10-16-2000

Photochemical production of gas phase NO x from ice crystal NO3 –

R E. Honrath
Michigan Technological University

S Guo
Michigan Technological University

Matthew C. Peterson
Michigan Technological University

M P. Dziobak
Michigan Technological University

Jack E. Dibb
University of New Hampshire, jack.dibb@unh.edu

See next page for additional authors

Recommended Citation

Authors

R E. Honrath, S Guo, Matthew C. Peterson, M P. Dziobak, Jack E. Dibb, and Matthew Arsenault

Photochemical production of gas phase NO_x from ice crystal NO_3^-

R. E. Honrath, S. Guo, M. C. Peterson, and M. P. Dziobak

Department of Civil and Environmental Engineering, Michigan Technological University, Houghton

J. E. Dibb and M. A. Arsenault

Institute for the Study of Earth, Oceans, and Space, University of New Hampshire, Durham

Abstract. Recent measurements have demonstrated that sunlight irradiation of snow results in the release of significant amounts of gas phase NO_x ($NO + NO_2$). We report here the results of a series of experiments designed to test the hypothesis that the observed NO_x production is the result of nitrate photolysis. Snow produced from deionized water with and without the addition of nitrate was exposed to natural sunlight in an outdoor flow chamber. While NO_x release from snow produced without added NO_3^- was minimal, the addition of 100 μM NO_3^- resulted in the release of >500 pptv NO_x in a 9 standard liter per minute (sLpm) flow of synthetic air exposed to the snow for 10–20 s; the rate of release was highly correlated with solar radiation. Further addition of radical trap reagents resulted in greatly increased NO_x production (to >8 ppbv in a flow of 20 sLpm). In snow produced from deionized water plus sodium nitrate, production of NO_2 dominated that of NO. The reverse was true in the presence of radical trap reagents; this suggests sensitivity of the NO_x release mechanism to pH, as a basic compound was added, or to the presence of free radical scavengers. A mechanism for NO_x release from NO_3^- photolysis consistent with these observations is presented. These results support previous suggestions that surface NO_x release may have a significant impact on boundary layer photochemistry in snow-covered regions and that nitrate photolysis on cirrus cloud particles may result in the release of gas phase NO_x. A potential for pH-dependent impacts on ice core records of oxidants and oxidized compounds is also suggested.

1. Introduction

A series of recent measurements indicate that photochemically mediated production of NO_x occurs in the surface snow of polar regions. NO_x ($NO + NO_2$) levels in the interstitial air of surface snow at Summit, Greenland, of magnitude 3 to >10 times those in ambient air have been observed [*Honrath et al.*, 1999], while more moderate production has been reported to occur within surface snow in Antarctica [*Jones et al.*, 2000]. Resulting emissions from surface snow apparently affect levels of NO_x in the ambient air of polar regions [*Ridley et al.*, 2000; *Davis et al.*, 1999].

The release of gas phase NO_x into snowpack interstitial air has been attributed to photolysis of NO_3^- present within the surface snowpack [*Honrath et al.*, 1999], a process that has also been identified as a potentially important source of OH in snow and ice [*Hoffman*, 1996].

However, the photochemistry of NO_3^- is complex [e.g., *Wagner et al.*, 1980; *Mark et al.*, 1996]. Although both NO_2 and NO are produced, each participates in further reactions to re-form NO_3^- and/or NO_2^-.

The present study was undertaken to determine whether NO_3^- alone is sufficient to account for observations of release of gas phase NO_x from surface snow. These experiments form part of the Snow Nitrogen and Oxidants in Winter (SNOW99) study, which took place during January–February 1999. The primary objectives of SNOW99 were to determine whether the photochemical activity observed in Arctic snow occurs in midlatitude regions and to investigate the mechanism and impacts of the process through measurements of a variety of inorganic and organic compounds. SNOW99 observations of the release of NO_x and aldehydes from natural snow are reported elsewhere [*Honrath et al.*, 2000; *Couch et al.*, 2000].

2. Experimental Methods

In short, the experimental procedure was as follows. Snow was artificially produced from deionized water or

from deionized water with nitrate added. The resulting snow was placed in a flow chamber, which was placed outdoors on a natural snow surface at the SNOW99 field site [*Honrath et al.*, 2000]. Low levels of natural sunlight irradiated the snow through a transparent Teflon cover, and breathing air quality synthetic air flowed through the snow at a constant rate, while NO and NO_2 mixing ratios were determined at the chamber outlet.

2.1. Snow Production

Snow was produced by spraying a fine mist of water or water solution into a pool of liquid nitrogen [*Laird and Sommerfeld*, 1995]. Since large amounts of snow were required to fill the flow chamber, a new, cleaned commercial paint spray gun was used to produce the mist. The snow produced appeared similar to fine, dry natural snow. Snow was made at night and stored outside overnight in a sealed flow chamber. Though the snow remained highly permeable, metamorphosis during storage resulted in consolidation. The snow was broken up and transferred into a second flow chamber at the field site using a clean scraper. Snow used in experiments I and II (described below) was kept dark prior to use; snow used in experiment III (described below) was illuminated without flow for a short period (see below).

2.2. Snow Photochemistry Chamber

Experiments were conducted in a high-cross-section 34 L Teflon-coated flow chamber designed to allow simultaneous sampling by multiple investigators during other SNOW99 experiments [*Honrath et al.*, 2000]. The chamber sides and bottom were constructed of perfluoroalkoxy (PFA) Teflon-coated aluminum; the top was sealed with a transparent fluorinated ethylene propylene (FEP) Teflon cover (transmittance > 75% at wavelengths ≥290 nm). During some experiments the chamber was darkened by placing an opaque sheet across a short aluminum wall that extended above and around the Teflon cover. Time-response experiments using step function addition of parts per billion-level NO at the inlet indicate that flow through the snow-filled chamber was not uniform: At 9 standard liters per minute (sLpm), a concentration pulse traveled through the chamber in 10–20 s, rather than the ≥170 s expected through uniform snow of typical densities in the 34 L chamber. In addition, a time constant of 70–130 s was observed in the increase in outlet mixing ratio following initial breakthrough. This is interpreted as the characteristic time for mixing of the full chamber volume. Thus the results presented below may reflect air-snow exchange in only a fraction of the flow chamber volume.

Although changes in appearance were not observed, metamorphosis of snow in the flow chamber may have occurred, induced by sublimation in the upstream region into the initially dry synthetic airflow. This could have resulted in volatilization of adsorbed compounds [*Hanot and Dominé*, 1999]. Laboratory measurements indicate that nitrate is not readily released from ice surfaces [*Abbatt*, 1997]. However, observations of rapid

changes in nitrate concentration in surface snowpacks [*Dibb et al.*, 1998; *Silvente and Legrand*, ; *De Angelis and Legrand*, 1995] have been interpreted as an indication of HNO_3 release and redeposition [*Silvente and Legrand*, ; *De Angelis and Legrand*, 1995]. Thus current understanding is incomplete regarding HNO_3 volatilization from the surface snowpack. However, HNO_3 was determined in the chamber effluent during one of the experiments (experiment III, described below); mixing ratios were <25 pptv, indicating that any HNO_3 volatilization that occurred was minimal and cannot explain the levels of NO_x reported below or their dependence upon solar radiation.

2.3. Chemical and Radiation Measurements

NO and NO_2 were determined in the chamber effluent and in the synthetic air flow upstream of the chamber. NO_y (total reactive nitrogen oxides) was measured concurrently in the ambient air; as expected under synthetic airflow, ambient [NO_y] was not correlated with [NO_x] exiting the flow chamber. NO, NO_2, and NO_y were determined sequentially, with one 20-s average measurement of each obtained once each iteration of a 5-min measurement cycle. NO and NO_2 measurements were referenced to a National Institutes of Standards and Technology (NIST) NO standard. Accuracy of the NO_x mixing ratios presented here is estimated to be 6%; precision was ≲12 pptv at low NO_x levels, and at high levels was much less than the uncertainty contributed by measurement accuracy. Additional measurement uncertainty was present at times when mixing ratios changed very rapidly, as was the case when the snow photochemistry chamber was first exposed to sunlight or covered in the experiments below. This is the case because [NO_2] is calculated from the difference between NO and NO_x measurements separated in time by approximately 1 min, and because calculation of [NO_2] depends on knowledge of [NO] at the same time, which is estimated by interpolation. Periods when this effect may have resulted in measurement uncertainty significantly greater than that cited above are excluded from the analyses below. These periods were ≲10 min in duration and their exclusion does not affect the conclusions presented. During one experiment (experiment III, described below), NO_x measurements were not made continuously in the chamber effluent, so that other species could be sampled occasionally by other investigators. This resulted in some gaps in the data coverage during that experiment. Details on the calibration and data reduction methods and measurement accuracy are provided by *Peterson and Honrath* [1999].

A hemispherical filterradiometer (Metcon USA) was used to determine the NO_2 photolysis rate constant (J_{NO_2}), as a measure of downwelling ultraviolet radiation. Calibration was provided by the manufacturer; no corrections were applied. The absorbance cross section for NO_2 extends further into the red than does that of NO_3^-, which has a local absorption maximum in liquid water at 302 nm [*Meyerstein and Treinin*, 1961]. J_{NO_2} is used here as the best indicator of ul-

traviolet actinic flux available during the present study, with the recognition that the greater sensitivity of nitrate to shorter wavelengths would result in a sharper dependence of nitrate photolysis on solar zenith angle, relative to NO$_2$. Nitrate [Dibb et al., 1994] and total organic carbon (TOC) were determined in the artificially produced snow prior to and/or following each experiment using established methods.

2.4. Experiments

Three batches of snow were produced, using (I) deionized (DI) water, (II) DI water with 100 μM NaNO$_3$ added, and (III) DI water with 100 μM NaNO$_3$, 25 mM dimethyl sulfoxide (DMSO), and 250 μM 3-amino-2,2,5,5-tetramethyl-1-pyrrolidinyloxy radical (3AP). DMSO and 3AP were included in the latter snow in an exploratory attempt to trap OH radicals produced by NO$_3^-$ photolysis [Vaughan and Blough, 1998]. No definitive evidence of OH production was observed (S. Green, private communication, 1999), but this method's detection limit for OH in ice is not characterized. However, as discussed below, the addition of these compounds resulted in greatly increased NO$_x$ release from the artificially produced snow and an apparent change in the mechanism of that release.

NO$_3^-$ concentrations measured in the snow produced without added nitrate (batch I) averaged 0.115 ± 0.057 μM (mean ± 3 standard errors of the mean) prior to use. After use, an increase in NO$_3^-$ was observed in the surface layer only, of magnitude 0.149 ± 0.075 μM. This may indicate volatilization and/or deposition of small amounts of nitrogen compounds present as contaminants in the snow or in the synthetic airflow. NO$_3^-$ concentrations in snow from batch II were measured only after the experiment was complete; they averaged 100.1 ± 2.1 μM. [NO$_3^-$] in three samples from batch III averaged 96.3 ± 1.8 μM prior to exposure and averaged 105.1 ± 13.5 μM in samples taken from the surface layer after exposure. Total organic carbon levels in the snow without added organics were 0.4–

0.7 ppm (experiment I) and approximately 0.2 ppm (experiment II) (S. Green, personal communication, 1999). An insufficient amount of snow was made in batch III; as a result, the bottom approximately one half of the flow chamber was filled with aged natural snow ([NO$_3^-$] = 3.08 ± 0.07 μM, TOC = 0.26 ppm) and covered with artificially produced snow. Nitrate concentrations measured in three samples from the lower snow layer following the experiment ranged from 12 to 53 μM, suggesting transfer of nitrogen oxides or snow particles between the surface and deeper snow layers.

Experiments I and II were conducted for 2 days. In experiment I, flow was continuous for the full period, while the snow remained without flow or illumination for a 2-day period between days of sampling in experiment II. NO$_x$ levels in experiment I declined from a maximum of 320 pptv (when $J_{NO_2} = 0.0013$–0.0019 s^{-1}) to 70 pptv (when $J_{NO_2} = 0.0010$ s^{-1}) over the first day of illumination; this is attributed to cleanout of the flow chamber, which had been exposed to part per billion-levels of ambient air NO$_x$ the previous day. For this reason, and because inconclusive experiments using filters to cover the chamber complicate the interpretation of data from day 1 of experiment II, only the second days of experiments I and II are discussed in the following sections. However, we note that use of the first day's results from experiments I and II would not alter the conclusions presented below regarding the source of NO$_x$ release observed in experiments II and III.

Snow temperatures during experiment I were -6° to 0°C (day 1) and approximately 0°C (day 2). Those during experiment II were -8° to 0°C (day 1) and -12° to -5°C (day 2), and those during experiment III were -19° to -11°C.

3. Results

NO$_x$ levels during experiments I and II are shown in Figure 1. Significant release of NO$_x$ from the
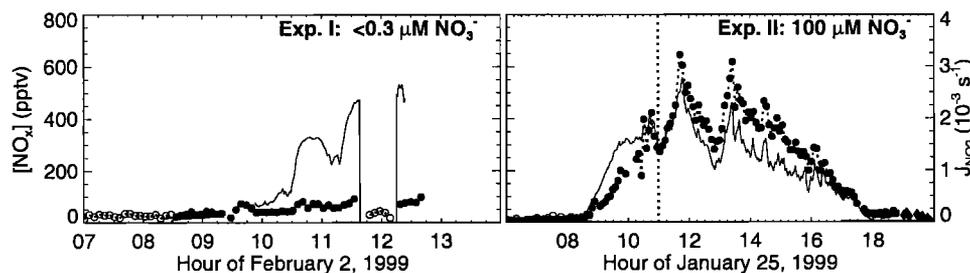

Figure 1. NO$_x$ measurements during experiments I and II. Solid circles indicate values during periods when the flow chamber was exposed to sunlight, open circles indicate observations during periods when the chamber was covered, and diamonds indicate measurements of synthetic air composition upstream of the chamber. Consecutive measurements are connected by dotted lines for clarity. The solid line indicates the downwelling component of J_{NO_2}; J_{NO_2} is set to zero during periods when the chamber was covered. The vertical dotted line indicates the beginning of the period used in the regression analyses of Figure 4. An interruption in the rise of [NO$_x$] just prior to 0900 in experiment II is the result of an increase of the flow rate through the chamber to 9 sLpm, from the flow rate of 6.5 sLpm which was used overnight.
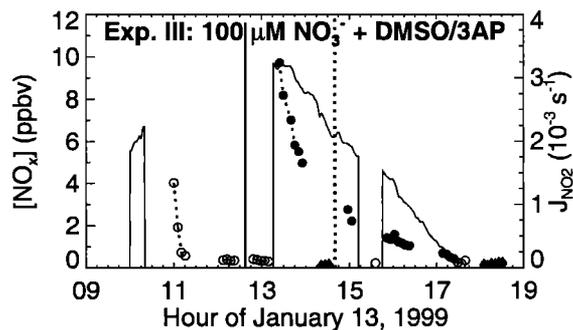
Figure 2. NO_x measurements during experiment III. Symbols are as described for Figure 1. The vertical dotted line indicates the beginning of the period used in the regression analyses of Figure 5. Nonzero J_{NO_2} values (indicated by the solid line) prior to 1300 indicate periods when the chamber was uncovered without flow (at ~1000) and was briefly uncovered with flow (at ~1240). Missing data during 1120–1205, 1405–1455, and 1630–1710 are the result of periods when the NO_x inlet was not connected to the flow chamber outlet. Missing data immediately following the time when the chamber was covered at 1510 result from the NO_x measurement cycle, which prevents accurate calculation of NO_x mixing ratios at times when mixing ratios change by large amounts.

NO_3^--containing snow was observed, with mixing ratios reaching >600 pptv and variations closely following variations in sunlight intensity. Much lower NO_x (<100 pptv) was detected from the low-NO_3^- snow. NO_x measurements during experiment III are shown in Figure 2. Extremely high levels, exceeding 8 ppbv, were observed when the cover was removed, allowing sunlight onto the snow. Elevated levels were also observed when the snow was first sampled while covered; this may have been due to irradiation of the snow without flow for a 25-min period around 1000. Levels of NO_x in the dark decayed rapidly after sampling commenced, reaching 600 pptv after 20 min, and <400 pptv when next sampled after 1 hour. After irradiation with airflow, NO_x levels returned to a baseline level of approximately 250 pptv, slightly higher than the inlet synthetic air mixing ratio of 150 pptv, within 10 min when the snow was covered at 1510, and rose to the sunlit values shown within 10 min when the chamber was uncovered at 1545.

The fraction of NO_x detected as NO is shown in Figure 3. There is a clear difference between the two experiments shown: NO_x was released primarily in the form of NO_2 in experiment II, while NO was the dominant product in experiment III. This observation is discussed below. There was no O_3 in the tank air used, and therefore gas phase conversion of NO to NO_2 is expected to be minimal within the flow chamber. Photodissociation of NO_2 could convert released NO_2 to NO, but this is also expected to be minimal. (Photodissociation of ≤22–34% of the NO_2 released is expected at J_{NO_2} = 0.004 s^{-1}, if flow in the chamber were well-mixed with the measured mixing time constant of 70–130 s, while much less photodissociation [4–8%] would occur under plug-flow flow conditions with residence time equal to the measured breakthrough period of 10–20 s). The lack of dependence of [NO]/[NO_x] upon J_{NO_2} shown in the left plot of Figure 3 confirms this expectation.

NO and NO_2 levels in the experiments with NO_3^- added were highly correlated to J_{NO_2}, as shown in Figures 4 and 5. There was a delay in the response of NO_2 to increasing sunlight in the morning of experiment II; the points during this ~2-hour period are indicated by open symbols and are excluded from the regressions shown in Figure 4. The first 1.5 sunlit hours of experiment III are also indicated by open symbols and excluded from the regression calculations in Figure 3. NO mixing ratios were initially extremely high when the chamber was uncovered in this experiment; these points may be affected by decay of that initial pulse, although they could alternatively indicate a greatly increased sensitivity to short-wavelength radiation, which declines following solar noon more quickly than does J_{NO_2}. Data from experiment I (no added NO_3^-) are also shown for comparison; mixing ratios on that day were both lower in magnitude and more weakly dependent on solar radiation than those in the experiments with NO_3^--containing snow.

4. Discussion

These results demonstrate that NO_3^- photolysis results in the release of NO_x from snow: Addition of NO_3^- to otherwise similar snow resulted in greatly increased NO_x release, and the rate of release was highly
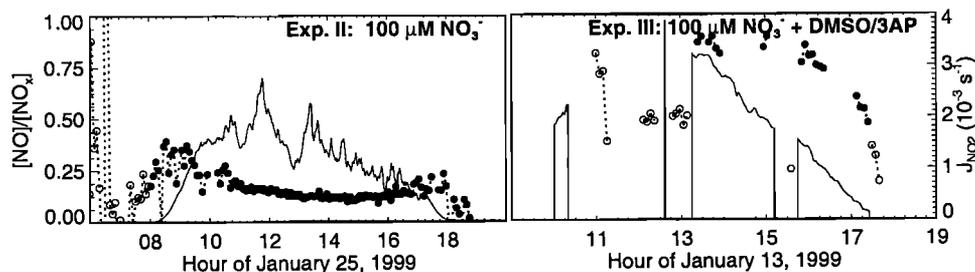

Figure 3. [NO]/[NO_x] ratios during the two experiments with $NaNO_3$ added. Increased scatter during periods of low mixing ratios (prior to 1000 and after 1700 on January 25, and after 1700 on January 13; see Figures 1 and 2) is the result of measurement imprecision. Symbols are as described for Figure 1.
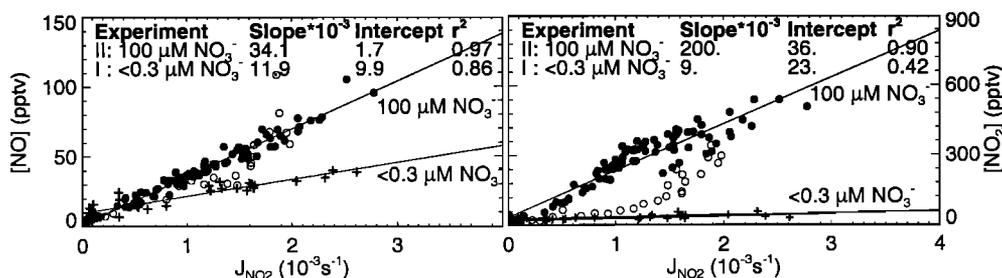
Figure 4. The dependence of [NO] and [NO₂] upon solar radiation during periods of experiments I and II when the chamber was exposed to sunlight. Solid circles are included in calculation of the regression lines for experiment II; observations before the vertical dotted line in Figure 1 are not included and are indicated here with open circles. Observations during experiment I are indicated by plus symbols.

correlated with solar radiation. In addition, the magnitude of the NO_x release observed, when normalized by snowpack NO_3^- concentration and flow rate, is approximately two thirds that observed from natural, mid-latitude snow during the SNOW99 study [*Honrath et al.*, 2000]. Given the small number of experiments conducted and significant variability observed in NO_x release from natural snow during that study, we consider these results consistent but deserving of further study.

In the following section we analyze these results in the context of previous work on nitrate photolysis. Before doing so, it is necessary to outline two important limitations: The physical and chemical structure of the ice surface is not well characterized, and the photochemistry of nitrate in ice has not been adequately studied.

At the temperatures at which these observations were made ($-10°$ to $0°C$), the surface of pure ice is disordered [e.g., *Lied et al.*, 1994; *Hobbs*, 1974]. In addition, solute-induced surface melting may occur, depending on the degree of solute exclusion to the surface upon freezing (although this effect may have been minimized as a result of rapid freezing in liquid nitrogen in the artificially produced snow analyzed here). Furthermore, the ice surface at near-freezing temperatures is active: Water evaporates and condenses at rates of the order of 10^4-10^5 monolayers per second [*Haynes et al.*, 1992]. As a result of these processes, there is considerable uncertainty regarding the physical and chemical state of

the ice surfaces in this work and in natural snowpacks. For example, while the ice surface has been successfully modeled as a layer of liquid water in at least one case [*Conklin and Bales*, 1993], the presence of an actual liquid has been disputed [e.g., *Knight*, 1996].

Uncertainty regarding the surface structure and composition of ice results in considerable uncertainty regarding the expected photochemistry of nitrate ion, which is known to differ with surface environment. For example, the photochemistry of nitrate species formed on solid NaCl surfaces by reaction with NO_2 was found to differ from that of solid $NaNO_3$ [*Vogt and Finlayson-Pitts*, 1995], and thin films of NH_4NO_3 behave differently than do films of neat HNO_3 [*Koch et al.*, 1996]. However, the surface layer of ice, while disordered relative to the solid, is apparently more ordered than is liquid water [*Lied et al.*, 1994], implying that a solvent cage is present. This suggests that the photochemistry of nitrate in liquid water may serve as a useful analog for that in ice surfaces. For this reason, and because of a lack of information on nitrate photochemistry in ice, we refer to previous work in liquid water in the following discussion. The purpose of this analysis is not to provide a definitive description of nitrate photochemistry in ice, but rather is to provide a starting point for future studies, by evaluating the extent to which aqueous nitrate photochemistry is consistent with the results of the present study.
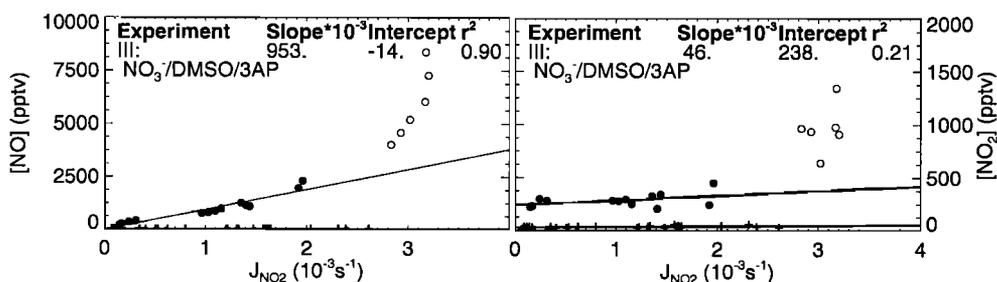

Figure 5. The dependence of [NO] and [NO₂] upon solar radiation during periods of experiment III when the chamber was exposed to sunlight. Open symbols indicate data prior to the vertical dotted line in Figure 2, which are not included in regression calculations. Measurements during experiment I (no $NaNO_3$ added) are indicated by plus symbols visible near the lower x axis.

4.1. Mechanism

The mechanism responsible for NO$_x$ release must explain the following observations: (1) NO$_{2\{g\}}$ release was dominant in snow made with NaNO$_3$ alone, and was moderately reduced by addition of DMSO and 3AP in experiment III; (2) NO$_{\{g\}}$ release closely followed variations in sunlight level; NO$_{2\{g\}}$ release behaved similarly, but only after an initiation period; and (3) J_{NO_2}-normalized NO$_{\{g\}}$ release was dominant in snow made with NaNO$_3$ plus DMSO and 3AP, being enhanced 30-fold relative to snow made with NaNO$_3$ alone.

Aqueous NO$_3^-$ photolysis in the 300 nm band is known to proceed via at least two channels [*Warneck and Wurzinger*, 1988]:

$$NO_3^-{}_{\{aq\}} + h\nu \;\rightarrow\; NO_{2\{aq\}} + O^-{}_{\{aq\}}, \qquad (1)$$

followed by

$$O^-{}_{\{aq\}} + H^+{}_{\{aq\}} \;\rightarrow\; OH_{\{aq\}}, \qquad (2)$$

$$NO_3^-{}_{\{aq\}} + h\nu \;\rightarrow\; NO_2^-{}_{\{aq\}} + O(^3P)_{\{aq\}}, \qquad (3)$$

where the subscript $\{aq\}$ is used to refer to the surface layer of an ice grain, which may, however, behave differently than liquid water. NO$_2$ formation is attributed to direct production via (1), followed by volatilization of NO$_2$. NO formation is attributed to the sequence of (3) followed by

$$NO_2^-{}_{\{aq\}} + h\nu \rightarrow NO_{\{aq\}} + O^-{}_{\{aq\}} \qquad (4)$$
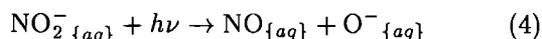
and volatilization. Nitrite formed in (3) may also result in volatilization of HONO, depending on pH. The quantum yield for (1) is significantly greater than that for (3) [*Warneck and Wurzinger*, 1988], which would account for greater formation of NO$_2$ than NO in experiment II.

Direct or nearly direct photochemical production is consistent with the strong dependence of NO and NO$_2$ mixing ratios upon ultraviolet actinic flux. However, it does not explain the delay in release of NO$_2$ during experiment II, relative to both the late morning increase of actinic flux and the increase in [NO]. While this behavior would be consistent with production via an accumulating intermediate, such a process is not observed in the bulk aqueous phase. An alternative explanation is that the tenfold greater Henry's law constant of NO$_2$, relative to NO [*Seinfeld and Pandis*, 1998], results in a capacity for NO$_2$ in the snow surface layer that is much greater than that for NO and that must be filled by NO$_2$ production prior to observation of significant gas phase release. This implies a delay period in NO$_2$ release that is a function of the time-integrated solar flux and would therefore be shorter under conditions of greater sunlight intensity than occurred during the present study.

Behavior during experiment III, in which DMSO and 3AP were added, was dramatically different: NO levels increased ~30-fold, and NO$_2$ levels dropped by 75%, together resulting in a fourfold increase in the J_{NO_2}-normalized NO$_x$ release rate. The reduction in NO$_2$ release may be due to the onset of second order loss processes, for example, [*Mark et al.*, 1996],

$$NO_{\{aq\}} + NO_{2\{aq\}} + H_2O \rightarrow 2NO_2^-{}_{\{aq\}} + 2H^+{}_{\{aq\}}. \qquad (5)$$
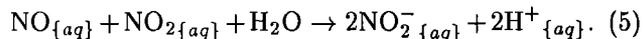
The cause of the large increase in NO levels during experiment III is not clear. Addition of 25 mM DMSO and 250 μM 3AP may have altered the snow surface structure, reduced the concentration of OH (DMSO was added as a radical scavenger), and/or increased the surface layer pH (3AP is a base with pK$_a$ $\simeq$ 9). Formation of NO under alkaline conditions has been observed in the aqueous phase through a mechanism involving formation of peroxynitrite ($^-$OONO); this may be the cause of the enhanced NO release observed here. Peroxynitrite is known to be formed during photolysis in the 200 nm band [*Mark et al.*, 1996]:

$$NO_3^-{}_{\{aq\}} + h\nu \rightarrow {}^-OONO_{\{aq\}}. \qquad (6)$$
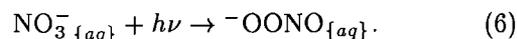
There is indirect evidence that peroxynitrite is also formed under 300 nm irradiation. *Warneck and Wurzinger* [1988] reported formation of significantly more nitrite than O(^3P) under 305 nm irradiation at pH 5-12, contrary to the ratio of unity expected from reaction (3). It was recently found that peroxynitrite is an interferent in the colorimetric nitrite analysis used in that and many other previous studies [*Plumb and Edwards*, 1992]. This interference may explain the observation of excess nitrite formation in the 300 nm band, as *Mark et al.* [1996] concluded was the case in the 200 nm band. Peroxynitrite may also be formed from the cage-constrained products of (1) [*Mark et al.*, 1996]:

$$\{NO_{2\{aq\}} + O^-{}_{\{aq\}}\}_{cage} \rightarrow {}^-OONO_{\{aq\}}. \qquad (7)$$

Peroxynitrite has a pK$_a$ of ~6.5, and the acid isomerizes rapidly to re-form NO$_3^-$ (τ $\simeq$ 1.2 s) [*Kissner et al.*, 1997]:

$$HOONO_{\{aq\}} \longrightarrow H^+{}_{\{aq\}} + NO_3^-{}_{\{aq\}}. \qquad (8)$$
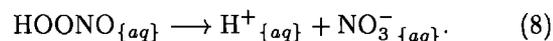
Under alkaline conditions, however, $^-$OONO has a significant lifetime and is photochemically active. *Mark et al.* [1996] identified NO as an intermediate in the 254 nm irradiation of NO$_3^-$, and concluded that $^-$OONO was a precursor. They hypothesized that decomposition of OONO, formed by reaction of $^-$OONO and OH, was the source of the NO. However, measurements of the decay of $^-$OONO formed from irradiation of solid KNO$_3$ indicate that $^-$OONO photodissociates under irradiation at both 254 and 300 nm [*Plumb and Edwards*, 1992]. Although previously believed to result in reformation of NO$_3^-$ [*Plumb and Edwards*, 1992], more recent work indicates that 355 nm irradiation of $^-$OONO results in the production of O$_2^-$, and presumably NO, through the reaction [*Kissner et al.*, 1997]

$$^-OONO + h\nu \longrightarrow NO + O_2^-. \qquad (9)$$

The addition of 3AP may, thus, have resulted in increased pH and the occurrence of reaction (9), which is prevented from occurring at low pH by HOONO isomerization (reaction (8)). Additional experiments are needed to determine whether increased pH alone re-

sults in greatly increased NO release from irradiated ice crystals and whether photoactive intermediates are involved.

4.2. Implications for Other Species

Production of NO_2 implies the production of OH through reaction (2). Thus we expect oxidation of organic compounds present within the snow surface layer to occur. OH and other oxidants may be enhanced in the gas phase as well, through volatilization of HONO produced via (3), followed by gas phase photodissociation to NO + OH, and as a result of OH-initiated production of photochemically active carbonyls within the snow, followed by volatilization. The occurrence of the latter process is also consistent with recent findings of elevated HCHO concentrations in snowpack interstitial air [Sumner and Shepson, 1999; Hutterli et al., 1999] and in the boundary layer at Summit, Greenland [Hutterli et al., 1999], although this is contrary to the process of temperature-dependent uptake and desorption of HCHO proposed by Hutterli et al. [1999] to explain those Greenland observations.

4.3. Environmental Implications

The NO_3^- concentrations used here (100 μM) were somewhat higher than those in natural snow at rural and remote sites. For example, concentrations in surface snow near the study site average 17 μM [Stottlemyer and Toczydlowski, 1990], concentrations in the snowpack of interior and Arctic Alaska [Jaffe and Zukowski, 1993] range from 3 to 11 μM, and concentrations in surface snow in Greenland [Silvente and Legrand, ; Dibb et al., 1998] and Antarctica [De Angelis and Legrand, 1995] range from 1 to 9 μM. On the other hand, solar intensity was quite subdued by lake-effect snow clouds. J_{NO_2} levels were only one tenth the peak values at Summit, Greenland, during mid-summer. We therefore expect that significant NO_x production occurs in the surface layer of snow in many regions, with resulting impacts on boundary layer photochemistry.

Concentrations of nitrate, H_2O_2, and HCHO in ice cores have been used to infer past atmospheric composition [Mayewski et al., 1990; Sigg and Neftel, 1991; Staffelbach et al., 1991]. Mass balance considerations imply that net NO_3^- deposition may not be changed greatly by NO_3^- photolysis, although it is not clear whether net export of NO_x from the boundary layer (which would imply an impact on net NO_3^- deposition) occurs. However, we expect enhanced OH and NO_x levels in snow grains and in the atmosphere to result in formation of H_2O_2 and HCHO, implying that impacts on ice core levels of those species could be significant. In addition, results during experiment III suggest that NO_x production may increase dramatically under alkaline conditions Such an effect would imply a different level of photoactivity of the surface snowpack and a different relationship between free atmospheric composition and near-surface composition between glacial periods, when the ice core record indicates that alkaline conditions were dominant [Wolff et al., 1997], and

nonglacial periods with neutral to acidic conditions, further complicating interpretation of the glacial record. Further experiments are necessary to test the hypothesis that NO_x release from snowpack nitrate is strongly dependent upon pH.

The present results imply that NO_3^- alone is sufficient for release of NO_x from ice crystals. As HNO_3 is scavenged by cirrus clouds [Weinheimer et al., 1998; Meilinger et al., 1999; Feigl et al., 1999], the potential for NO_x release due to NO_3^- photolysis on cirrus crystals should be investigated. Slow release of NO_x from cirrus clouds in the upper troposphere, where the NO_x lifetime is long, may be responsible for inability of current photochemical models to adequately simulate $[NO_x]:[HNO_3]$ ratios observed in that region [e.g., Liu et al., 1992; Chatfield, 1994; Jaeglé et al., 1998; Lawrence and Crutzen, 1998; Hauglustaine et al., 1998].

References

Abbatt, J. P. D., Interaction of HNO_3 with water-ice surfaces at temperatures of the free troposphere, Geophys. Res. Lett., 24, 1479-1482, 1997.

Chatfield, R. B., Anomalous HNO_3/NO_x ratio of remote tropospheric air: Conversion of nitric acid to formic acid and NO_x?, Geophys. Res. Lett., 21, 2705-2708, 1994.

Conklin, M. H., and R. C. Bales, SO_2 uptake on ice spheres: Liquid nature of the ice-air interface, J. Geophys. Res., 98, 16,851-16,855, 1993.

Couch, T. L, A. L. Sumner, T. M. Dassau, P. B. Shepson, and R. E. Honrath, An investigation of the interaction of carbonyl compounds with the snowpack, Geophys. Res. Lett., in press, 2000.

Davis, D. D., M. Buhr, J. Nowak, G. Chen, R. Mauldin, F. Eisele, and D. Tanner, Unexpected high levels of NO at South Pole: Observations and chemical consequences, Eos Trans. AGU, 80(46), Fall Meet. Suppl., F190, 1999.

De Angelis, D., and M. Legrand, Preliminary investigations of post depositional effects on HCl, HNO_3, and organic acids in polar firn layers, in Ice Core Studies of Global Biogeochemical Cycles, NATO ASI Ser., Ser. I, vol. 30, edited by R. J. Delmas, pp. 361-381, Springer-Verlag, New York, 1995.

Dibb, J. E., R. W. Talbot, and M. H. Bergin, Soluble acidic species in air and snow at Summit, Greenland, Geophys. Res. Lett., 21, 1627-1630, 1994.

Dibb, J. E., R. W. Talbot, J. W. Munger, D. J. Jacob, and S.-M. Fan, Air-snow exchange of HNO_3 and NO_y at Summit, Greenland, J. Geophys. Res., 103, 3475-3486, 1998.

Feigl, C., H. Schlager, H. Ziereis, J. Curtius, F. Arnold, and C. Schiller, Observation of NO_y uptake by particles in the Arctic tropopause region at low temperatures, Geophys. Res. Lett., 26, 2215-2218, 1999.

Hanot, L., and F. Dominé, Evolution of the surface area of a snow layer, Environ. Sci. Technol., 33, 4520-4255, 1999.

Hauglustaine, D. A., G.P. Brasseur, S. Walters, P.J. Rasch, J.F. Müller, L.K. Emmons, and M.A. Carroll, MOZART, a global chemical transport model for ozone and related chemical tracers, 2, Model results and evaluation, J. Geophys. Res., 103, 28,291-28,335, 1998.

Haynes, D. R., N. J. Tro, and S. M. George, Condensation and evaporation of H$_2$O on ice surfaces, *J. Phys. Chem.*, *96*, 8502-8509, 1992.

Hobbs, P. V., *Ice Physics*, Clarendon, Oxford, 1974.

Hoffman, M. R., Possible chemical transformations in snow and ice induced by solar (UV photons) and cosmic irradiation (muons), in *Chemical Exchange Between the Atmosphere and Polar Snow, NATO ASI Ser., Ser. I*, vol. 43, edited by E. W. Wolff and R. C. Bales, pp. 353-377, Springer-Verlag, New York, 1996.

Honrath, R. E., M. C. Peterson, S. Guo, J. E. Dibb, P. B. Shepson, and B. Campbell, Evidence of NO$_x$ production within or upon ice particles in the Greenland snowpack, *Geophys. Res. Lett.*, *26*, 695-698, 1999.

Honrath, R. E., M. C. Peterson, M. P. Dziobak, S. Green, J. E. Dibb, and M. A. Arsenault, NO$_x$ production in sunlight-irradiated mid-latitude snow during the SNOW99 study, *Geophys. Res. Lett.*, in press, 2000.

Hutterli, M. A., R. Röthlisberger, and R. C. Bales, Atmosphere-to-snow-to-firn transfer studies of HCHO at Summit, Greenland, *Geophys. Res. Lett.*, *26*, 1691-1694, 1999.

Jaeglé, L., D.J. Jacob, Y. Wang, A.J. Weinheimer, B.A. Ridley, T.L. Campos, G.W. Sachse, and D. Hagen, Origin of NO$_x$ in the upper troposphere over the central United States, *Geophys. Res. Lett.*, *25*, 1709-1712, 1998.

Jaffe, D. A., and M. D. Zukowski, Nitrate deposition to the Alaska snowpack, *Atmos. Environ.*, *27A*, 2935-2941, 1993.

Jones, A. E., R. Weller, and H.-W. Jacobi, Speciation and rate of photochemical NO and NO$_2$ production in Antarctic snow, *Geophys. Res. Lett.*, *27*, 345-348, 2000.

Kissner, R., T. Nauser, P. Bugnon, P. G. Lye, and W. H. Koppenol, Formation and properties of peroxynitrite as studied by laser flash photolysis, high-pressure stopped-flow technique, and pulse radiolysis, *Chem. Res. Toxicol.*, *10*, 1285-1292, 1997.

Knight, C. A., Surface layers on ice, *J. Geophys. Res.*, *101*, 12,921-12,928, 1996.

Koch, T. G., N. S. Holmes, T. B. Roddis, and J. R. Sodeau, Low-temperature photochemistry of submicrometer nitric acid and ammonium nitrate layers, *J. Phys. Chem.*, *100*, 11,402-11,407, 1996.

Laird, S. K., and R. A. Sommerfeld, Nitric acid adsorption on ice: A preliminary study, *Geophys. Res. Lett.*, *22*, 921-923, 1995.

Lawrence, M. G., and P. J. Crutzen, The impact of cloud particle gravitational settling on soluble trace gas distributions, *Tellus*, *50B*, 263-289, 1998.

Lied, A., H. Dosch, and J. H. Bilgram, Surface melting of ice I$_h$ single crystals revealed by glancing angle X-ray scattering, *Phys. Rev. Lett.*, *72*, 3554-3557, 1994.

Liu, S. C., M. Trainer, M. A. Carroll, G. Hubler, D. D. Montzka, R. B. Norton, B. A. Ridley, J. G. Walega, E. L. Atlas, B. G. Heikes, B. J. Huebert, and W. Warren, A study of the photochemistry and ozone budget during the Mauna Loa Observatory photochemistry experiment, *J. Geophys. Res.*, *97*, 10,463-10,471, 1992.

Mark, G., H.-G. Korth, H.-P. Schuchmann, and C. von Sonntag, The photochemistry of aqueous nitrate ion revisited, *J. Photochem. Photobiol. A*, *101*, 89-103, 1996.

Mayewski, P. A., W. B. Lyons, J M. Spencer, M. S. Twickler, C. F. Buck, and S. Whitlow, An ice-core record of atmospheric response to anthropogenic sulphate and nitrate, *Nature*, *346*, 554-556, 1990.

Meilinger, S. K., A. Tsias, V. Dreiling, M. Kuhn, C. Feigl, H. Ziereis, H. Schlager, J. Curtius, B. Sierau, F. Arnold, M Zöger, C. Schiller, and T. Peter, HNO$_3$ partitioning in cirrus clouds, *Geophys. Res. Lett.*, *26*, 2207-2210, 1999.

Meyerstein, D., and A. Treinin, Absorption spectra of NO$_3^-$ in solution, *Trans. Faraday Soc.*, *57*, 2104-2112, 1961.

Peterson, M. C., and R. E. Honrath, NO$_x$ and NO$_y$ over the northwestern North Atlantic: Measurements and measurement accuracy, *J. Geophys. Res.*, *104*, 11,695-11,707, 1999.

Plumb, R. C., and J. O. Edwards, Color centers in UV-irradiated nitrates, *J. Phys. Chem.*, *96*, 3245-3247, 1992.

Ridley, B., J. Walega, D. Montzka, F. Grahek, E. Atlas, F. Flocke, V. Stroud, J. Deary, A. Gallant, H. Boudries, J. Bottenheim, K. Anlauf, D. Worthy, A. L. Sumner, and P. Shepson, Is the Arctic surface layer a source and sink of NO$_x$ in winter/spring?, *J. Atmos. Chem.*, *36*, 1-22, 2000.

Seinfeld, J. H., and S. N. Pandis, *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, John Wiley, New York, 1998.

Sigg, A., and A. Neftel, Evidence for a 50% increase in H$_2$O$_2$ over the past 200 years from a Greenland ice core, *Nature*, *351*, 557-559, 1991.

Silvente, E., and M. Legrand, A preliminary study of the air-snow relationship for nitric acid in Greenland, in *Ice Core Studies of Global Biogeochemical Cycles, NATO ASI Ser., Ser. I*, vol. 30, edited by R. J. Delmas, pp. 225-240, Springer-Verlag, New York, 1995.

Staffelbach, T., A. Neftel, B. Stauffer, and D. Jacob, A record of the atmospheric methane sink from formaldehyde in polar ice cores, *Nature*, *349*, 603-605, 1991.

Stottlemyer, R., and D. Toczydlowski, Pattern of solute movement from snow into an Upper Michigan stream, *Can. J. Fish. Aquat. Sci.*, *47*, 290-300, 1990.

Sumner, A., and P.B. Shepson, Snowpack production of formaldehyde and its impact on the Arctic troposphere, *Nature*, *398*, 230-233, 1999.

Vaughan, P. P., and N. V. Blough, Photochemical formation of hydroxyl radical by constituents of natural waters, *Environ. Sci. Technol.*, *32*, 2497-2953, 1998.

Vogt, R., and B. J. Finlayson-Pitts, Unique photochemistry of surface nitrate, *J. Phys. Chem.*, *99*, 17,269-17,272, 1995.

Wagner, I., H. Strehlow, and G. Busse, Flash photolysis of nitrate ions in aqueous solution, *Z. Phys. Chem.*, *123*, 1-33, 1980.

Warneck, P., and C. Wurzinger, Product quantum yields for the 305-nm photodecomposition of NO$_3^-$ in aqueous solution, *J. Phys. Chem.*, *92*, 6278-6283, 1988.

Weinheimer, A. J., T. L. Campos, J. G. Walega, F. E. Grahek, B. A. Ridley, D. Baumgardner, C. H. Twohy, and B. Gandrud, Uptake of NO$_y$ on wave-cloud ice particles, *Geophys. Res. Lett.*, *25*, 1725-1728, 1998.

Wolff, E. W., J. C. Moore, H. B. Clausen, and C. U. Hammer, Climatic implications of background acidity and other chemsitry derived from electrical studies of the Greenland Ice Core Project ice core, *J. Geophys. Res.*, *102*, 26,325-26,332, 1997.

M. A. Arsenault and J. E. Dibb, Institute for the Study of Earth, Oceans, and Space, University of New Hampshire, Durham, NH 03824.

M. P. Dziobak, S. Guo, R. E. Honrath, and M. C. Peterson, Department of Civil and Environmental Engineering, Michigan Technological University, 1400 Townsend Drive, Houghton, MI 49931. (reh@mtu.edu)