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# Tracing the Origin and Fate of $\text{NO}_x$ in the Arctic Atmosphere Using Stable Isotopes in Nitrate

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Atmospheric nitrogen oxides ( $\text{NO}_x = \text{NO} + \text{NO}_2$ ) play a pivotal role in the cycling of reactive nitrogen (ultimately deposited as nitrate) and the oxidative capacity of the atmosphere. Combined measurements of nitrogen and oxygen stable isotope ratios of nitrate collected in the Arctic atmosphere were used to infer the origin and fate of  $\text{NO}_x$  and nitrate on a seasonal basis. In spring, photochemically driven emissions of reactive nitrogen from the snowpack into the atmosphere make local oxidation of  $\text{NO}_x$  by bromine oxide the major contributor to the nitrate budget. The comprehensive isotopic composition of nitrate provides strong constraints on the relative importance of the key atmospheric oxidants in the present atmosphere, with the potential for extension into the past using ice cores.

The atmospheric cycle of reactive nitrogen (1) has a profound influence on the chemical composition of the lower atmosphere and the deposition pattern of nutrients at Earth's surface.  $\text{NO}_x$  contributes to the formation of ozone and particulate matter (2) and is thus important for regional air quality (3) and radiative balance (4). Atmospheric nitrate, produced upon oxidation of  $\text{NO}_x$ , is the main source of reactive nitrogen to remote ecosystems (5). Understanding the budget of  $\text{NO}_x$  and nitrate in the Arctic atmosphere is necessary to assess their environmental impact.

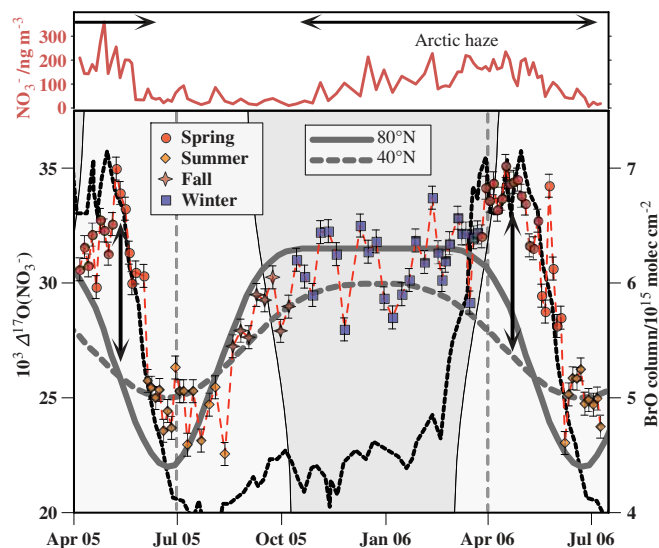
The input of reactive nitrogen to the Arctic proceeds mainly through long-range transport within the troposphere (6) and the deposition of atmospheric nitrate, associated with the so-called Arctic haze phenomenon (7, 8), which has hitherto been confined to winter and spring. A substantial direct contribution from the stratosphere to the budget of reactive species in the Arctic

marine boundary layer has been ruled out on the basis of meteorological evidence and patterns of atmospheric transport (6). Local oxidation of  $\text{NO}_x$  is generally thought to be limited because the release of appreciable amounts of  $\text{NO}_x$  to the Arctic atmosphere from the thermal decomposition of peroxyacetyl nitrate [PAN, the main reservoir species of  $\text{NO}_x$  in the atmosphere (9)] is prevented by the low temperatures pre-

vailing during winter and spring (10) and because PAN levels are too low during summer. However, the possible recycling of nitrate deposited on snow, leading to the release of  $\text{NO}_x$  to the atmosphere (11–14) and interactions with halogen oxides such as bromine oxide (BrO) during the spring (15), complicates the atmospheric budget of reactive nitrogen in the Arctic atmosphere (16). In situ emissions of  $\text{NO}_x$  may occur in the future during the summer, with the development of shipping routes associated with the reduction of sea-ice cover (17).

In general, closing the budget of atmospheric species requires the quantification of both the burden and the fluxes (that is, source/sink rates) associated with the different processes acting on them, such as emissions, chemical reactions, and transport. Conventional methods rely mostly on models that are evaluated and constrained with atmospheric concentration measurements, because there is no direct means of measuring chemical fluxes associated with individual reactions. In contrast, the measurement of isotopic ratios (18) provides direct insights into the nature and importance of individual fluxes (19). First, changes in the  $\delta^{15}\text{N}$  values during the conversion of  $\text{NO}_x$  to nitrate are minor, therefore  $\delta^{15}\text{N}$  traces  $\text{NO}_x$  sources (20). Second, because of mass-independent fractionation during its formation process (21),

**Fig. 1.** Seasonal cycle of concentrations and  $\Delta^{17}\text{O}$  of atmospheric nitrate at Alert. Also shown is the day length (from 0 to 24 hours, the shaded area corresponding to nighttime conditions). The black dashed line represents a satellite-retrieved column of BrO north of 70°N (32). Thick gray lines correspond to the calculated  $\Delta^{17}\text{O}$  value in atmospheric nitrate formed at 40° and 80°N, respectively. The black vertical arrows indicate the strong deviation from these seasonal cycles in spring, due to the interaction of BrO with snowpack-emitted  $\text{NO}_x$ . The vertical dotted lines are identical to those in Fig. 2 (delineating periods of snowpack  $\text{NO}_x$  emissions from April to June).



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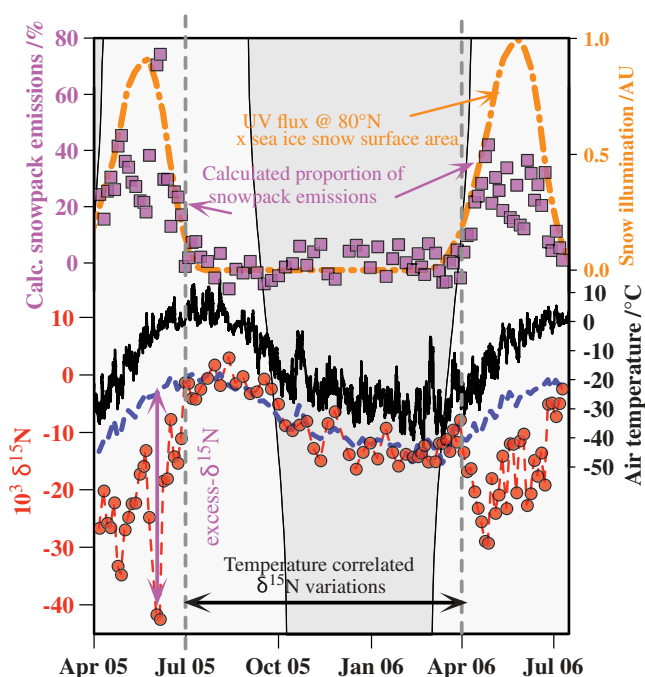
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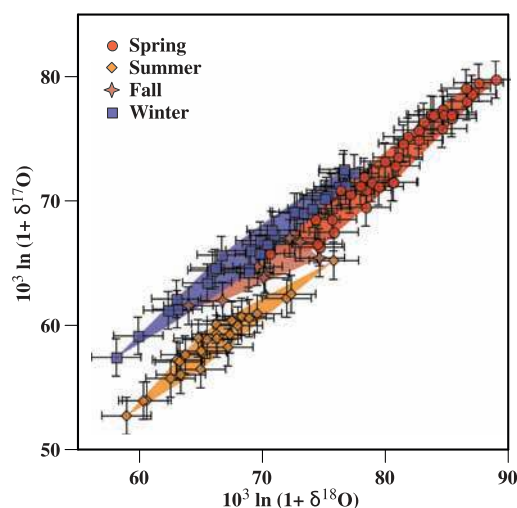
ozone possesses a strong isotope anomaly ( $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$ ), which is transferred to most short-lived oxygen-bearing species, including  $\text{NO}_x$  and nitrate. The isotope anomaly of nitrate depends on the relative importance of ozone and other key oxidants in  $\text{NO}_x$  oxidation, thus  $\Delta^{17}\text{O}$  measurements in nitrate allow researchers to identify and apportion  $\text{NO}_x$  sinks (16, 22).

This study combines atmospheric concentration and isotopic composition ( $\delta^{15}\text{N}$ ,  $\Delta^{17}\text{O}$ ) of nitrate sampled at Alert, Nunavut, Canada (82.5°N, 190 m above sea level), in order to infer a detailed budget of  $\text{NO}_x$  and nitrate on a seasonal time scale (23). The nitrate concentrations measured at Alert are typical of the yearly cycle in the Arctic lower atmosphere (Fig. 1) (8). They show a marked seasonal cycle with maximum values between November and May (on average  $140 \pm 50 \text{ ng m}^{-3}$ ) and minimum values between June and October ( $40 \pm 20 \text{ ng m}^{-3}$ ).

**Fig. 2.** Temporal evolution of  $\delta^{15}\text{N}$  of atmospheric nitrate at Alert (red dots). Shaded areas are identical to those in Fig. 1. Also shown is the air temperature record (black solid line). The blue dashed line represents the seasonal cycle of  $\delta^{15}\text{N}$  inferred from temperature variations (between July and March). Purple squares represent the calculated contribution of snowpack emissions inferred from an isotopic mass balance, which qualitatively correlates with the normalized UV radiation at 80°N interacting with snow surfaces in the Arctic basin (termed snow illumination).



**Fig. 3.** Three-isotope plot of atmospheric nitrate oxygen isotopes at Alert. Symbols and colors refer to the seasons delineated in Fig. 1. Summer, spring, and winter correspond to  $\text{NO}_x$  oxidation pathways involving OH, BrO, and  $\text{NO}_3$ , respectively, so that reporting oxygen isotopic measurements on this plot offers a way to unambiguously identify (and possibly apportion)  $\text{NO}_x$  oxidation pathways. The slopes (intercepts) of the linear regression lines are 0.88, 0.71, and 0.74 (2.4, 11.6, and 15.0) for spring, summer, and winter, respectively.



Throughout the year,  $\delta^{15}\text{N}$  exhibits pronounced variations, spanning a very large range [between  $-42$  and  $3$  per mil (‰)], which encompasses previous measurements carried out in the Arctic (Fig. 2) (24, 25). Summer months exhibit the highest values (on average  $-1\%$  in July and August), smoothly decreasing to reach values on the order of  $-15\%$  in winter (until March), which is consistent with seasonal variations inferred from a Greenland snowpit (25). This seasonal cycle is more pronounced than and opposite to seasonal variations observed at industrialized mid-latitude sites (26, 27) that are driven by isotopic exchange between  $\text{NO}$  and  $\text{NO}_2$  (26). During most of the year (between July and March),  $\delta^{15}\text{N}$  variations are strongly correlated with air temperature ( $T$ ) [ $10^3 \delta^{15}\text{N} = 0.37 \times T (\text{in } ^\circ\text{C}) - 1.8$ ,  $R^2 = 0.81$ ,  $n = 41$ ,  $P < 0.001$ , fig. S2]. This relationship points toward an isotopic effect arising from physicochemical transformations

within the Arctic region and during the transport of nitrate and reactive nitrogen species from mid-latitudes (26), although the driving factor cannot be identified on the basis of this sole data set. The compact relationship between  $\delta^{15}\text{N}$  and temperature breaks down completely during spring, suggesting the onset and predominance of a process anomalous with respect to the rest of the year.  $\delta^{15}\text{N}$  becomes extremely variable and reaches record low values: They are matched only by measurements carried out in coastal Antarctica (28, 29) that have unambiguously been attributed to emissions of reactive nitrogen from the snowpack (11, 14, 29). The  $^{15}\text{N}$  isotopic effect associated with this snowpack recycling loss is large, with a fractionation constant ( $\epsilon$ ) on the order of  $-54\%$  in central Antarctica (30), leading to elevated  $\delta^{15}\text{N}$  values in nitrate remaining in the snow (30) and, as a consequence of mass conservation, depleted  $\delta^{15}\text{N}$  values in the emitted species (29). Assuming that, without snowpack emissions,  $\delta^{15}\text{N}$  would correlate with temperature year-round, and using the ratio of the deviation of  $\delta^{15}\text{N}$  data from this seasonal trend with  $\epsilon$  measured in Antarctica (30) (due to the lack of Arctic measurements), it is found that snowpack emissions can contribute to at least a third of the budget of  $\text{NO}_x$  and nitrate during spring [Fig. 2 and supporting online material (SOM) text]. Although snowpack emissions do not represent a net source of reactive nitrogen to the Arctic, they do have a substantial impact on the seasonality of its concentrations and the oxidative capacity of the lower Arctic troposphere, especially in spring. In the same way, this phenomenon can also explain the absence of a correlation between the atmospheric nitrate concentration record and the concentration time series of other anthropogenic species (31). As shown by Fig. 2, the derived contribution of snowpack emissions correlates with the amount of ultraviolet (UV) (calculated for 80°N) interacting with snow surfaces in the Arctic basin, suggesting that snow photochemistry drives much of these reactive nitrogen emissions: The calculated impact of snowpack emissions is maximal when both snow and UV radiation coexist during spring. During winter, permanent nighttime conditions prevent photochemistry, and in summer and fall the snow cover is minimal.

Oxygen isotopic data are represented as a function of the season (Figs. 1 and 3). Summer corresponds to permanent sunlight conditions, and fall corresponds to the sharp transition into the winter, during which sunlight is permanently absent. The spring period corresponds to polar sunrise, when frequent surface ozone depletion events (ODEs) are observed at Alert, due to active halogen chemistry (15, 32). The seasonal pattern of  $\Delta^{17}\text{O}$  (Fig. 1) is strongly asymmetrical, with lowest values in summer, whereas the highest  $\Delta^{17}\text{O}$  values correspond to the spring, followed by the winter and fall. The highest variability is observed during spring. Variations of the  $\Delta^{17}\text{O}$  of nitrate can be understood in terms of the transfer of the isotope anomaly from ozone to nitrate through different formation pathways (16, 22).

Regardless of the  $\text{NO}_x$  source,  $\Delta^{17}\text{O}$  of  $\text{NO}_2$  is a direct function of the isotope anomaly of ozone and the concentration of  $\text{NO}$  oxidants ( $\text{O}_3$ ,  $\text{BrO}$ , and  $\text{RO}_2$ ) due to rapid photochemical recycling (16, 22, 33). When  $\text{NO}_2$  is oxidized to nitrate, an additional O atom is incorporated from various source molecules, depending on the  $\text{NO}_2$  oxidation pathway (16, 22), which results in characteristic  $\Delta^{17}\text{O}$  values in the nitrate produced. Three groups of nitrate formation pathways need to be considered, depending on the nature of the  $\text{NO}_2$  oxidant: (i) OH radicals, (ii)  $\text{O}_3$ , and (iii)  $\text{BrO}$ . The first case (i) corresponds to the reaction of OH with  $\text{NO}_2$  (directly producing  $\text{HNO}_3$ ), which operates only during the day because OH levels are negligible at night. The reaction of  $\text{NO}_2$  with ozone (ii) yields the nitrate radical, which can react either with hydrocarbons and reduced sulfur compounds to give  $\text{HNO}_3$  or with  $\text{NO}_2$  to form dinitrogen pentoxide,  $\text{N}_2\text{O}_5$ , whose heterogeneous hydrolysis leads to nitrate formation (3). These channels (ii) essentially operate at night because  $\text{NO}_3$  is rapidly photolysed back to  $\text{NO}_2$  during the day. The reaction of  $\text{NO}_2$  with  $\text{BrO}$  (iii) yields the reservoir species bromine nitrate ( $\text{BrONO}_2$ ), which can in turn hydrolyze into nitrate. Each of these channels results in a different  $\Delta^{17}\text{O}$  value in the produced nitrate, thus providing an easy way to tabulate the isotopic signature of each  $\text{NO}_x$  sink (table S1). An atmospheric chemistry box model was used to compute the  $\Delta^{17}\text{O}$  of nitrate produced in winter and summer at middle ( $40^\circ\text{N}$ ) and polar ( $80^\circ\text{N}$ ) latitudes (SOM text). These two extreme cases represent the two sources of Arctic nitrate that is, long-range transport and local production, respectively). Halogen chemistry was not taken into account because it does not operate significantly in summer and winter (15, 32). In winter,  $\text{NO}_x$  is mostly oxidized through the ozone channels (ii). In summer, the reaction  $\text{OH} + \text{NO}_2$  (i) is the main  $\text{NO}_x$  oxidation channel. The seasonal contrast is more pronounced in polar regions as compared to middle latitudes because of permanent nighttime conditions in winter and permanent daytime in summer, so that predominant channels are more exclusive. Under the assumption that changes in actinic flux are the main drivers of the seasonal changes in  $\text{NO}_x$  oxidation pathways (22), the annual cycle of  $\Delta^{17}\text{O}$  can then be inferred from the two model-calculated values (winter and summer) and the solar zenith angle. These calculations are shown in Fig. 1, along with the field measurements. For most of the year (from July to March), measured  $\Delta^{17}\text{O}$  values fall by and large between the modeled values, with a tendency to better follow the temporal evolution of the modeled  $\Delta^{17}\text{O}$  at  $40^\circ\text{N}$ , especially in summer, despite some scatter in the data. Oxygen isotopic measurements are consistent with the idea that atmospheric nitrate mostly originates from long-range transport from mid-latitudes at this time of the year (6, 8). In contrast,  $\Delta^{17}\text{O}$  measurements during spring are found far away from the range of model-calculated values. The concurrence of elevated  $\Delta^{17}\text{O}$  values and

large-scale observations of enhanced  $\text{BrO}$  levels in the polar lower atmosphere (Fig. 1) (32) strongly suggests that  $\text{NO}_x$  is mainly oxidized to nitrate within the Arctic basin through the hydrolysis of  $\text{BrONO}_2$  (16).

Scrutiny of the  $\delta^{15}\text{N}$  and  $\Delta^{17}\text{O}$  time series shows that abnormally high  $\Delta^{17}\text{O}$  values, indicative of local  $\text{NO}_x$ -halogen chemistry, are recorded only when low  $\delta^{15}\text{N}$  values, indicative of snowpack  $\text{NO}_x$  emissions, occur. The scenario emerging from this dual isotopic approach, complemented by the regional  $\text{BrO}$  measurements (32), is that interactions of UV light with snow surfaces drive photochemical loss of nitrate in the snowpack and the concomitant release of  $\text{NO}_x$  during spring. In turn,  $\text{NO}_x$  interacts with  $\text{BrO}$  to profoundly modify the budget of atmospheric nitrate, which is then formed almost exclusively by  $\text{BrONO}_2$  hydrolysis. This implies that snowpack  $\text{NO}_x$  emissions are key to the atmospheric budget of  $\text{NO}_x$  and nitrate at high latitudes during springtime, confirming the significant impact of snow on the ground on the overlying atmosphere (12).  $\text{NO}_x$  emissions also play a role in the recycling of atmospheric reactive halogen species, in particular through the role of  $\text{BrONO}_2$ , thereby forming a link between the chemistry of  $\text{NO}_x$  and reactive halogens. The latter observation may explain why ODEs do not occur in fall, because at this time of the year the interaction of UV light (maximal in June) and snow surfaces is minimal (see Fig. 2, fig. S3, and SOM text for details). It could imply either that bromine activation requires the simultaneous occurrence of UV light and the presence of snow, as for snowpack  $\text{NO}_x$  emissions, or that snowpack  $\text{NO}_x$  emissions themselves play a role in bromine explosion.

Another important implication of oxygen isotopic measurements is the determination of purely chemical budgets. The data set can be used to identify the isotopic signature of almost pure  $\text{NO}_x$  oxidation channels. Figure 3 summarizes all the oxygen isotopic data on a three-isotope plot, where seasonally labeled data plot on distinct arrays. Each of these seasonal arrays broadly represents the signature of predominant nitrate formation mechanisms at the hemispheric scale (summer,  $\text{OH} + \text{NO}_2$ ; winter,  $\text{NO}_3$  radical; spring, halogen chemistry). Hence the oxygen isotopic composition of atmospheric nitrate offers a way to identify and apportion  $\text{NO}_x$  oxidation pathways. In contrast to elaborate in situ concentration measurements [as in (3)], this “geochemical” approach relies on standard aerosol sampling techniques, which are easy to implement on large geographical scales and for long-term studies, and on stable isotope measurements, which can be performed in the laboratory weeks or months after the sampling. The isotope tool is thus able to assist in identifying sources and sinks of reactive nitrogen in complex environments or matrices, such as polluted areas or polar ice cores.

#### References and Notes

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23. Nitrate (both particulate and gas-phase  $\text{HNO}_3$ ) trapped on Whatman 41 filters by means of high-volume sampling at a subweekly resolution between April 2005 and July 2006 was dissolved in ultrapure water and analyzed for its oxygen and nitrogen isotope ratios using an automated version of the denitrifier technique (34). Uncertainties ( $1\sigma$ ) pertaining to  $\delta^{18}\text{O}$ ,  $\Delta^{17}\text{O}$ , and  $\delta^{15}\text{N}$  measurements are 2, 0.4, and 0.5‰, respectively (see SOM for details).
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35. Thanks are due to the Alert Global Atmospheric Watch station personnel for aerosol field sampling in rough conditions; to E. Vince for help with bacterial cultures; to J. Kaiser, D. Sigman, and M. Hastings for their help with setting up the analytical technique; to G. Picard, F. Dominé, and M. Thiemens for helpful discussions; and to J.-Ph. Balestrieri for technical support. Funding was provided by the Institut Polaire–Paul-Émile Victor, Institut National des Sciences de l’Univers LEFE-CHAT, and the European Science Foundation under the EUROCORES Programme EuroCLIMATE, through contract no. ERAS-CT-2003-980409 of the European Commission, DG Research, FP6. S.M. acknowledges the Ecole National des Ponts et Chaussées for financial support.