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Evidence of NO_x Production Within or Upon Ice Particles in the Greenland Snowpack

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Abstract. NO_x and NO_y were determined in the interstitial air of surface snow and in ambient air at Summit, Greenland. NO_x levels in interstitial air were 3 to >10 times those in ambient air, and were generally greater than ambient NO_y levels. $[\text{NO}_y]$ in interstitial air varied diurnally in a manner consistent with photochemical generation within the snowpack. These observations imply that photochemical reactions occurring within or upon the ice crystals of surface snow produced NO_x from a N-reservoir compound within the snow. Average $[\text{NO}_x]:[\text{HNO}_3]$ and $[\text{NO}_x]:[\text{NO}_y]$ ratios in ambient air above the snow were elevated relative to other remote sites, indicating that NO_x release within the snowpack may have altered NO_x levels in the overlying atmospheric boundary layer. We suggest that the observed release of NO_x may have been initiated by photolysis of nitrate, present in relative abundance in surface snow at Summit. Such a process may affect levels of nitrate and other compounds in surface snow, the overlying atmosphere, and glacial ice, and its potential role in cirrus cloud chemistry should be investigated.

Introduction

The occurrence of photochemical reactions involving nitrogen oxide species on ice crystals under tropospheric conditions would be of interest for two reasons. First, nitrate deposited in snow and stored in glacier ice has been used to indirectly assess past atmospheric levels of NO_x ($\text{NO} + \text{NO}_2$) (e.g., [Mayewski et al., 1990; Fischer et al., 1998]), as HNO_3 is the sink for most atmospheric NO_x . However, there is evidence that nitrate is redistributed within the snowpack after deposition [Dibb et al., 1994; De Angelis and Legrand, 1995]. In addition, evidence suggests that nitrate may be produced within the snowpack from other reactive nitrogen species [Dibb et al., 1998]. Second, laboratory studies indicate that HNO_3 is adsorbed onto ice particles to such an extent that cirrus clouds should rapidly remove more than 100 pptv HNO_3 if present [Abbatt, 1997; Zondlo et al., 1997], and in-situ measurements of total reactive nitrogen oxides (NO_y) indicate the uptake of 25–75 pptv NO_y by

cirrus clouds, interpreted as HNO_3 uptake [Weinheimer et al., 1998]. HNO_3 scavenging of this magnitude is sufficient to alter the tropospheric distribution of HNO_3 and NO_x through particle settling, even in the absence of chemical reactions on the ice particles [Lawrence and Crutzen, 1998]. However, given that NO_3^- is known to undergo photolysis to produce aqueous free radicals in solution [Wagner et al., 1980], the permanency of NO_3^- as a tropospheric NO_x sink should be evaluated.

In order to investigate the potential occurrence of reactions involving nitrogen oxides within surface snow, we conducted measurements of the composition of ambient air, surface snow, and snow interstitial air in central Greenland. We present here results that indicate that interconversion of nitrogen species occurred within the snow and resulted in the release of NO_x into the interstitial air.

Methods

NO , NO_2 , and NO_y were determined at the Summit ATM site (72.33 N, 38.75 W, 3210 m asl) in ambient air 10 m above the snow surface, in ambient air less than 1 m above the snow surface, and in interstitial air sampled from pore spaces within the snow. These species were determined using an instrument designed for use in the remote, clean troposphere [Peterson et al., 1998]. Interstitial air was sampled for a two-day period at the end of the study, using two methods. A 55 L transparent FEP Teflon chamber was placed on a pristine snow surface and lightly sealed by tamping snow around the outside edges. Air sampled from the chamber with a chamber residence time of 15–35 min was pulled through the highly permeable snow below and/or around the chamber. Interstitial air was also sampled near the base of three holes cored into the snow. The NO_x inlet was placed just above the hole base, and air from above the hole was excluded by insertion of a small balloon into the hole, above the sampling inlet [Bales et al., 1995]. Abrupt increases in NO_x were observed within the chamber when pollution from the camp generator impacted the site. These spikes decayed in $\lesssim 1$ hr, demonstrating that ambient air flowed through a minimal pore volume of surface snow prior to reaching the chamber. A similar NO_x increase due to camp emissions was observed in a cored hole. NO_y measurements at 10 m height were made with an inlet designed to pass HNO_3 [Peterson and Honrath, 1999]. NO_y measurements within the cham-

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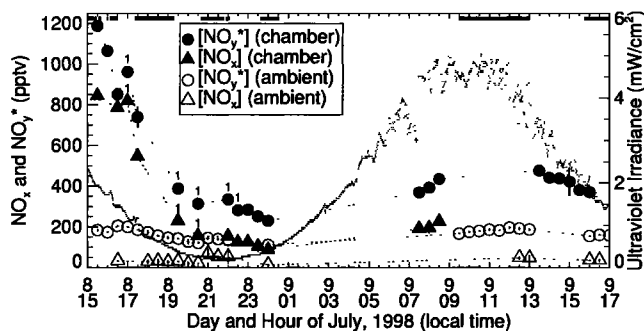


Figure 1. NO_x (triangles) and NO_y^{*} (circles) determined in the snow chamber (solid symbols) and in ambient air (open symbols). Mixing ratios are averaged over 30-minute periods. Points based on a single 30-s measurement are indicated with a numeral 1 above; vertical bars extend two standard errors above and below the mean of other points (most bars are obscured by the symbols). Dotted lines connect adjacent averages and indicate the linear interpolations used to calculate the enhancements above ambient shown in Figure 2. Ultraviolet irradiance above the snow surface is plotted with small dots. Periods when the chamber was sealed or left uncapped but without flow are indicated with horizontal lines along the top x-axis. Missing NO_x measurements during July 9 reflect periods when NO_x was sampled within the snowpack (Figure 3).

ber and just above the snow surface were made using a 5 cm unheated PFA Teflon inlet extension, which likely partially or wholly adsorbed HNO₃ at the low ambient temperatures (<-8 C) [Neuman *et al.*, 1999]. To underscore this possibility, NO_y measurements using the inlet extension are referred to as NO_y^{*}.

Results

Snow Chamber Sampling

Figure 1 shows the results of alternating measurements within the snow chamber and in ambient air near the chamber during July 8–9, 1998. Ambient NO_x and NO_y^{*} levels during the first 9 hours of measurements were relatively stable and low. Levels within the chamber were greatly elevated relative to ambient air, dropping from initial values of more than 800 pptv NO_x in the afternoon of July 8 to approximately 100 pptv near midnight. Periods of flow from the camp generator occurred during 00:00–07:20 July 9 and have been screened from the figure.

A diurnal cycle in [NO_y^{*}] within the chamber is indicated by the data in Figure 1. Chamber-air NO_y^{*} declined during periods of declining ultraviolet irradiance, measured using an Eppley radiometer ~1 m above the snow surface, and rose during periods of increasing sunlight. (Trends in [NO_y^{*}] were less consistent with trends in air temperature, which varied between -22 and -11 C during this period.) The decline in NO_x and NO_y^{*} during the first 9 hours continued even during periods when the chamber was sealed or left uncapped but without flow (indicated along the top of Figure 1). This suggests that release of NO_x into the interstitial air was photolytically driven and that NO_x produced during the periods when the chamber was sealed was released to the ambient atmosphere. NO_x and NO_y^{*} levels were significantly

higher when the chamber was first sampled, suggesting that a depletable reservoir of NO_x or NO_x-producing compounds was initially present in the snowpack. However, the increase in chamber NO_y^{*} during July 9 implies the continued release of NO_x during the second day of measurements.

The enhancement of chamber-air NO_y^{*} above ambient levels is mainly due to NO_x. Figure 2 shows the NO_y^{*} enhancement ($[\text{NO}_y^*]_{\text{chamber}} - [\text{NO}_y^*]_{\text{ambient}}$), estimated at the time of each chamber NO_x measurement using linear interpolation, as a function of NO_x enhancement ($[\text{NO}_x]_{\text{chamber}} - [\text{NO}_x]_{\text{ambient}}$). With the exception of measurements during the four hours prior to 19:00 July 8, when rapidly changing chamber concentrations make estimation of NO_y^{*} enhancement uncertain, the NO_y^{*} enhancement is highly correlated to NO_x enhancement ($r^2 = 0.89$), with a regression slope not significantly different from unity.

Pore Air Sampling

NO_x levels measured in air sampled at the base of three holes cored in the snow are shown in Figure 3. Holes 1 and 2 were cored to successively lower depths; there was no reproducible trend of NO_x levels with depth. Hole 3 was cored to a depth of 10 cm and sampled until exhaust from the site generator impacted the site after 9 hours. Ambient NO_x was determined between hole tests, and ambient NO_y^{*} was determined continuously during most of this period. NO_x levels in air sampled from the holes were much higher than those in ambient air, and generally exceeded ambient NO_y^{*} levels. Given the low ambient HNO₃ levels observed during this (ambient [HNO₃] < 35 pptv during the entire week before these experiments) and prior studies [Dibb *et al.*, 1998], it is extremely likely that NO_x levels in interstitial air exceeded ambient NO_y^{*} as well.

While ambient NO_y^{*} levels were relatively constant, NO_x levels continuously measured in hole 3 were highly variable. Both the magnitude and the standard deviation of NO_x mixing ratios in the interstitial air declined after approximately

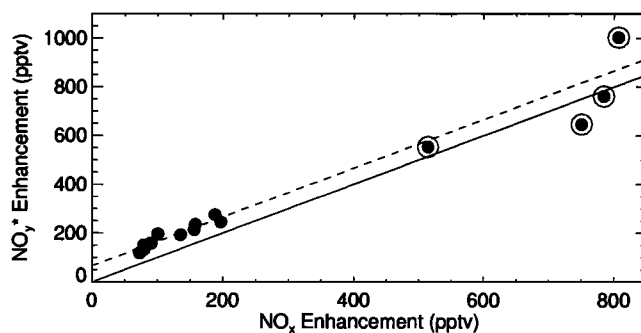


Figure 2. The relationship between the enhancements above ambient levels of NO_x and NO_y^{*} in chamber air. NO_x and NO_y^{*} enhancements are calculated at the time of each 30-minute-average NO_x measurement in the chamber (shown in Figure 1); values not measured at that time are linearly interpolated. Measurements made before 7/8 19:00 have higher uncertainty due to rapidly changing NO_x and NO_y^{*} levels in the chamber and are circled. The solid line indicates equal NO_x and NO_y^{*} enhancements above ambient; the dashed line indicates an additional constant 66 pptv NO_y^{*} enhancement.

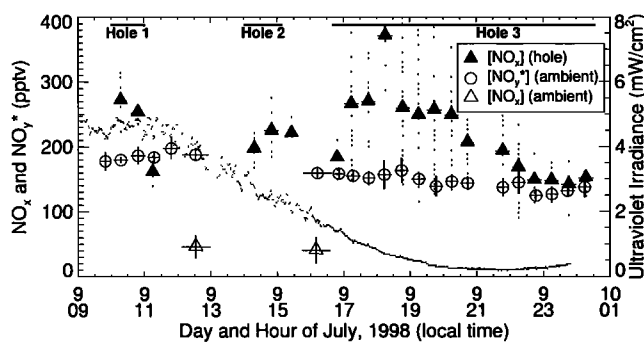


Figure 3. NO_x levels determined in air sampled at the base of holes cored into the snow. Average levels measured at each depth in holes 1 and 2 and each 30 minutes in hole 3 are indicated by solid triangles. Ambient air measurements of NO_x (triangles) and NO_y* (circles) are shown with open symbols. Horizontal and vertical lines indicate the averaging period and twice the sample standard deviation, respectively. Measurements in hole 1 were made at depths of 11, 23, and 32 cm (left to right), and measurements in hole 2 were made at depths of 22, 30, and 43 cm (left to right); all measurements in hole 3 were at a depth of 10 cm. Ultraviolet irradiance above the snow surface is plotted with small dots.

21:00. This decrease may have resulted from a decline in the magnitude of ambient air flow through the snow—average wind speed dropped from 2.6 m/s during 17:00–20:00 to 0.5 m/s during 21:00–23:30—or from a decline in insolation. The high variability in interstitial NO_x observed during 17:00–20:00 implies that either the production of NO_x within the snow was spatially heterogeneous or that dilution of the interstitial NO_x source was variable.

Discussion

The presence of NO_x in interstitial air at levels in excess of ambient NO_y* implies the release of NO_x from a N-reservoir compound within the snow. A candidate for this reservoir compound is nitrate, the most abundant soluble anion in summer snow at Summit [Dibb and Jaffrezo, 1997]. It is likely that this process is related to the budget of nitrate within the upper layers of snow and firn, which is currently inadequately understood. Previous observations indicate that HNO₃ is lost from the surface snow layer [Dibb et al., 1994; De Angelis and Legrand, 1995]. This loss has been attributed to HNO₃ volatilization [De Angelis and Legrand, 1995; Wagenbach et al., 1998], although recent laboratory measurements indicate that HNO₃ adsorbed to ice crystals is not readily released [Diehl et al., 1995; Laird and Sommerfeld, 1995; Abbatt, 1997].

The present measurements imply the photochemical production of NO_x within the snow. Significant ultraviolet radiation is available to at least the upper 5 cm [Beaglehole et al., 1998], and wind-driven advective ventilation of the firn results in mixing to lower depths [Albert 1996]. Conversion of a small fraction of the surface-snow nitrate to NO_x could explain the NO_x levels observed in this study—just 3×10^{-4} nmol NO₃⁻/g snow would produce ≥ 1000 pptv NO_x in the undisturbed pore volume of snow with density \geq

0.1 g/cm³. In contrast, loss of nitrate from buried surface snow on the order of at least 5 nmol/g over short periods ($\lesssim 1$ week) is indicated by surface snow and snowpit measurements made in this and prior studies [Dibb et al., 1994; De Angelis and Legrand, 1995]. If the observed nitrate loss were due to NO_x production, then the amount of NO_x remaining in the interstitial air is insufficient to account for the amount produced. Additional NO_x may have been released to the ambient atmosphere by wind pumping of the interstitial air. Such a process is consistent with the observed loss of surface-snow NO₃⁻ and with the elevated and variable ambient-air ratios of [NO_x]:[HNO₃] and [NO_x]:[NO_y] we found during this study (7.6 ± 5.5 and 0.22 ± 0.09 , respectively, mean \pm standard deviation of observations during the prior week), which are much higher than expected for a remote, cold location [Chatfield, 1994; Peterson and Honrath, 1999].

Additional work is needed to determine whether nitrate is the source of the observed NO_x production. However, we note that photolysis of aqueous nitrate is known to result in the formation of NO₂, NO₂⁻, and OH [Wagner et al., 1980] in the 300–350 nm absorption band. In addition to this direct formation of NO₂, NO₂⁻ photodissociates at wavelengths of 295–410 nm to form NO, which has been detected in air bubbled through irradiated seawater [Zafriou et al., 1980]. If photolysis of NO₃⁻ and/or NO₂⁻ occurred on or near the surface of an ice crystal, it is likely that the NO₂ and/or NO produced would volatilize into the interstitial air.

Implications

These measurements potentially have broad implications. Emission of NO_x from surface snow would affect NO_x and HO_x photochemical cycles within the boundary layer over Greenland, altering interpretation of ice-core H₂O₂ [Stigg and Neftel, 1991] and HCHO [Staffelbach et al., 1991] records. Depending on magnitude, such emissions throughout Greenland could affect atmospheric composition on a larger scale. In surface waters, photolysis of nitrate produced sufficient OH to result in significant degradation of trace organic compounds in a eutrophic lake [Zepp et al., 1987]. If OH production occurs in Summit surface snow, the resulting free radical chemistry would likely play an important role in the fate of organic compounds and H₂O₂ deposited onto the ice sheet, as discussed from measurements of HCHO in the Canadian Arctic snowpack [Sumner and Shepson, 1999].

The potential for release of NO_x in the free troposphere through reactions on ice crystals should also be considered. Laboratory measurements indicate that HNO₃ is rapidly adsorbed onto ice crystals [Diehl et al., 1995; Abbatt, 1997; Zondlo et al., 1997] to such an extent that cirrus clouds should rapidly remove more than 100 pptv HNO₃ if present, as noted in the Introduction. NO_x release from cirrus cloud particles could help explain discrepancies between observed and predicted [NO_x]:[HNO₃] ratios in the free troposphere [Chatfield, 1994].

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