Nitrate in Greenland and Antarctic ice cores: a detailed description of post-depositional processes

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ABSTRACT. A compilation of nitrate (NO$_3^-$) data from Greenland has shown that recent NO$_x$ concentrations reveal a temperature dependence similar to that seen in Antarctica. Except for sites with very low accumulation rates, lower temperatures tend to lead to higher NO$_3^-$ concentrations preserved in the ice. Accumulation rate, which is closely linked to temperature, might influence the concentrations preserved in snow as well, but its effect cannot be separated from the temperature imprint. Processes involved in NO$_3^-$ deposition are discussed and shown to be temperature- and/or accumulation-rate-dependent. Apart from scavenging of nitric acid (HNO$_3$) during formation of precipitation, uptake of HNO$_3$ onto the ice crystal’s surface during and after precipitation seems to contribute further to the NO$_3^-$ concentrations found in surface snow. Post-depositional loss of NO$_3^-$ from the top snow layers is caused by release of HNO$_3$, and by photolysis of NO$_3^-$. It is suggested that photolysis accounts for considerable losses at sites with very low accumulation rates. Depending on the site characteristic, and given that the temperature and accumulation-rate dependence is quantified, it should be possible to infer changes in atmospheric HNO$_3$ concentrations.

INTRODUCTION

The nitrate (NO$_3^-$) record in polar ice cores is expected to contain information about past atmospheric concentrations of nitrogen oxides (NO$_x$ = NO + NO$_2$) due to the close link between NO$_3^-$ and NO$_x$. The increase in atmospheric NO$_x$ concentrations in the Northern Hemisphere caused by rising fossil-fuel combustion since approximately 1940, for example, is reflected in higher NO$_3^-$ concentrations in Greenland snow (Neftel and others, 1985). However, past studies have shown that factors other than atmospheric NO$_x$ concentrations also influence NO$_3^-$ concentrations in Greenland snow (Wolf, 1995). In Greenland as well as in Antarctica, reversible deposition of NO$_3^-$ and net losses in the top snow layers have been observed. It has been suggested that either re-evaporation of nitric acid (HNO$_3$) (Dibb and others, 1998; Mulvaney and others, 1998; Röthlisberger and others, 2000a) or photolysis of NO$_3^-$ in the top few centimetres of the snowpack (Honrath and others, 2000; Jones and others, 2000) causes such post-depositional alterations.

In earlier studies, relationships between NO$_3^-$ and accumulation rate have been proposed (Herron, 1982; Legrand and Kirchner, 1990; Yang and others, 1993), with generally higher accumulation rates associated with lower NO$_3^-$ concentrations and higher NO$_3^-$ depositional fluxes. In a more recent study based on a macroscopic deposition model, Fischer and others (1998) found a second-order polynomial dependence of average firn concentration and inverse snow accumulation.

Based on a compilation of NO$_3^-$ data from more than 50 Antarctic sites covering various temperature and accumulation regimes, it has recently been suggested that temperature is also a key parameter in defining NO$_3^-$ concentrations in Antarctic snow and ice, with lower temperatures leading to higher NO$_3^-$ concentrations preserved in the snow (Rothlisberger and others, 2000a). Elevation has also been linked to NO$_3^-$ concentrations, for both Greenland and Antarctica (Mulvaney and Wolff, 1994; Yang and others, 1996), but no statistically significant relationship has been found in a more recent study (Kreutz and Mayewski, 1999). The inherent connection between temperature, accumulation rate and elevation makes it difficult to distinguish between the separate effects, and no firm conclusions about their relative importance have yet been reached.

Here, we provide a detailed description of the processes involved in NO$_3^-$ re-emission and a discussion of how temperature and accumulation rate affect those processes. In analogy to the compilation of NO$_3^-$ data from Antarctic...
sites, NO\textsubscript{3} data from many Greenland sites have been gathered in order to illustrate the effect of temperature. Also, we outline how calcium (Ca\textsuperscript{2+}) can inhibit NO\textsubscript{3} re-emission. Another aspect that has been discussed lately is the effect on NO\textsubscript{3} concentrations of snow layers containing large amounts of sulphuric acid (H\textsubscript{2}SO\textsubscript{4}) of volcanic origin. Most studies focused on a few well-known volcanic eruptions during the Holocene which showed post-depositional dis-placement of NO\textsubscript{3} away from the H\textsubscript{2}SO\textsubscript{4} peak. This behaviour has been found in single events in Greenland and Antarctica (Legrand and Kirchner, 1990; Clausen and others, 1997; Rothlisberger and others, 2000a). However, the mechanisms leading to this effect are only vaguely understood, and hypotheses have not been tested on a large number of cases, because of a lack of sufficient high-resolution data.

In this paper, new high-resolution data from the North-
GRIP (North Greenland Ice Core Project) ice core are used to investigate in more detail the effect of volcanic H$_2$SO$_4$ on NO$_3^-$.

Volcanic events from the early Holocene, the Last Glacial Maximum (LGM) and some earlier glacial periods are compared and a hypothesis of the mechanism is given.

DATA

Many of the NO$_3^-$ data used in this paper are compiled from earlier studies (see Table 1 for sources). Furthermore, data from selected sections of the NorthGRIP ice core (75.1° N, 42.05° W; 2978 m a.s.l.) are presented. These sections were analyzed during the NorthGRIP 2000 field season with a continuous flow analysis (CFA) system, as described in Rothlisberger and others (2000b). Among other compounds, nitrate (NO$_3^-$), sulphate (SO$_4^{2-}$) and calcium (Ca$^{2+}$) have been measured at a resolution of approximately 1 cm.

In Figure 1, average NO$_3^-$ concentrations for different Greenland locations are indicated. In order to account for the anthropogenic increase in NO$_3^-$ concentrations in Greenland, the data have been split into two separate sets, one indicating concentrations from before 1940, which are unaffected by the anthropogenic emissions, and one from after 1970. The data and their sources are listed in Table 1. For both pre-1940 and post-1970, a decreasing trend in NO$_3^-$ concentration with increasing temperature is found (Fig. 2). A similar trend has been found in Antarctica (Rothlisberger and others, 2000a).

NO$_3^-$, TEMPERATURE AND ACCUMULATION RATE

In Figure 1, average NO$_3^-$ concentrations for different Greenland locations are indicated. In order to account for the anthropogenic increase in NO$_3^-$ concentrations in Greenland, the data have been split into two separate sets, one indicating concentrations from before 1940, which are unaffected by the anthropogenic emissions, and one from after 1970. The data and their sources are listed in Table 1. For both pre-1940 and post-1970, a decreasing trend in NO$_3^-$ concentration with increasing temperature is found (Fig. 2). A similar trend has been found in Antarctica (Rothlisberger and others, 2000a).
where also generally higher concentrations are found at sites with lower temperatures, except for very low-accumulation sites (e.g. Dome C). At Dome C, the concentrations in the top few centimetres can be very high (up to 1000 ppb), but at greater depths, only 15 ppb are preserved, despite the low temperatures (annual mean temperature \( \approx -5.4 \, ^\circ \text{C} \)).

When \( \text{NO}_3^- \) concentrations are plotted against accumulation rate, higher \( \text{NO}_3^- \) concentrations are found at sites with lower accumulation rates (Fig. 3), but again, \( \text{NO}_3^- \) concentrations at very low-accumulation sites do not agree with the general trend. Considering the close relationship between temperature and accumulation rate (Fig. 4), it seems difficult to separate their effects on \( \text{NO}_3^- \) concentrations. Only a detailed consideration of the underlying microphysical processes allows for assigning a temperature or accumulation-rate dependence.

In the following discussion, we analyze the temperature and accumulation-rate dependence of processes involved in \( \text{NO}_3^- \) deposition and re-emission, aiming for a better understanding of:

- the cause of the relationship between \( \text{NO}_3^- \) concentrations and mean annual temperature and accumulation rate at a site
- the generally higher \( \text{NO}_3^- \) levels in summer snow than in winter snow
- the net loss of \( \text{NO}_3^- \) from snow after deposition.

\( \text{NO}_3^- \) can either be predominantly incorporated in the bulk or adsorbed to the surface of a snow crystal, depending on the deposition pathway. In a cloud with a liquid-water content of \( >0.01 \, \text{g m}^{-2} \) and \( \text{pH} > 1 \), \( \text{HNO}_3 \) would be completely dissolved in water droplets due to its high solubility, leaving virtually no \( \text{HNO}_3 \) in the gas phase (Seinfeld and Pandis, 1998). Thus, in the case of liquid or mixed clouds, essentially all \( \text{HNO}_3 \) is removed from the gas phase independent of the cloud temperature. While there is no specific information about the conditions at cloud level, typical liquid-water contents of \( 0.1 \, \text{g m}^{-2} \) and initial \( \text{HNO}_3 \) concentrations of 20 ppbv in the air would lead to \( \text{NO}_3^- \) concentrations of approximately 350 ppbw in fresh snow. On the other hand, the co-condensation of \( \text{HNO}_3 \) and water (\( \text{H}_2\text{O} \)) molecules on ice crystals (Thibert and Domine, 1998) would lead to a bulk concentration of 20 ppbv only. In the absence of liquid water, i.e. in ice clouds, the high \( \text{NO}_3^- \) concentrations found in surface snow could not be explained. However, Abbatt (1997) observed a temperature dependence of adsorption of \( \text{HNO}_3 \) on ice surfaces with higher uptake at lower temperatures. For typical summer temperatures at South Pole (246 K; data obtained from http://www.cmdl.noaa.gov), the uptake capacity on fresh snow crystals exceeds the amount of \( \text{HNO}_3 \) available in the cloud, implying that at very cold temperatures where ice clouds predominate, essentially all \( \text{HNO}_3 \) is bound to the surface of the snow crystal. While co-condensation, riming and adsorption of \( \text{HNO}_3 \) determine the distribution of \( \text{NO}_3^- \) within the ice crystal, its concentration is defined by the initial atmospheric concentration of \( \text{HNO}_3 \) and the amount of condensed water in the cloud. An imprint of temperature is expected for surface uptake and co-condensation, but not for the \( \text{HNO}_3 \) taken up in liquid cloud droplets. Based on the results of Abbatt (1997), the snow crystals are expected to efficiently scavange atmospheric \( \text{HNO}_3 \) on their way to the surface, potentially further increasing the \( \text{NO}_3^- \) concentration of the fresh snow.

Once on the ground, the formation of surface hoar frost (co-condensation), rime (deposition of supercooled fog droplets) as well as dry deposition (adsorption of \( \text{HNO}_3 \) onto the crystal's surface) leads to additional \( \text{NO}_3^- \) deposition to surface snow. For a given atmospheric \( \text{HNO}_3 \) concentration, the hoar-frost \( \text{NO}_3^- \) concentration is determined by the water-
vapour concentration (Thibert and Domine, 1998), which is mainly a function of temperature $T$. Assuming that the relative humidity at the site is similar throughout the year, the NO$_3^-$ concentration should depend linearly on $1/T$ in a first-order approach. However, assuming that the HNO$_3$ concentrations in the atmosphere as in Table 2 are representative for the site, the estimated concentrations resulting from co-condensation are lower than observed surface snow concentrations, thus leading to dilution of the surface snow (Table 2). Rime deposition, on the other hand, which is likely to remove all HNO$_3$ from the air, shows concentrations similar to those in fresh snow, provided that the atmospheric HNO$_3$ concentration is similar to that at cloud level. A net dry deposition of HNO$_3$ (adsorption of HNO$_3$ onto snow crystals) has the potential to increase the NO$_3^-$ concentration in snow. However, it will only contribute where the surface is undersaturated, i.e. at very cold sites and during winter. The contribution in winter is small, due to low atmospheric HNO$_3$ concentrations. During the summer, the contribution of dry deposition to the NO$_3^-$ concentrations in snow at South Pole might be considerable. However, according to Hauglustaine and others (1994), the dry-deposition velocity of 0.5 cm s$^{-1}$ for HNO$_3$ on snow has to be considered as an upper limit. At sites with higher accumulation rates, a specific surface snow layer is buried more rapidly, leaving less time to adsorb additional HNO$_3$ from the atmosphere, given that no saturation has been reached. Therefore, a tendency to higher concentrations at lower accumulation rates is expected.

Besides the diluting effect of co-deposition, processes capable of reducing the NO$_3^-$ concentration in snow are desorption of HNO$_3$ from the snow crystal (Dibb and others, 1998; Mulvaney and others, 1998; Rothlisberger and others, 2000a) and photolysis (Honrath and others, 2000; Jones and others, 2000). In both cases, the NO$_3^-$ ion has to be at the surface of a snow crystal, since photolysis of NO$_3^-$ in the bulk is not effective (Dubowski and others, 2001). If a NO$_3^-$ ion recombines with a H$^+$ ion to form HNO$_3$, it then may desorb into the firm air and eventually diffuse into the air above the snow. Diffusion of NO$_3^-$ in ice has been investigated by Thibert and Domine (1998), who found that diffusion of NO$_3^-$ in ice is slower at colder temperatures, with the diffusion coefficient $D$ given by $D = 1.37 \times 10^{-26} 10^{-26} T^2$ cm$^2$ s$^{-1}$, with $T$ being the temperature in K. During the summer, the typical time a NO$_3^-$ molecule needs to reach the ice surface (diffusion length of 40 $\mu$m, corresponding to an average crystal radius (Harder and others, 1996)) is of the order of a couple of hours (e.g. Neumayer) to a few days (e.g. South Pole).

The solubility of NO$_3^-$ in ice has been determined for various temperatures (Thibert and Domine, 1998). For summer conditions, not only the surface snow but also deeper layers are supersaturated with respect to the solubility of NO$_3^-$ in ice (Table 2). In the case of South Pole, the surface remains undersaturated, suggesting that NO$_3^-$ that is expelled from the bulk is simply transferred to the surface without affecting the NO$_3^-$ concentration. At warmer sites (e.g. Neumayer or Summit), the ice surface also might become supersaturated during the summer, leading to release of HNO$_3$ from the snow into the interstitial air. From a thermodynamic point of view, warmer temperatures during the summer should facilitate the release of HNO$_3$ from the ice surface. But according to the uptake experiment of Abbatt (1997), only up to 25% of the

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Fig. 5. Examples of the influence of volcanic H$_2$SO$_4$ on NO$_3^-$ in the NorthGRIP ice core. H$^+$ concentrations have been inferred from electrical conductivity measurements on the solid ice. Due to very low H$^+$ concentrations, the scale of the y-axis had to be adjusted for the section shown in (b). Of 28 events selected with SO$_4^{2-}$ concentrations exceeding 20 $\mu$eq L$^{-1}$, H$^+$ showed a pattern similar to (a), 12 similar to (b), and 2 similar to (c). The data are shown against depth, as the absolute age is not critical to the illustration of the effect and an absolute time-scale is not yet available.
HNO$_3$ that has been taken up is released again afterwards. However, his study emphasized the uptake rather than the release of HNO$_3$, and a temperature dependence of the release has not been discussed. Once released from the snow crystal’s surface, the HNO$_3$ molecule might make its way out of the snowpack, leading to a net loss of NO$_3$ in the snow. The molecular diffusion of HNO$_3$ in the interstitial air is temperature-dependent as well, but probably this is not the limiting factor controlling the transfer out of the snowpack. It is conceivable that temperature-dependent, repeated adsorption and subsequent desorption of a HNO$_3$ molecule on ice crystals will determine the removal from the snowpack.

Photolysis of NO$_3$ in the top snow layers results in the production of nitrogen dioxide (NO$_2$) and hydroxyl radical (OH). NO$_2$ is expected not to interact with the surrounding snow but to be mixed into the boundary layer rather quickly, leading to a NO$_3^-$ depletion in surface snow. The influence is presumably largest at low-accumulation sites, where surface snow is exposed to sunlight for a long time. Furthermore, photolysis should become more efficient at lower latitudes due to more incoming ultraviolet radiation. At Dome C, the top few centimetres of snow seem to reach saturated surface coverage (concentrations in the range of several hundred ppbw) (Roselhisberger and others, 2000b). Deeper layers are then dramatically undersaturated considering surface coverage and solubility in the bulk. No quantitative estimate has yet been made of how much NO$_3^-$ can be lost by photolysis. It therefore remains unclear whether photolysis alone can account for the NO$_3^-$ profile seen in the snow at Dome C. The estimate of the maximum surface uptake relies very much on the surface area in recrystallization, which has not yet been taken into account.

Although elevation may affect the atmospheric HNO$_3$ concentration, there is no obvious mechanism by which it can have a direct physical influence on post-depositional processes. A minor influence is expected on the photolysis rate due to changes in the irradiance with altitude and on the gas-phase diffusion due to lower pressure, but both effects might only slightly modulate the changes in NO$_3^-$ concentrations.

INTERACTIONS OF NO$_3^-$ WITH DUST

Recent studies have reported that NO$_3^-$ and Ca$^{2+}$ concentrations are correlated in ice from the last glacial period from Vostok and Dome C, Antarctica (Legrand and others, 1999; Roselhisberger and others, 2000a). During the last glacial period, the Ca$^{2+}$ deposited on the East Antarctic plateau is mainly of terrestrial origin and can thus be used as a proxy for dust. It has been suggested that the reaction of HNO$_3$ and CaCO$_3$ to form Ca(NO$_3$)$_2$ prevents NO$_3^-$ from being released from the snow into the gas phase.

In principle, the reaction could take place in the atmosphere or in the snow. For it to occur in the atmosphere, high dust concentrations would need to be in the same season as the maximum nitrate concentrations. A recent paper that studied the reaction of CaCO$_3$ with HNO$_3$ derived a formula for the lifetime for removal of HNO$_3$ by dust (Hanisch and Crowley, 2000). Based on this, and using very rough estimates for the surface area of dust (assuming spherical particles of 1 mm diameter, a typical density of 2 g cm$^{-3}$, and atmospheric dust concentrations of 10 ng m$^{-3}$), we can estimate a HNO$_3$ lifetime vs removal by dust in the present-day Antarctic atmosphere of around 50 days. This is unlikely to be important relative to other removal processes. However, this could be reduced to 2 days under the drier conditions of the LGM, and in Greenland under LGM conditions one could estimate a lifetime for this removal of only a few hours. It seems possible therefore that under LGM conditions much of the atmospheric HNO$_3$ could be converted to aerosol calcium nitrate in the atmosphere. In addition, the reaction to form Ca(NO$_3$)$_2$ might take place in the snow, in which case HNO$_3$ has to make its way to the snow layer where the Ca$^{2+}$ has been deposited and, if Ca$^{2+}$ is inside the snow grain rather than on its surface, diffuse through it.

INFLUENCE OF VOLCANIC H$_2$SO$_4$ ON NO$_3^-$

As shown lately in an Antarctic high-resolution record from Dome C (Roselhisberger and others, 2000a), H$_2$SO$_4$ of volcanic origin can cause NO$_3^-$ to move in the ice. Several examples of very low NO$_3^-$ concentrations coinciding with H$_2$SO$_4$ peaks and increased NO$_3^-$ concentrations above and below this layer have been found in the Dome C as well as the NorthGRIP record (Fig. 5a). At Dome C, the effect is first seen at 12 m depth, where the deposits of the Tambora (Indonesia) eruption (AD 1815) are located. This indicates that the processes involved take place or at least start in the firn.

Our hypothesis of the mechanism for NO$_3^-$ displacement in the firn relies on processes similar to those described above, as it includes diffusion of HNO$_3$ in the firn air. The high concentration of H$_2$SO$_4$ in a volcanic layer causes the equilibrium of H$^+$ + NO$_3^-$ $\rightleftharpoons$ HNO$_3$ to shift towards the righthand side, as a large amount of H$^+$ from the H$_2$SO$_4$ is present. Therefore, a locally elevated concentration of HNO$_3$ in the firn air is caused, which prompts gas-phase diffusion of the HNO$_3$ away from the volcanic layer towards either side. In an adjacent layer with no excessive H$_2$SO$_4$, HNO$_3$ favours dissociation into H$^+$ and NO$_3^-$, thus maintaining the gradient in the firn air by removing HNO$_3$ from the gas phase. It is possible that the movement of NO$_3^-$ progresses via a different mechanism in the ice after pore close-off, possibly by diffusion of ions in the veins.

Figure 5b shows an event where no NO$_3^-$ displacement occurred. In this section, large amounts of alkaline material are present in the ice, as seen by the high Ca$^{2+}$ and negligible H$^+$ concentrations. In the context of the above hypothesis, the high concentrations of alkaline material (presumably CaCO$_3$) neutralize the H$_2$SO$_4$ and prevent the formation of HNO$_3$. The assumption that in this case H$_2$SO$_4$ undergoes some reactions is supported by the significantly narrower SO$_4^{2-}$ peak compared to the ones seen in acid ice (personal communication from P. Barnes, 2001).

Our hypothesis is challenged by the example shown in Figure 5c. Although much excess H$_2$SO$_4$ is present and far too little Ca$^{2+}$ to compensate, no marked NO$_3^-$ displacement is seen. It is possible that the Ca$^{2+}$ was unable to neutralize the H$_2$SO$_4$, but that it managed to bind NO$_3^-$, thus preventing it from being transferred into the gas-phase. The occurrence of ice layers limiting HNO$_3$ diffusion in the interstitial air is rather unlikely in NorthGRIP.

CONCLUSIONS

The spatial distribution of nitrate concentrations in Greenland is shown to be strongly related to site temperature, just as it is
for Antarctica. Because temperature and snow-accumulation rate are so closely linked, we cannot determine which of these factors is the one exerting physical control on the concentrations seen. In either case, the relationship changes at the very lowest accumulation rates, where it is clear that post-depositional losses are the dominant control on the subsurface concentration.

By examining the individual processes that could contribute to the nitrate concentration in snow, we find that many of them are indeed temperature-dependent, with higher concentrations predicted at lower temperatures, as observed. Some processes could also depend on the accumulation rate, if a longer exposure time at the surface allows additional uptake. Of the processes identified, either uptake by liquid droplets in cloud, if present, or uptake onto the ice surface in the cloud or after deposition can lead to concentrations in fresh snow that are as high as or higher than those observed. However, the role of surface uptake at higher temperatures, as encountered in coastal Antarctica and in Greenland in summer, needs to be quantified. Co-condensation of nitric acid and water, and dissolution of nitric acid within the ice lattice appear to give concentrations that are too low compared to those observed. This suggests tentatively that surface uptake and retention might be rather important in determining the concentrations we see. This process has a temperature dependence (approximately threefold greater uptake at −55 °C compared to −25 °C (Abbatt, 1997)) similar to that seen in Figure 2. However, according to Abbatt (1997), the uptake is not dependent on the nitric acid concentration in air. The higher nitrate concentrations in post-1970 Greenland snow compared to pre-1940 snow suggest that the snow concentration is somehow related to atmospheric concentrations, and we suggest that this is simply a question of limited supply to the ice surface, because nitric acid is scavenged so efficiently. In that case, a temperature- and accumulation-rate-corrected Holocene nitrate ice-core record of a site with adequate snow-accumulation rate should reflect the flux of nitrate to the surface, which should in turn be related to atmospheric NOx input.

For sites with very low accumulation rate, losses, possibly due to photoysis, control the concentration seen in the Holocene in such a dominant way that it is unlikely that information about atmospheric nitrate or NOx can be extracted. Once the ice becomes less acidic (in the last glacial period), the concentration of nitrate seems to be controlled by processes in the snow (11) 3475–3486. Dubowski, V., A. J. Colussi and M. R. Hoffmann. 2001. Nitrogen dioxide release in the 302 nm band photolysis and spray-frozen aqueous nitrate solutions: atmospheric implications. J. Phys. Chem., Ser. A, 105(20), 4926–4932.


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