

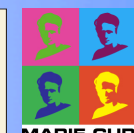


# Comprehensive Isotopic Composition of Nitrate in Antarctic Snow and Atmospheric Aerosol Samples:

## Towards Interpretation of the Polar Ice Core Record

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### Abstract

The nitrogen ( $\delta^{15}\text{N}$ ) and triple oxygen ( $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$ ) isotopic composition of nitrate ( $\text{NO}_3^-$ ) has been measured year-round in the atmosphere and surface snow at Dome C, Antarctica. Results indicate that seasonal variations of the oxygen isotopic composition of  $\text{NO}_3^-$  in the surface snow ("skin layer") closely follow those of atmospheric  $\text{NO}_3^-$ , suggesting that the upper-most snow layer acts as an integrator of the atmospheric signal. Maximum values for surface snow  $\Delta^{17}\text{O}(\text{NO}_3^-)$  (40-45 ‰) are observed in the winter due to the increased oxidation of  $\text{NO}_x$  by ozone ( $\text{O}_3$ ), which possesses a strongly positive oxygen isotope anomaly. The lowest  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values (25-30 ‰) for surface snow are observed in the late spring and early summer when  $\text{O}_3$  concentrations are low and atmospheric  $\text{NO}_3^-$  production occurs predominantly through reaction of  $\text{NO}_x$  with the hydroxyl radical ( $\text{OH}$ ). Conversely, skin layer  $\delta^{15}\text{N}$  ( $\text{NO}_3^-$ ) values are consistently enriched by 10-20 ‰ over the atmospheric signal throughout most of the year. Information on these cycles is critical to the development of a conceptual view of  $\text{NO}_3^-$  recycling at the snow surface on the Antarctic plateau.

### Introduction

Atmospheric nitrogen oxides ( $\text{NO}_x = \text{NO} + \text{NO}_2$ ) play a key role in the biogeochemical cycling of reactive nitrogen and can have a significant impact on the oxidative capacity of the atmosphere. Nitrate ( $\text{NO}_3^-$ ) is the final product of the atmospheric oxidation of  $\text{NO}_x$  and is one of the most abundant ions present in polar ice and snow. There has been a great amount of interest in using the polar ice core record of  $\text{NO}_3^-$  concentration (Figure 1) and isotopic composition to assess past levels of atmospheric  $\text{NO}_x$  and to infer historic variations in  $\text{NO}_3^-$  production pathways.  $\Delta^{17}\text{O}$  values for  $\text{NO}_3^-$  are deemed especially important as they are indicative of  $\text{NO}_x$  interactions with important atmospheric oxidants (e.g.,  $\text{O}_3$  and  $\text{OH}$ ) and may reflect the overall oxidative capacity of the atmosphere. However, strong post-depositional processing (photolysis of  $\text{NO}_3^-$  and desorption/evaporation of  $\text{HNO}_3$ ) in snow can lead to significant isotopic fractionation within the upper snow pack, particularly for nitrogen isotopes (Figure 2), thus obscuring the isotopic signal and complicating the interpretation of long-term ice core records of nitrate. This is particularly true for sites with low snow accumulation rates, such as Dome C. It is hypothesized that the upper-most snow layer maintains an approximate equilibrium with the lower atmosphere and thus the isotopic signal is preserved in this "skin layer," however this has yet to be established in field studies. A primary goal of this project was to establish the atmosphere/snow transfer of the  $\text{NO}_3^-$  isotopic signal, particularly the  $\Delta^{17}\text{O}$  anomaly, which reflects the relative importance of different  $\text{NO}_3^-$  formation pathways (Figure 3).

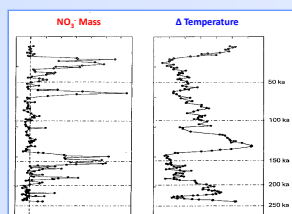


Figure 1: Depth profile of  $\text{NO}_3^-$  from the Vostok ice core (Antarctica) along with co-variations in temperature over the last two climatic cycles (Legrand et al., Ann. Glaciol., 1999).

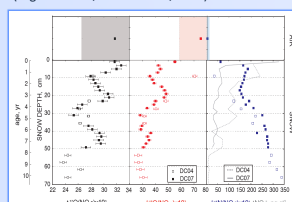


Figure 2: Depth profiles of the nitrogen and triple oxygen isotopic composition of  $\text{NO}_3^-$  from DC snow pits showing isotopic fractionation (particularly for nitrogen) and mass loss with depth (Frey et al., Atmos. Chem. Phys., 2009).

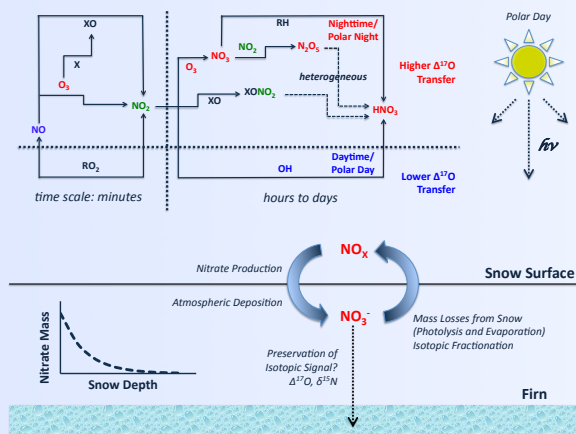


Figure 3: Conceptual model of atmospheric  $\text{NO}_x$  production and post-depositional processing on the Antarctic plateau.  $\text{NO}_x$  production results from the interaction of  $\text{NO}_x$  with various atmospheric oxidants ( $\text{O}_3$ ,  $\text{OH}$ , etc.), with preferred day- and nighttime reaction pathways. These various mechanisms leading to  $\text{NO}_3^-$  production result in different levels of  $\Delta^{17}\text{O}$  transfer. After deposition, nitrate at the snow surface is subject to photolysis ( $\text{NO}_3^-$ ) and desorption/evaporation (nitric acid), leading to the depletion of nitrate mass in the upper-most layers. The surface snow is thus a source of  $\text{NO}_x$  to the local atmosphere where it is again subject to atmospheric oxidation.

### Methods

◆ Snow and atmospheric sampling was conducted at regular intervals throughout 2009 at Dome C, Antarctica (75.1° S, 123.3° E). Atmospheric particle samples were collected on glass fiber filters using a high volume sampler operated at 1 m<sup>3</sup> min<sup>-1</sup>. Surface snow (approximately the first 3-5 mm) samples were collected at regular intervals.

#### ◆ $\text{NO}_3^-$ extraction and analysis

- Aerosol samples extracted with 40 ml of ultra-pure water
- Snow samples melted and preconcentrated via quantitative trapping of  $\text{NO}_3^-$  on anion exchange resin
- $\text{NO}_3^-$  concentrations determined for snow and aerosol samples using a colorimetric method via continuous flow analysis

#### ◆ Isotopic measurements

- Comprehensive  $\text{NO}_3^-$  isotopic composition ( $\delta^{17}\text{O}$ ,  $\delta^{18}\text{O}$ ,  $\delta^{15}\text{N}$ ) determined using the bacterial denitrifier method, where sample  $\text{NO}_3^-$  is converted to  $\text{N}_2\text{O}$  via denitrification by *Pseudomonas aureofaciens*, then cryofocused using a liquid nitrogen trap
- $\text{N}_2\text{O}$  decomposed to  $\text{O}_2$  and  $\text{N}_2$  in a purified helium flow using a gold furnace (900° C)
- Chromatographic separation and injection into Isotope Ratio Mass Spectrometer (Thermo Finnigan™ MAT 253)

### Isotopic Definitions

$$\delta = (R_{\text{sample}} / R_{\text{reference}}) - 1$$

where  $R = {}^{17}\text{O}/{}^{16}\text{O}$ ,  ${}^{18}\text{O}/{}^{16}\text{O}$ , or  ${}^{15}\text{N}/{}^{14}\text{N}$

$$\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$$

### Results and Discussion

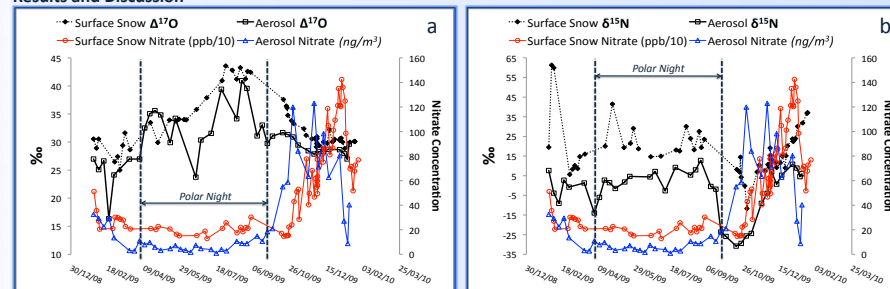


Figure 4: Seasonal variations in  $\Delta^{17}\text{O}$  (a) and  $\Delta^{15}\text{N}$  (b) of  $\text{NO}_3^-$  in skin layer snow and aerosol samples collected at DC during 2009, referenced against VSMOW and atmospheric  $\text{N}_2$ , respectively, and reported as ‰ (left y-axis). Surface snow and atmospheric  $\text{NO}_3^-$  concentrations are plotted on the right y-axis in each graph. Variations in the oxygen isotopic composition of  $\text{NO}_3^-$  in surface snow closely follow those of atmospheric  $\text{NO}_3^-$ . In the winter, the  $\Delta^{17}\text{O}(\text{NO}_3^-)$  of both surface snow and aerosols reach maximum values (40-45 ‰), reflecting an increased interaction of  $\text{NO}_x$  with ozone ( $\text{O}_3$ ), possibly of a stratospheric origin, which possesses a strongly positive oxygen isotope anomaly ( $\Delta^{17}\text{O}$ ). The lowest  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values (25-30 ‰) for surface snow and aerosols are observed in the late spring/summer when  $\text{O}_3$  concentrations are at a seasonal low and atmospheric  $\text{NO}_3^-$  production occurs predominantly through reaction of  $\text{NO}_x$  with the hydroxyl radical ( $\text{OH}$ ). Conversely, skin layer  $\delta^{15}\text{N}(\text{NO}_3^-)$  values are consistently enriched by 10-20 ‰ over the atmospheric signal throughout most of the year. This observation may indicate a loss of lighter  $\text{NO}_3^-$  isotopologues from the skin layer due to photolysis. Alternatively, this offset could be explained by the existence of a thermodynamic equilibrium between  $\text{HNO}_3$  in the condensed and gaseous phases, which can lead to a fractionation of ~20 ‰, with the heavy isotope in the condensed phase. For both the  $\Delta^{17}\text{O}$  and  $\delta^{15}\text{N}$  of  $\text{NO}_3^-$ , an approximate equilibrium between the atmosphere and skin layer is achieved in the late spring/early summer, when atmospheric  $\text{NO}_3^-$  concentrations reach their annual maxima (> 100 ng m<sup>-3</sup>). This strongly suggests that  $\text{NO}_3^-$  removal and subsequent recycling is very intense and most likely composed of more than one cycle (i.e., deposition, removal, atmospheric processing, redeposition or possibly export).

### Summary

- ◆ The atmospheric  $\Delta^{17}\text{O}(\text{NO}_3^-)$  signal is preserved in the surface skin layer (Figure 3a)
- ◆ Maximum values in winter concurrent with high  $\text{O}_3$  concentrations, minimum values in spring/summer concurrent with high solar radiation (maximum  $\text{OH}$  concentration)
- ◆  $\delta^{15}\text{N}(\text{NO}_3^-)$  values of surface snow also reflect the basic atmospheric trend, with lowest values occurring during the late spring/early summer, when photolysis of snowpack  $\text{NO}_3^-$  results in high levels of atmospheric  $\text{NO}_x$  and  $\text{NO}_3^-$  (Figure 3b)
- ◆ 10-20 ‰ offset throughout most of the year indicates strong post-depositional processing of nitrogen isotopes, even in the skin layer

### Acknowledgement

The authors would like to thank Jean Martins and Erwann Vince of the Laboratoire d'étude des Transferts en Hydrologie & Environnement (LTHE) for their assistance in preparing bacterial cultures. The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant n° 237890. This work was also supported by the French Polar Institute (IPEV) NITDC program under grant n° 1011 and by the Institut national des sciences de l'Univers (INSU) program LEFE.