Isotopic view on nitrate loss in Antarctic surface snow

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[1] Massive post-depositional processes alter the nitrate concentration in polar firn where the annual snow accumulation is low. This hinders a direct atmospheric interpretation of the ice core nitrate record. Fractionation of nitrate isotopes during post-depositional nitrate loss may allow estimating the amount of nitrate loss in the past. We measured $\delta^{15}N$ of nitrate in two Antarctic surface cores from the Dome C area. In concert with the known concentration decrease with depth we observe an increase in the isotopic signature. Assuming a Rayleigh type process we find an isotope effect of $\varepsilon = -54‰$. We measured the fractionation factor for photolysis in the laboratory and obtained $\varepsilon = -11.7 \pm 1.4‰$. As the observed fractionation factor in the firn is much lower this rules out that photolysis in the surface snow is the main process leading to the dramatic nitrate loss in the top centimeters of the firn. **Citation:** Blunier, T., G. L. Floch, H.-W. Jacobi, and E. Quansah (2005), Isotopic view on nitrate loss in Antarctic surface snow, *Geophys. Res. Lett.*, *32*, L13501, doi:10.1029/2005GL023011.

1. Introduction

[2] Nitrate (NO_3^-) deposition is the final fate of various N species in polar regions [*Wolff*, 1995]. Therefore, NO_3^- from polar ice cores can potentially be used to investigate the atmospheric cycle of reactive nitrogen compounds. Nitrogen compounds have an important impact on atmospheric chemistry and the oxidation capacity of the atmosphere. Unfortunately, it turned out that NO_3^- undergoes massive depositional and post-depositional processes in the firn. This hinders a direct atmospheric interpretation of the ice core NO_3^- records [*Röthlisberger et al.*, 2002].

[3] In Antarctica's low accumulation areas most of the NO_3^- deposited at the surface is lost when the snow reaches a few decimeters depth [*Mayewski and Legrand*, 1990; *Röthlisberger et al.*, 2000]. On the other hand, high accumulation sites (e.g., Summit, Greenland) presently preserve more than 90% of the initial NO_3^- [*Burkhart et al.*, 2004]. Here the annual cycle in the concentration is preserved and also the isotopic composition of NO_3^- appears largely unaffected by post-depositional processes [*Hastings et al.*, 2004].

[4] *Mulvaney et al.* [1998] describe the depositional processes affecting NO_3^- in surface snow as a short-term equilibrium between the atmosphere and the snowpack where uptake and loss operate over the daily cycle with a net loss over weeks and months. The seasonal NO_3^- signal is preserved in this process although smoothed by diffusion. At very low accumulation sites the net loss of NO_3^- continues over several years and results in a complete loss of the annual signal for very low accumulations sites like Vostok, or Dome C.

[5] Key parameters determining NO_3^- loss are established but are not clearly quantified [*Dibb and Whitlow*, 1996; *Mayewski and Legrand*, 1990; *Röthlisberger et al.*, 2000]. They include temperature-accumulation, near surface air concentration, elevation, and presence of other species in snow (see *Burkhart et al.* [2004] for a compilation). Major candidates for the loss process in Antarctica as well as in Greenland are photolysis and re-evaporation. The latter may be related to wind driven effects [*Mulvaney et al.*, 1998].

[6] In low accumulation sites snow remains relatively long in close proximity to the surface and thus in range of radiation of intense UV. Therefore, it seems possible that photolysis is the main process leading to the NO_3^- loss [*Röthlisberger et al.*, 2002]. Nonetheless, a model study suggests that only 40% of the NO_3^- content can be depleted by photolysis for conditions found at Dome C [*Wolff et al.*, 2002].

[7] The isotopic composition of NO_3^- deposited on the snow depends on the NO_3^- sources and the chemical reactions taking place during the transport to the deposition site [*Freyer et al.*, 1996]. The isotope composition in freshly fallen snow is expected to equal the one in the atmosphere above the snow [*Hastings et al.*, 2004]. *Wagenbach et al.* [1998] present Antarctic atmospheric $\delta^{15}N$ values varying from 0 to $-50‰$. In a pioneer study *Freyer et al.* [1996] measured $\delta^{15}N$ of NO_3^- in ice cores from Greenland, Antarctica and the Alps. They found increasing $\delta^{15}N$ values with the inverse accumulation rate for Holocene samples. This increase goes along with a NO_3^- concentration decrease for most sites, which is interpreted as originating from a loss process in the freshly fallen snow. Thus, the changes in the nitrogen (and oxygen) isotope composition of NO_3^- may allow for the reconstruction of the atmospheric NO_3^- concentration once the fractionation processes in the firn are understood.

[8] Here we investigate the first 15 cm of a firn core taken at the EPICA-DC site in the austral summer of 2003 by means of isotope analysis. Dome C (75°06′S, 123°21′E, altitude 3233 m a.s.l.) has an annual mean temperature of $-54.5°C$ and a snow accumulation rate of 25.0 kg m^{-2} year^{-1} (corresponding to about 7.4 cm of snow per year at the surface). At this low accumulation site the NO_3^- concentration decreases by orders of magnitude over the first 10 cm of firn. Release in the form of HNO_3 and photolysis of NO_3^- have been proposed as the cause for this loss [*Röthlisberger et al.*, 2002]. Further we determined the fractionation factor for $\delta^{15}N$ of NO_3^- associated with photolysis of NO_3^- in snow. Based on laboratory and

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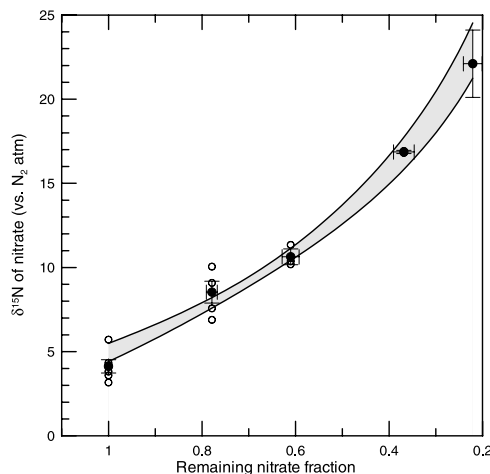[2]Alfred Wegener Institute for Polar and Marine Research, Bremerhaven, Germany.

Figure 1. $\delta^{15}N$ of NO_3^- measured in artificial snow versus the remaining NO_3^- fraction after exposure to radiation. Circles are replicate isotope measurements using the same snow sample. Dots are mean values with error bars. The gray area represents the one sigma spread of the Monte Carlo simulations for the Rayleigh type process. The calculated fractionation factor is $\varepsilon = -11.7 \pm 1.4‰$, where $\varepsilon = (\alpha - 1)$.

firn measurements we are able to show that photolysis is not the sole process responsible for the NO_3^- loss in the firn.

2. Measurements

[9] We measure NO_3^- isotopes using a microbiological method developed by Sigman et al. [*Sigman et al.*, 2001]. The method is based on the isotopic analysis of nitrous oxide (N_2O) generated from NO_3^- by denitrifying bacteria. We use *Pseudomonas Chlororaphis*, which lacks N_2O reductase activity, and follow the protocol for bacteria cultivation by *Sigman et al.* [2001]. 2 ml aliquots of bacteria slush are added to 20 ml sample vials. Remnant N_2O in the vials is removed by purging ultrapure helium carrier gas at 20 ml/min for 2–4 hours, before melt water from the samples (or artificial snow) is added to the cultures. After an overnight incubation, the bacteria quantitatively converted NO_3^- to N_2O. A poison (NaOH) is injected to lysis the bacteria and stop the reaction. Using a helium carrier gas, N_2O is stripped from each sample vial and analyzed by a GC/MS system (Thermo Finnigan MAT 253). With standards we obtain a reproducibility of ± 15 ppb for the concentration and $\pm 0.2‰$ for $\delta^{15}N$. All measurements are made versus a N_2O standard gas. Each batch of samples includes samples with NO_3^- standards (IAEA-N3), which have an assigned $\delta^{15}N$ of 4.7‰ versus atmospheric N_2.

[10] Our system is designed to work with a sample amount of 10 nmole of NO_3^-. To obtain 10 nmole of NO_3^- the volume of the sample (i.e., the amount of snow) added to the bacteria slush varies depending upon the concentration of each sample. As the concentration in the snow decreases rapidly over the first few centimeters, the sample volumes vary between 1 and 8 ml from the surface to 15 cm depth. We observe that for low concentration samples the transfer of NO_3^- to N_2O is slightly reduced. Along with the

reduced transfer comes a strong $\delta^{15}N$ fractionation of several per mil. We overcame this problem by adding more bacteria to the low NO_3^- concentration samples. The bacteria concentration was kept constant at values corresponding to the sample protocol of *Sigman et al.* [2001] regardless of the sample size.

3. Laboratory Experiment

[11] Fractionation factors for the various possible reactions in firn are unknown. We determined the fractionation factor for photolysis of NO_3^- in a laboratory experiment. At AWI artificial snow was produced from a solution of $NaNO_3$ in ultrapure water (MilliQ) with an initial concentration of about 780 ppb. The solution was sprayed into a Styrofoam cup filled with liquid nitrogen. The generated ice chunks were ground and passed through a sieve. After storage over night, the artificial snow samples were exposed to intense UV and visible radiation in the range of 200 nm to ~900 nm [see *Jacobi et al.*, 2005]. The experiments were performed at $-20°C$ with exposition times ranging from 0.5 to 3 h.

[12] Previous experiments performed under identical conditions regarding initial NO_3^- concentration, radiation intensity, and temperature demonstrated an exponential decay of NO_3^- within the first 5 h of the experiments with a photolysis rate of 0.5 h^{-1} [*Quansah*, 2004]. This photolysis rate was used to calculate remaining NO_3^- fractions in the snow samples used for the isotope analyses. In the previous experiments, nitrite concentrations showed a steep increase followed by a fast decrease leading to a maximum in the nitrite concentrations after experiments lasting between 0.5 and 1 h. Using the previously observed nitrite concentrations, we estimate that the nitrite-to-nitrate ratios are equal to or smaller than 0.08 in all samples used for the isotope analysis. Since the experiments were performed in closed cells, it is not clear if the detected nitrite is a decay product or if it is formed from decay products, which were not removed during the experiments. We also do not completely rule out that some NO_3^- is reformed from gaseous decay products like NO_2. The exposed snow was transported to Bern for isotope analysis (Figure 1).

[13] We calculate the fractionation factor of the photolysis reaction for this Rayleigh type experiment.

$$\frac{R_f}{R_0} = f^{(\alpha-1)} \qquad (1)$$

R_0 and R_f are the isotope ratios $^{15}N/^{14}N$ of the initial NO_3^- and the remaining NO_3^- fraction f. The same equation can be written with concentrations and δ-values versus an arbitrary standard with the isotope ratio value R_{St}.

$$\frac{R_f}{R_{St}} \cdot \frac{R_{St}}{R_0} = \frac{\delta_f + 1}{\delta_0 + 1} = f^{(\alpha-1)} \qquad (2)$$

$$\ln(\delta_f + 1) = (\alpha - 1) \cdot \ln f + \ln(\delta_0 + 1) \qquad (3)$$

[14] A simple linear regression of the data allows the calculation of the fractionation factor (Equation 3). However, this method does not account for the individual
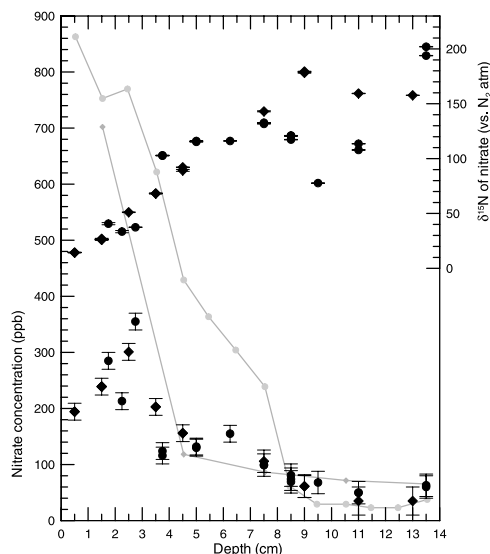
Figure 2. $\delta^{15}N$ and concentrations of NO_3^- from the Dome C area versus depth. Grey dots and diamonds are concentration measurements from a snow pit taken in 1999 [*Röthlisberger et al.*, 2000]. Dots and diamonds are individual samples from adjacent cores taken in 2003. Error bars show one sigma analytical errors. Concentrations were estimated from the mass spectrometer measurements.

uncertainties for $\delta^{15}N$ values and concentrations, which are quite substantial. Therefore, we do a Monte Carlo simulation taking into account these uncertainties (Figure 1). The exposition times are used to calculate the NO_3^- concentrations, which are accurate to the 2% range. We obtain a fractionation factor of $\varepsilon = -11.7 \pm 1.4‰$, where $\varepsilon = (\alpha - 1)$. Our bacteria do feed on NO_3^- and nitrite forming finally N_2O. Therefore the calculated fractionation factor includes a fraction of maximal 8% nitrite in our samples (see above). Depending on how this nitrite is formed we may under- or overestimate the photolytic fractionation factor for NO_3^-.

4. Antarctic Samples

[15] Two adjacent firn cores were sampled at Dome C during the austral summer of 2003. The cores were stored in polyethylene tubes and kept below $-20°C$ until analyzed. We measured the first 15 cm of both cores, which covers about two years of precipitation. Both concentration profiles are typical for Dome C and low accumulations sites, with a drastic drop of 350 ppb to 50 ppb in the first ten centimeters of the firn (Figure 2). In deeper strata the concentration remains stable at low levels [*Röthlisberger et al.*, 2000].

[16] Samples were taken from the inner and the outer part of the core. We observe systematically higher NO_3^- concentrations and lower isotopic values in the outer section of the cores. On average the concentration difference between outer and inner sample is 41 ± 11 ppb with an average $\delta^{15}N$ difference of $-26 \pm 6‰$. Apparently the polyethylene tube is a source of light NO_3^-. In a core sampled and stored in a similar way than the Dome C samples discussed here, we investigated how deep the contamination entered the core. We found that the contamination has entered the outermost 2 cm of the core. As these measurements have been made

six months later than the isotope measurements, we are confident that our Dome C results from the inner core section are free from a contamination from the sampling tubes.

[17] In Figure 3, $\delta^{15}N$ values of the inner section are plotted against NO_3^- concentrations. The resolution depends on the NO_3^- concentration of the ice core. In the top 2 cm we measured samples every 0.5 cm. Further down the core the resolution decreases due to the lower concentration in order to match the sample size minimum of about 10 nmoles of NO_3^-.

5. Results and Discussion

[18] At high accumulation sites annual variations in concentration and isotope values are visible in the first meter of firn [*Hastings et al.*, 2004]. No annual variations are obvious in the concentration [*Röthlisberger et al.*, 2000] or nitrogen isotope records (Figure 2) at Dome C. The two cores and similar concentration studies show, that both concentration and isotope signals are highly variable in adjacent cores. Nevertheless, a clear trend of lower concentrations with increasing isotope values is visible. Apparently the removal process for NO_3^- prefers the lighter isotope. Assuming that NO_3^- is removed irreversibly from the firn we can use the Rayleigh equation to calculate the fractionation coefficient α of the sum of the processes involved. For the natural samples we do not know the original surface concentration and, therefore, the fraction f. However, the fractionation coefficient can also be calculated without that knowledge. We substitute $f = C_f/C_0$ where C_0 and C_f are the original surface concentration and the concentration of the remaining fraction f, respectively and obtain:

$$\ln(\delta_f + 1) = (\alpha - 1)\ln C_f + \underbrace{[\ln(\delta_0 + 1) - (\alpha - 1)\ln C_0]}_{b} \quad (4)$$

[19] We find $\varepsilon = -53.9‰$, where $\varepsilon = (\alpha - 1)$ (Figure 3). Due to the high local variability the uncertainty of this isotope effect is relatively large (9.7‰). As the fractionation
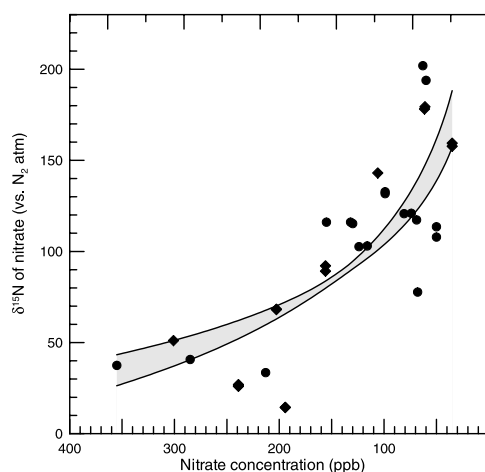

Figure 3. $\delta^{15}N$ of NO_3^- versus concentration for samples taken in the austral summer of 2003 (Figure 2). The gray area represents the one sigma spread of the Monte Carlo simulations for a Rayleigh type process.

coefficient for photolysis is only $\varepsilon = -11.7 \pm 1.4‰$ we conclude, that photolysis is probably not the dominant loss process in the near surface snow.

[20] There is, however, the possibility that photolysed NO_3^- is recycled, accumulating photolytic fractionations to the observed isotope effect. Such a process would involve the photolysis of NO_3^- in the snow generating nitrogen oxides (NO_x), its release to the firn air [*Jones et al.*, 2000], the reoxidation of NO_x to NO_3^- in the gas phase, which then is again deposited to the snow. Such a recycling in the atmosphere could explain the strong fractionation observed in the natural snow only, if it involves at least one step with a strong $\delta^{15}N$ enrichment. Such an enrichment has been observed, however, not under conditions that lead to a significant NO_3^- production. Under conditions that lead to a significant production of NO_3^- the redeposited NO_3^- is isotopically light [*Heaton et al.*, 2004]. This is in line with a recent finding from *Hastings et al.* [2004] and makes it unlikely that recycling of photolysed NO_3^- explains the observed isotope fractionation in the firn.

[21] At Neumayer Station (70°39′S, 08°15′W) the isotope values of NO_3^- vary between about 0‰ in the austral summer and $-50‰$ in the austral winter. The annual mean value for the time period 1986 to 1992 is $-21.6 \pm 9.9‰$ [*Wagenbach et al.*, 1998]. First measurements on filter samples from the Dome C site show a similar signal. The top samples ("surface") show relatively low concentrations compared to the values found by *Röthlisberger et al.* [2000] with elevated isotope values of up to +40‰. It is likely that we did not catch the surface snow or that the first sample suffered from loss processes during the transport. The Rayleigh approach allows also the calculation of a surface concentration based on a surface isotope value from the intercept b of the regression (Equation 4).

$$C_0 = \left(\frac{\delta_0 + 1}{e^b} \right)^{1/(\alpha - 1)} \tag{5}$$

[22] Assuming that the initial $\delta^{15}N$ signature of NO_3^- in fresh snow corresponds to the annual mean value found for Neumayer Station, we calculate a surface NO_3^- concentration of about 900 ppb consistent with published data for the Dome C area [*Röthlisberger et al.*, 2000].

[23] We are aware that assuming a Rayleigh type fractionation is an oversimplification of the processes in the firn. Nevertheless, this simple approach demonstrates that photolysis alone is not responsible for the loss process in the near surface snow. *Wolff et al.* [2002] estimate that only 40% of the NO_3^- is removed by photolysis reactions. With our data this would result in a fractionation factor of the other non photolytic process(es) of about $-80‰$. The most promising candidate is re-evaporation of NO_3^-. The next step will be to simulate re-evaporation in the lab and to determine its fractionation factor.

[24] Once fractionation factors for individual loss processes in the firn are known they will help to disentangle their relative contribution to the total NO_3^- loss. If we understand the fractionation of NO_3^- isotopes during post-depositional processes isotope measurements from ice cores may ultimately allow estimating the amount of post-depositional NO_3^- loss in the past. Combined with the existing high resolution NO_3^- concentration records it may be possible to reconstruct the true past atmospheric NO_3^- concentration in polar areas.

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