

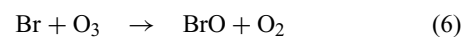
Since the discovery of the mass-independent fractionation of oxygen stable isotopes during the formation of ozone, a variety of atmospheric species were found to bear isotope anomalies.^[1] In most cases in the troposphere, the existence of an oxygen isotope anomaly (Δ¹⁷O = δ¹⁷O - 0.52δ¹⁸O)¹ is a result of the transmission of the ozone isotope anomaly during oxidation reactions. It has been shown that atmospheric nitrate possesses a high isotopic anomaly, which is attributed to the intimate coupling between ozone and nitrogen oxides (NO_x), the precursors of atmospheric nitrate.^[2]

To test the ability of Δ¹⁷O(NO₃⁻) to be influenced by variations in the mixing ratio of ozone itself, we carried out field measurements of Δ¹⁷O in atmospheric nitrate in the place on Earth where surface ozone naturally varies the most on a day-to-day basis, namely the coastal Arctic troposphere in springtime, where ozone is subject to frequent and rapid destruction shortly after polar sunrise ('ozone depletion events', ODEs). This unexpected behaviour was discovered in the early 1980s,^[3] and triggered many field studies, laboratory experiments and modelling efforts devoted to the understanding of these events. Tropospheric ozone is now known to be destroyed by halogen atoms (mostly bromine) through a catalytic cycle very

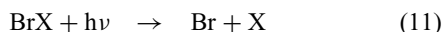
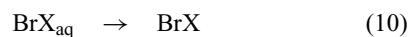
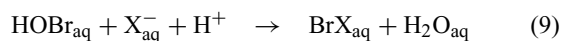
similar to the reaction scheme responsible for the destruction of stratospheric ozone by chlorine atoms:



Current research focuses on the identification of processes responsible for the trigger of such episodes and their amplification. Heterogeneous reactions (at the surface of the sea-ice seasonal snowpack and aerosols) are believed to be key in this regard, notably the 'bromine explosion' mechanism (X_{aq}⁻ denotes a liquid-phase halogen ion, either Cl⁻ or Br⁻):



¹δ^xO refers to the isotopic enrichment of a given oxygen isotope, calculated as R_{sample}^x/R_{ref}^x - 1, where R^x is the isotope ratio ^xO/¹⁶O (x = 17 or 18) for the sample and an international reference material (Standard Mean Ocean Water for oxygen isotopes). δ^xO values are expressed in ‰.



The main aspect of this sequence of reactions is the ability of the dissolved hypobromous acid (HOBr) to activate a dissolved halogen anion into the gas-phase (reactions 9 and 10). For each bromine atom entering this sequence of reaction, one molecule of ozone is destroyed and two reactive halogen atoms are released into the atmosphere, where they can in turn destroy two molecules of ozone while releasing four reactive halogen atoms; one understands the exponential nature of this chain reaction. An extensive review of the chemistry at play during ODEs is given by Simpson et al.^[4]

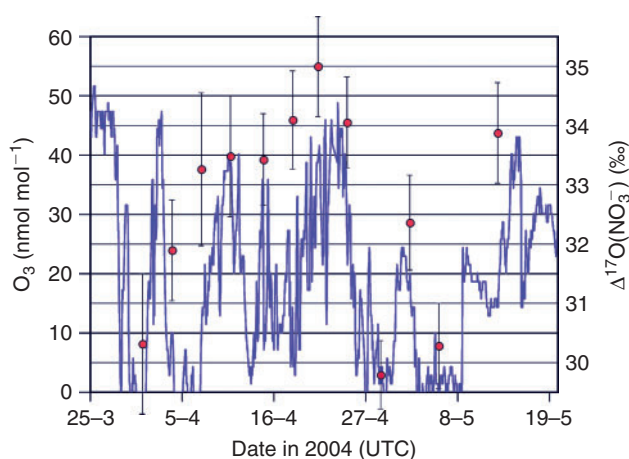


Fig. 1. Times series of ozone (line) and $\Delta^{17}\text{O}(\text{NO}_3^-)$ (symbols) for the Alert 2004 measurement campaign.

The triple oxygen isotopic composition of atmospheric inorganic nitrate was measured in samples collected at Alert, Nunavut, Canada (82.5°N), and at Barrow, Alaska (71°N) in springtime, together with measurements of ozone and BrO in the boundary layer (see Experimental section). At both stations, several ODEs were experienced during the course of the measurement campaign, with average ozone mole fractions over the 3 days of inorganic nitrate sampling reaching values as low as 5 nmol mol⁻¹ at Alert (see Fig. 1), and even lower values (down to 2 nmol mol⁻¹ on daily average) at Barrow (see Fig. 2). We see a discernible anti-correlation between the ozone mixing ratio and the concentration of particulate bromide, which is consistent with previous studies.^[3] At both stations, significantly high $\Delta^{17}\text{O}(\text{NO}_3^-)$ measurements are reported (29–35‰ at Alert, 26–36‰ at Barrow), in comparison with mid-latitude measurements carried out at the same period of the year (23–25‰).^[2] Fig. 2 presents the correlation plot between $\Delta^{17}\text{O}(\text{NO}_3^-)$ and the average mixing ratio of ozone during the collection of each sample, for the Barrow and Alert campaigns. With the very noticeable exception of a data point from Barrow, we observe a significant (possibly non-linear) correlation between $\Delta^{17}\text{O}(\text{NO}_3^-)$ and the ozone mixing ratio. At Alert, in permanent sunlight conditions after polar sunrise, the oxygen anomaly in nitrate follows the evolution of ozone mixing ratio during ODEs, with $\Delta^{17}\text{O}(\text{NO}_3^-) [\text{‰}] = (0.15 \pm 0.03) \text{O}_3 [\text{nmol mol}^{-1}] + (29.7 \pm 0.7)$ ($R^2 = 0.7$, $n = 12$). At Barrow, interestingly, during the most intense ODE ($\text{O}_3 < 2 \text{ nmol mol}^{-1}$), we measured the highest value of $\Delta^{17}\text{O}(\text{NO}_3^-)$ (36‰) which appears to be in complete contradiction with the correlation derived with the other data points. We will show later that this outlier reveals a change in oxidation pathway for NO.

In a previous study, we described and analysed the sources of the correlation in the case of Alert in spring 2004.^[5] We indicated in that analysis a plausible cause for the values of $\Delta^{17}\text{O}(\text{NO}_3^-)$, based on the mechanisms that lead to nitrate and their isotopic signatures. We found that the variability in $\Delta^{17}\text{O}(\text{NO}_3^-)$ over

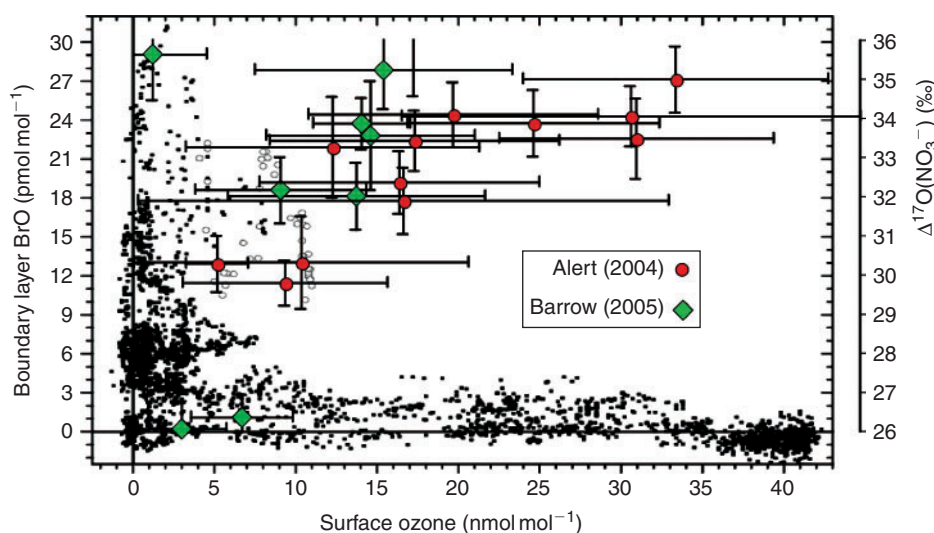
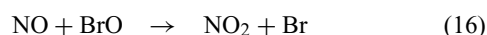
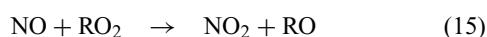
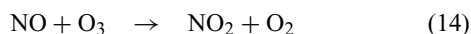
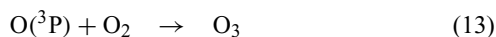
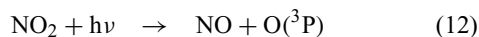


Fig. 2. Overview of the Alert and Barrow $\Delta^{17}\text{O}(\text{NO}_3^-)$ datasets. $\Delta^{17}\text{O}$ data are plotted v. the mean ozone mixing ratio during the collection period, along with BrO 'instantaneous' (integration times of a few minutes) mole fractions (black and white dots – white dots were discriminated as 'transitional periods' shortly before or after ODEs, a feature not captured by our aerosol collection periods of 1–3 days) from Hönninger and Platt.^[11] This highlights the drastic transition between the 'normal' regime (ozone > 5 nmol mol⁻¹, BrO ~2 pmol mol⁻¹) and the 'bromine explosion' regime (ozone < 5 nmol mol⁻¹, BrO > 10 pmol mol⁻¹). Horizontal error bars represent the 1 σ deviation around the mean ozone mole fraction. Vertical error bars represent experimental uncertainty for the $\Delta^{17}\text{O}(\text{NO}_3^-)$ measurements (see Experimental section).

the course of the measurement campaign is mostly accounted for by variations in $\Delta^{17}\text{O}(\text{NO}_2)$. In the Arctic troposphere, NO_2 is in photochemical equilibrium with ozone, BrO , and RO_2 (the latter representing all peroxy radicals, including HO_2) through the following series of reactions:



Each of the three last reaction pathways results in a different isotope anomaly in NO_2 . Indeed $\Delta^{17}\text{O}(\text{RO}_2) = 0\text{‰}$ and $\Delta^{17}\text{O}(\text{O}_3)$ and $\Delta^{17}\text{O}(\text{BrO})$ are expected to be different, although both in the 25–40‰ range: the terminal oxygen atom in ozone is expected to carry an isotope anomaly on the order of 1.2 times the anomaly of bulk ozone.^[6] Since reaction 1 is a direct atom transfer, and since Br most likely attacks a terminal oxygen atom in O_3 to form BrO ,^[7] BrO should carry an anomaly higher than $\Delta^{17}\text{O}$ in bulk ozone. At steady state conditions, the value of $\Delta^{17}\text{O}(\text{NO}_2)$ depends on the respective importance of its main formation channels (i.e. reactions 14, 15 and 16).^[5]

The termination reactions that ultimately produce atmospheric nitrate from NO_2 and a variety of compounds, result in an additional oxygen atom being supplied to form the nitrate. Given the generally elevated values of $\Delta^{17}\text{O}(\text{NO}_3^-)$ during both measurement campaigns, the additional oxygen atom must carry a high isotopic anomaly. BrO has the possibility of reacting with NO_2 :



In turn, BrONO_2 produced in the gas phase reacts with H_2O on ice surfaces to yield HOBr and HNO_3 .^[8] Model studies have predicted a significant influence of bromine nitrate on ODEs, since its hydrolysis promotes the formation of HOBr , which is known to be a key player of the ‘bromine explosion’ mechanism.^[4,9] However, in terms of nitrate formation, this reaction has only recently received the attention it deserves.^[10] A detailed analysis of the possible channels that lead to the formation of nitrate and its isotopic composition has led our group to confirm that the hydrolysis of bromine nitrate (BrONO_2), formed by reaction of BrO (high isotope anomaly) with NO_2 as shown in reaction 17, is a major source of nitrate in the Arctic troposphere in springtime.^[5]

The data from Barrow corroborate this new isotopic evidence, since the major role of BrO in the chemistry of nitrogen oxides explains the reversal of the correlation between $\Delta^{17}\text{O}(\text{NO}_3^-)$ and the surface ozone mixing ratio, which was only observed there. Indeed, at Alert, during the collection of a given sample, the mean ozone mixing ratio did not drop below 5 nmol mol^{-1} . This value (5 nmol mol^{-1}) is the threshold observed by Hönninger and Platt^[11] to be the limit between the regime of ‘bromine explosion’ (below this value), in which BrO mole fractions as high as 30 pmol mol^{-1} were detected, and the ‘normal’ regime characterised by moderate ODEs, for which the BrO mixing ratio does not significantly increase above the value of 2 pmol mol^{-1} . In contrast, at Barrow, one major ODE was experienced, during which the average mixing ratio of ozone dropped below 5 nmol mol^{-1} over the course of an entire sample collection

period. For that sample we measured the highest $\Delta^{17}\text{O}(\text{NO}_3^-)$ value ever recorded in the Arctic troposphere in springtime (36‰). According to the recommended kinetic data,^[12] for 10 pmol mol^{-1} of BrO and 2 nmol mol^{-1} of ozone, the rate of reaction 16 is more than one order of magnitude faster than that of reaction 14. Consequently, in this situation, NO_x is in isotopic equilibrium with BrO only. It is expected that during very low O_3 ‘bromine explosion’ events, BrO transfers a large $\Delta^{17}\text{O}$ to NO_2 and, hence, to nitrate. The anomalously high $\Delta^{17}\text{O}(\text{NO}_3^-)$ data point at low O_3 in Fig. 2 corresponds to these exceptional conditions with the highest value of $\Delta^{17}\text{O}(\text{NO}_3^-)$ and an extremely intense ODE. It is indicative of this change in oxidation pathway of NO .

Our measurements and analysis of the $\Delta^{17}\text{O}$ budget of atmospheric nitrate confirm the importance of BrO in the cycling of nitrogen oxides and ultimately in the formation of nitrate (through the hydrolysis of BrONO_2), in the Arctic troposphere in springtime. Conversely, strong interactions between NO_x and BrO and the hydrolysis of bromine nitrate support the chemistry at play during ODEs, by providing recycling agents (HOBr) and acidity (HNO_3) to ice surfaces where the ‘bromine explosion’ occurs. On the isotope side, this study shows the usefulness of mass balance approaches^[2,5] for the interpretation of $\Delta^{17}\text{O}$ in atmospheric nitrate, even if many crucial data are desperately needed to achieve further advances. For instance, $\Delta^{17}\text{O}$ in tropospheric ozone has been seldom measured,^[13] and modelling predictions^[6,14] would require further developments and field validations to be used in such studies. Large uncertainties pertain to the rates of isotope anomaly transfer during chemical reaction, which sometimes result in contradictory parameterisations. Therefore, it is possible that new results in the fast-moving research front on isotope anomalies in atmospheric species could alter the conclusions reached here.

Experimental

Samples were collected on filter material by means of high-volume sampling ($\sim 1\text{--}2 \text{ m}^3 \text{ min}^{-1}$). At Alert, Nunavut, Canada (82.5°N), we used cellulose acetate filters on a semi-weekly basis, in April–May 2004. Near Barrow, Alaska (71°N) daily sampling was performed on fibreglass filters in March 2005. Nitrate trapped in/on the filter was analysed for its triple isotopic composition using the silver nitrate thermal decomposition method.^[15] First, soluble species were extracted from the filter medium using ultra pure water (Millipore). An ion-chromatography technique was used to separate nitrate from other anionic species, and the obtained nitric acid aqueous solution was converted into silver nitrate using an ion-exchange membrane. Silver nitrate was then evaporated in silver cups, and subsequently decomposed at 550°C in a vacuum line, to yield a mixture of O_2 and NO_x . After purification, O_2 was transferred to an isotopic ratio mass spectrometer (IRMS, Dual Inlet, Thermo-Finnigan MAT 253). This method has proven to be accurate in terms of $\Delta^{17}\text{O}(\text{NO}_3^-)$ for samples as small as a few $\mu\text{mol}(\text{NO}_3^-)$, but its reliability is questionable for samples containing less than $4 \mu\text{mol}(\text{NO}_3^-)$, because of the existence of a blank effect, attributed to the formation of O_2 -derived silver oxide on the surface of the silver cup. Therefore, samples that contained too little nitrate were discarded for this analysis. The resulting uncertainty for both campaigns lies between 1 and 2‰ for $\Delta^{17}\text{O}(\text{NO}_3^-)$, mainly because of the uncertainty associated with the correction for the blank effect.^[5] The surface mixing ratio of ozone was measured using a standard UV-absorption

ozone monitor. At Barrow, tropospheric BrO was estimated using multi-axis differential optical absorption spectrometry (MAX-DOAS).^[11]

Acknowledgements

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