Nitrate, a member of the oxidized nitrogen family (NO$_3^-$), is one of the primary species involved in the nitrogen cycle and thus plays a key role in ecosystem processes, globally. It exists as nitrate salts and as nitric acid (HNO$_3$) in both aerosols and the gas phase. It is formed from the NO$_3^-$ radical/N$_2$O$_5$ or directly from the oxidation of NO$_2$ and is lost by photolysis, OH oxidation, and deposition. In regions covered with snow/ice it has a significant impact on air quality, atmospheric oxidizing capacity, greenhouse gas concentrations, and paleoclimate/isotopic data. Snow/ice environments can, at seasonal maximum, comprise ~ 30% of Earth’s surface area while 10% is covered with ice/snow found at the polar cryosphere. Nitrate makes up 75–100% of the nitrogen budget deposited from the atmosphere and measured at the Arctic and Antarctica. Its concentrations in Greenland ice have risen by a factor of 2–3, reflecting the long-ranged transport of increased anthropogenic NO$_x$ (NO + NO$_2$) emissions.

The polar cryosphere is an active medium for the movement of traces gases, such as nitrate, between the snowpack/sea-ice and overlying atmosphere. Field, laboratory, and modeling efforts have quantitatively shown that the exchange of trace species between the snowpack and the air above is governed by photochemistry in combination with air moving gases between these two matrices. Polar tropospheric chemistry and dynamics immensely impact processes governing chemical composition, isotopic signatures, oxidizing capacity, and thus regional climate. This study presents a comprehensive review of laboratory and modeling efforts – contextualized by field measurements – that have elucidated physicochemical processes governing nitrate photochemistry and its impact on the polar snowpack. Specifically, after an Introduction to nitrate photochemistry in ice, we discuss the: 1) initial Arctic field measurements that sparked interest in ice photolysis in the polar regions; 2) suite of follow-up field studies that catalyzed laboratory and snow-chamber investigations that gave deeper understanding of the effects of snow/ice – air trace gas exchange due to nitrate photochemistry; 3) complementary laboratory, snow-chamber investigations; and 4) a detailed review of recent nitrate ice photolysis laboratory experiments and the potential impact of utilizing laboratory and computational models to study the role of nitrate in the nitrogen cycle.

1. Introduction

Global snow/ice coverage fluctuates over seasonal and climatic timescales. For example, over long timescales, ice sheets covered ~ 32% of the Earth’s surface year-round during the glacial periods, compared to the present of ~ 10% with additional extensive seasonal snow and sea-ice coverage (https://nsidc.org/cryosphere/glaciers/quickfacts.html). The decrease in the global sea ice extent is a major concern (http://nsidc.org/data/seaice_index/) as the cryosphere plays an important role in global climate, hydrology and ecosystems through the snow-albedo feedback and snow-hydrological effects. Future model scenarios, therefore, predict considerably less snow/ice coverage compared to the past and present.

In the past, the cryosphere was perceived as an inert sink, inhibiting emissions from land and ocean surfaces below and acting as a permanent sink of atmospheric species. Snow itself was not considered beyond its effect on radiative transfer through albedo. Throughout the last two decades, it has been shown that the polar cryosphere can have a major influence on the overlying atmosphere (Grannas et al., 2007). These findings exemplify the photochemically-active nature of snow and ice, rather than how it was viewed—that is, it being an inert sink for impurities. However, snowpack constituents are photolyzed by sunlight and oxidized via heterogeneous processes to release reactive trace gases to the polar boundary layer (PBL). This fact is globally important as seasonal snow can over covers up to a maximum of ~ 30% of the Earth’s surface (Dozier, 1989), whereas ~ 15% of the world’s oceans are covered by sea ice (https://nsidc.org/cryosphere/seaice/index.html), and 10% of Earth’s surface is covered with glacial ice (https://nsidc.org/cryosphere/glaciers/quickfacts.html).

Field measurements of trace gases in the cryosphere/high latitude snow/ice-covered regions aimed at enhancing our understanding of ice core data and atmospheric chemistry in a clean background.
atmosphere. The first polar field measurements at the Arctic (Honrath and Jaffe, 1992) and Antarctic (Jefferson et al., 1998) revealed low concentrations (less than 5 ppt) of ambient NO, which supported the longstanding assumption that dominant NO sources there were pre-
dominantly from downward transport from the stratosphere and long-
range transport from lower latitudes. The initial discoveries of NO (= NO + NO₂) and HCHO within polar snow and subsequent release provided the first evidence for the photochemical production and release of trace gases from the cryosphere (Furher et al., 1996; Sumner and Shepson, 1999; Honrath et al., 1999; Mauldin et al., 2004; Domine and Shepson, 2002). The snowpack was deemed the source of NO, and HCHO as their concentrations in the snow were enhanced when compared to the ambient air (just above the snow surface). Moreover, in less polluted, high-latitude regions, emissions from the snowpack can dominate boundary layer chemistry. For instance, on the Antarctic plateau, some oxidants are as abundant as they are in the tropical troposphere (Mauldin et al., 2004).

There has been growing interest in atmospheric photochemistry of the polar regions (Domine and Shepson, 2002). One of the primary reasons for this increased interest is the relevance of this chemistry to the interpretation of chemical signatures in polar ice core records (Wolff, 2012). Ice core records can provide insights about major geophysical events in earth's past as well as point to changes that have occurred in the planet's climate (e.g., fluctuations in atmospheric oxidative capacity) (LeGrand and Delmas, 1987; Legrand and Feniet-Saigne, 1991). An understanding of atmospheric chemistry is relevant, because it provides one of the critical inputs for evaluating the air-to-

3. Production of NO₃ via nitrate photolysis

The initial field studies that showed that photochemistry made the snowpack a dynamic environment also revived interest in the nitrogen cycle over the polar regions. Nitrate is a primary driver for the photochemical production of other trace gases in and above the snowpack; it is one of the dominant anions present in the snowpack with an even
distribution with latitude and longitude at both polar regions (Legrand and Mayewski, 1997; Mulvaney et al., 1999). HNO₃(g), the atmospheric reservoir species for nitrate, is completely miscible in water and, thus, readily dissociates to produce nitrate ions (Mack and Bolton, 1999; Mark et al., 1996). In the polar snowpack, HNO₃(g) dissociates in surface and interfacial thin films surrounding ice nuclei to produce NO₃-, which photolyzes to produce NOx, which are limiting reagents for the photochemical production of boundary layer ozone. In the aqueous phase, it was also known that nitrate photolysis produces nitrite (NO₂−) and the OH radical (Mack and Bolton, 1999; Mark et al., 1996).

These initial studies heightened the interest in accurately modeling photochemistry in the polar regions, which in turn, increased the need for additional field measurements to the Arctic and Antarctic in the late 1990s (Jones et al., 1999; Ridley et al., 2000; Davis et al., 2001). These field investigations demonstrated enhanced release of NOₓ and HCHO within, and above, the snowpack to the atmosphere. Given these initial field measurements and studies describing the mechanistic release of NOₓ, NO₂−, OH, and HCHO (Mack and Bolton, 1999; Mark et al., 1996; Quan, 1996), nitrate photochemistry became a focal point for later polar photochemical field, laboratory, and modeling work.

2. What sparked the interest on polar snow photochemistry studies?

Snowpacks were assumed to be an inert sink for atmospheric gases – that is, there was no bi-directional exchange with the overlying atmosphere. Thus, there was not sufficient motivation to conduct extensive field measurements of atmospheric trace gases over the polar snowpack. Polar snowpack studies were, therefore, primarily focused on understanding how ice/snow – air exchange might affect glacial ice core composition (Neftel et al., 1985, 1988; Raynaud et al., 1988; Stauffer et al., 1988; Chappellaz et al., 1990). Concomitantly, early studies were conducted under conditions that did not highlight the impact of snowpack emissions (e.g., under unstable boundary layer scenarios or conditions where pollution transport dominates (Dickerson, 1985; Beine et al., 1997; Solberg et al., 1997; Beine et al., 1996). Additional measurements involved instruments that (at the time) were insensitive to the snowpack trace gas emission levels (Bottenheim et al., 1986, 1990; Leaitch et al., 1994). However, the discovery that NO (Honrath et al., 1999) and HCHO (Sumner and Shepson, 1999) were photolytically-produced in the polar snowpack changed this previously held view. This paradigm shift demonstrated that the polar snowpack not only preserves climatic signatures of Earth's past but actively interacts with the overlying boundary layer through photochemical processing of trace gases contained in snow/ice. Since this time, a wide range of trace gases have been measured via a suite of field (Honrath et al., 1999; Davis et al., 2001; Jones et al., 2000; Honrath et al., 2000a,b,c; 2002; Davis et al., 2004a,b; Zhou et al., 2001; Dibb et al., 1998, 2004; Qiu et al., 2002; Beine et al., 2002a,b; 2003; Jacobi et al., 2004; Wang et al., 2007; Bausguitte et al., 2012), laboratory (Bartels-Rausch and Donaldson, 2006; France et al., 2007; Honrath et al., 2000a,b,c; Dubovski et al., 2001, 2002; Chu and Anastasio, 2003; Boxe et al., 2003, 2005a,b; 2006; McCabe et al., 2005; Jacobi et al., 2006; Jacobi and Hilker, 2007; Marcotte et al., 2015; Berhanu et al., 2014; Meusinger et al., 2014; Svoboda and Slavicek, 2014; Abida et al., 2011; Yabushita et al., 2008; Minero et al., 2007; Matykiewiczova et al., 2007), and modeling studies (Thomas et al., 2011, 2012; Boxe and Saiz-Lopez, 2008; Bock and Jacobi, 2010; King et al., 2005; Wolff et al., 2002).

The even distribution of nitrate (NO₃-) across Greenland and Antarctica arises from remote sources, which are convolved with long distance atmospheric transport (Platt, 1986; Logan, 1983; LeGrand and Mayewski, 1997; Mulvaney et al., 1999). HNO₃(g), the atmospheric reservoir species for nitrate, is completely miscible in water and, thus, readily dissociates to produce nitrate ions (Mack and Bolton, 1999; Mark et al., 1996). In the polar snowpack, HNO₃(g) dissociates in surface and interfacial thin films surrounding ice nuclei to produce NO₃-, which photolyzes to produce NOx, which are limiting reagents for the photochemical production of boundary layer ozone. In the aqueous phase, it was also known that nitrate photolysis produces nitrite (NO₂−) and the OH radical (Mack and Bolton, 1999; Mark et al., 1996).
have all shown elevated NOx emissions, diurnally correlated with solar actinic flux, in and over the polar snowpack.

Snow chamber measurements further demonstrated that the amount of NOx released from the snowpack was directly dependent on initial nitrate concentrations (Honrath et al., 2000a,b,c; Beine et al., 2002a,b). NOx levels within the snowpack (~10–30 cm depth) at Summit, Greenland, Greenland ice sheets, North America, coastal Antarctica, South Pole range between 100 and 1000 pptv, correspondingly. These studies also show that the NOx/NO ratio exceeded what was measured in the overlying air (ambient air) above the snowpack due to the fact that: i) NOx is produced by way of nitrate's primary photolytic pathway with a 90% branching (Mack and Bolton, 1999; Mark et al., 1996); and that ii) the photolysis rate of NO2 decreases as a function of depth within the snowpack. In contrast, NO mixing ratios are usually twice that of NOx as NO photolyzes in the UV while NO2 photolyzes in both the UV and visible wavelengths (Oncley et al., 2004). These analyses show that the NO2/NO ratio is governed by emissions, NOx–NO2–O3 photochemistry, and additional reactions with peroxy and/or halogen radicals.

NO mixing ratios are highest at the South Pole due to its limited vertical mixing, weak but continuous sunlight, and, potentially, long length of upwind fetch containing snowpack emissions. Deeper boundary layers and a smaller fetch yield much lower NOx concentrations in other areas of the polar environment (5 pptv to 25 pptv) (Jones et al., 1999, 2007; Jefferson et al., 1998; Weller et al., 2002). The Arctic region exhibits a similar pattern with higher values on the high-altitude ice sheet and lower values at coastal locations.

Although early measurements were pivotal in spawning the field of ice/snow photochemistry, incongruent measurement techniques (e.g., volumetric flow rate of air sampled), accessibility to the polar snowpack, and varying snowpack properties (described in more detail in Section 5) made it difficult to interpret these results. These confounding issues make it difficult to use field data to quantify relative NO and NO2 production rates within snowpack interstitial air. Firstly, at any given time, there is a limited amount of funded field campaigns in the Arctic and Antarctic, which prevents detailed analyses of physico-chemical properties and processes. Moreover, scientists should ideally have access to uncontaminated ice, snow, and air. It becomes hard to provide truly “clean” air as field sites also emit trace gases. Year-round studies are also needed, which is difficult due to the harsh winter conditions at the polar regions. Flux measurements of trace gases in the field are also pivotal for model parameterizations. Interpreting flux data is tough as well since they are influenced by a several variables, including frequency of snowfall events, snowpack solute concentrations, changes in irradiance, and atmospheric stability; furthermore, a method is needed for the fast and selective measurement of species of interest for eddy correlation measurements or flux measurements determined by tower gradient methods. Measurements of trace gas fluxes also need be decoupled, quantitatively providing physical and photochemical sources. Within the context of inherent instrument sampling errors/differences, actual measurements are confounded by artificial ventilation. This issue becomes more pronounced for sampling gases at low mixing ratios, especially when considering typical gas sampling flow rates are many liters per minute.

A suite of laboratory investigations were carried out to explore the mechanisms governing the photochemical production of NOx in and above the polar snowpack (France et al., 2007; Honrath et al., 2000a,b,c; Dubowski et al., 2001, 2002; Chu and Anastasio, 2003; Boxe et al., 2003, 2005a,b, 2006; McCabe et al., 2005; Jacob et al., 2006, Jacob and Hilker, 2007; Marcotte et al., 2015; Berhanu et al., 2014; Meusinger et al., 2014; Svoboda and Slavicek, 2014; Abida et al., 2011; Yabushita et al., 2008; Minero et al., 2007; Matykieviczowa et al., 2007, etc.). The foundation of these studies was based on aqueous phase nitrate and nitrite photochemistry (Mack and Bolton, 1999; Mark et al., 1996). These studies showed that NO, NO2, OH, and NO•- are the primary photoproducts formed during the photolysis of aqueous phase solutions doped with NO3- or NO2-. Dissolved nitrate has two primary absorption bands in the ultraviolet (UV). The first occurs in the far UV via the strong \( \lambda \approx \pi \cdot \pi \) transition, centered at 201 nm (\( \lambda_{max} = 9500 \ M-1 \ cm^{-1} \)), and the second is a weaker absorption band that occurs via the highly forbidden \( \lambda \approx \pi \cdot \pi \) transition, centered at 302 nm (\( \lambda_{max} = 7.14 \ M-1 \ cm^{-1} \)) (see Fig. 1 for UV–visible spectrum of NO3- and NO2-).

![Fig. 1. The UV–visible absorption spectrum of NO3-, NO2-, and H2O2. The solid lines refer to the left y-axis, and the broken lines refer to the right y-axis](Adapted with permission from Mack and Bolton (1999) Copyright, 2000 Elsevier.)

In the absence of OH scavengers this stoichiometry is maintained over the entire pH range (Mack and Bolton, 1999). For \( \lambda < 280 \ nm \), the major reaction pathway is through isomerization of [NO3•]-, generated via r2, to form ONOO•-, peroxynitrite, and at low pH, peroxynitrous acid, HONOO (r3). HONOO can also be produced from the recombinant of O• OH and NO2 within a solvent cage as shown in reaction r4, HONOO isomerizes rapidly back to NO3 (reaction r5) (Mack and Bolton, 1999).

\[
\begin{align*}
\text{NO}_3^- & \xrightarrow{hv} \text{[NO3•]}^{-} & r2 \\
\text{NO}_3^- & \rightarrow \text{ONOO}^- + \text{H}^+ + \rightarrow \text{HONOOC} & r3 \\
\text{OH} + \text{NO}_2 & \rightarrow \text{HONO} & r4 \\
\text{OH} + \text{NO}_2 & \rightarrow \text{NO}_3^- + \text{H}^+ & r5 \\
\end{align*}
\]

Yet, in the lower troposphere, all \( \lambda < 290 \ nm \) is completely attenuated by stratospheric ozone. Therefore, \( \lambda \geq 290 \ nm \) are pertinent for the study of nitrate photochemistry in the polar regions. In aqueous solutions at pH < 6 and \( \lambda \geq 290 \ nm \), nitrate photolysis proceeds via two primary photolytic pathways as illustrated in reaction r6 and r7, through the generation of nitrate in the excited state, [NO3•]- from r2. As shown in r8, O• reacts rapidly with water to form the hydroxyl radical.

\[
\begin{align*}
[\text{NO}_3^-]^+ + \text{H}^+ & \rightarrow \text{NO}_2^- + \text{O}^- & r6 \\
[\text{NO}_3^-]^+ & \rightarrow \text{NO}_2^- + \text{O}(^3\text{P}) & r7 \\
\text{O}^- + \text{H}_2\text{O} & \rightarrow \text{OH} + \text{OH}^- & r8 \\
\text{Atomic oxygen produced in reaction r7 can react with molecular oxygen ([O2]_water \sim 0.3 \text{ mM}) via r9 or with nitrate by way of r10 (Chu and Anastasio, 2003) } & \\
\text{O}_2 + \text{O}(^3\text{P}) & \rightarrow \text{O}_3 & r9 \\
\text{NO}_3^- + \text{O}(^3\text{P}) & \rightarrow \text{NO}_2^- + \text{O}_2 & r10 \\
\end{align*}
\]

Ozone, generated by r9, is either consumed by reaction with NO2-
The UV absorption spectrum of nitrite displays three absorption bands: the first involves a $\pi \rightarrow \pi^*$ transition with maxima at 220 nm, and the latter two peaks are maxima at 318 nm ($\varepsilon_{\text{max}} = 10.90 \text{ M}^{-1} \text{ cm}^{-1}$) and 354 nm ($\varepsilon_{\text{max}} = 22.90 \text{ M}^{-1} \text{ cm}^{-1}$), both corresponding to $n \rightarrow \pi^*$ transitions. Similar to nitrate, nitrite undergoes direct photolysis as shown in reaction r12 to produce NO, and it also oxidized by reaction with $\cdot OH$ via r13. The photolysis of NO2 also produces NO (r14) (see Fig. 2 for UV–visible spectrum of NO and NO2).

\[
\begin{align*}
\text{NO}_2^+ + \text{O}_3 & \rightarrow \text{NO}_3^- + \text{O}_2 \quad \text{(r11)} \\
\text{NO}_2^- + \text{O}_3 & \rightarrow \text{NO}_3^- + \text{O}_2 \\
\text{NO}_2^- + \text{OH} & \rightarrow \text{NO}_2 + \text{OH}^- \\
\text{NO}_2^- & \rightarrow \text{NO} + \text{O}^{(P)}
\end{align*}
\]

The initial studies, utilizing nitrate and nitrite aqueous photochemistry, as a basis, addressed whether NO$_3^-$ impurities in snow/ice matrices could produce NO$_2$ when irradiated. For instance, Honrath et al. (2000a,b,c) made artificial snow samples using: 1) deionized water alone; 2) deionized water with 100 $\mu M$ NaNO$_3$ added; 3) and deionized water with 100 $\mu M$ NaNO$_3$, 25 mM dimethyl sulfoxide (DMSO) and 250 $\mu M$ 3-aminio-2,2,5,5-tetramethyl-1-pyrroolidinylxoy radical (3AP). DMSO and 3AP were included to trap OH radicals produced during NO$_3^-$ photolysis. These artificially-made snow samples were placed in a flow chamber, which was located outdoors on a natural snow surface at the Snow Nitrogen and Oxidants in Winter (SNOW99) field site. 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. This rapidly frozen “snow” (or spray-frozen solutions) of only deionized water released minimal NO, that did not exhibit a diurnal solar dependence, while the spray-frozen deionized water with 100 $\mu M$ NaNO$_3$ released > 500 pptv of NO$_2$ (Fig. 3), which had a high correlation to solar radiation. The radical trap reagents, DMSO and 3AP, resulted in NO$_2$ levels of > 8 ppbv (Fig. 4), consistent with nitrate aqueous phase photochemistry experiments (Mack and Bolton, 1999; Mark et al., 1996). This was the first study to show that the photolysis of artificial snow samples doped with nitrate produces NO$_2$.

Dubowski et al. (2001, 2002) conducted subsequent nitrate photochemistry ice experiments measuring NO$_2$ and NO$_3^-$. They quantified NO$_2$ fluxes released into the gas phase during the continuous $\lambda$ ∼ 300 nm photolysis of NO$_3^-$ in submillimeter ice layers by spray-freezing KNO$_3$ solutions on a temperature controlled coldfinger. Between 5 ≤ [NO$_3^-$]/mm ≤ 50 NO$_2$ fluxes increase weakly, but increase more drastically between 248 ≤ T/K ≤ 268. Supporting Honrath et al. (2000a,b,c), Dubowski et al. (2001) showed that NO$_3^-$ photo-decomposed into NO2 and NO$_2^-$. Moreover, NO$_2$ produced in the uppermost region of the spray-frozen ice samples was able to escape to the gas phase, while NO$_2$ produced at greater depths was photolized to NO. They also quantified NO$_2$ and NO$_2^-$ quantum yields at 263 K, $\phi_{\text{NO}_2} \sim 4.8 \times 10^{-3}$ and $\phi_{\text{NO}_2^-} \sim 1.3 \times 10^{-3}$, respectively, which are similar to their respective quantum yields in the aqueous phase. These
findings suggested that NO$_3^−$ photolysis in ice takes place in a liquid-like environment. Using the quantum yields measured in this study, Dubowski et al. (2001) also concluded that nitrate photolysis on cirrus clouds is a minor NO$_2$ source due to the small amount of NO$_2$ that could be deposited on the cirrus cloud surface and the slow NO$_2$ production rate, thus not impacting the over-prediction of the [HNO$_3$]/[NO$_2$] ratio by photochemical models. Dubowski et al. (2002) conducted another study solely focused on the nitrate photoproduct NO$_2$$. This study quantified $\phi$NO$_2$ between 238 ≤ T/K ≤ 294 in the 302 nm photolysis band of aqueous and frozen nitrate solutions. Dubowski et al. (2002) also concluded that the nitrate photodecomposition takes place in a similar liquid-like media at all temperatures when considering that the detection of NO$_2$ is only possible after the initial photofragments (i.e., NO$_2^−$ and O) escape the solvent cage and that the diffusivity of ice is approximately 6 orders of magnitude smaller than that of supercooled water at the same temperature. Again, supporting Honrath et al. (2000a,b,c), the addition of the radical scavenger for OH, formate (HCO$_2$−), increased initial rate constants for nitrite production by 5-fold (Fig. 5). Reaction 13 proceeds efficiently with a rate constant of 2 × 10$^{-10}$ M$^{-1}$ s$^{-1}$, while the presence of HCO$_2$− also proceeds efficiently to not only scavenge OH radicals but also convert NO$_2$, the primary photolytic product of nitrate photolysis, into additional nitrate via r15-17.

HCOO$^−$ + OH $→$ H$_2$O + CO$_2^−$  
\[ \text{r15} \]

CO$_2^−$ + O$_2$ $→$ O$_2$ + CO$_2$  
\[ \text{r16} \]

O$_2^−$ + NO$_2$ $→$ O$_2$ + NO$_2$  
\[ \text{r17} \]

Dubowski et al. (2001) quantified lower-bounds of $\phi$NO$_3^−$ because of incomplete recoveries of NO$_2$. They showed that nitrogen dioxide produced photochemically and released into the gas phase was condensed in a liquid nitrogen trap at 77 K containing a frozen NaOH solution. The condensing trap was evacuated, sealed, and thermalized at 298 K, and kept in the dark for 12 h to allow any NO$_2$ present to dissolve in the NaOH solution. The contents of the trap, as well as the melted ice left from the coldfinger, were then analyzed for nitrate using the Saltzman reagent (Saltzman, 1954). Chu and Anastasio (2003) used an alternative approach by following the formation of OH radicals. Hydroxyl radicals react with a chemical probe, benzoic acid (BA), to form stable, measurable p-hydroxybenzoic acid (p-HBA) and m-hydroxybenzoic acid (m-HBA) as shown in reaction r18.

BA+OH $→$ p-HBA + m-HBA + other  
\[ \text{r18} \]

At the end of each illumination period, ice samples were melted and measured in the dark and room temperature and then analyzed for p-HBA using High Performance Liquid Chromatography (HPLC) with UV detection. Temperature dependence experiments between 239 and 318 K at pH 5.0 showed that $\phi$NO$_3^−$ and $\phi$OH in ice pellets and aqueous solutions were both well described by the same regression line (Fig. 6),

\[ \ln(\phi_{\text{OH}}) = \ln(\phi_{\text{NO}_3^−}) = -(2400 \pm 480)/(1/T) + (3.6 \pm 0.8), \]  

suggesting that the photolysis of nitrate on ice occurs in the quasi-liquid layer (QLL), rather than in the bulk ice. Chu and Anastasio (2003) measured NO$_3^−$ and OH quantum yields that were 3–9 times higher than Dubowski et al. (2001) and were able to account for past field studies that measured NO$_x$ from sunlit snow at coastal Antarctica and Summit, Greenland, but concluded that nitrate photolysis was a minor snowpack source of NO$_x$ when compared to field campaigns during Alert 2000 in the Canadian Arctic.

Chu and Anastasio (2007) later quantified quantum yields of OH during the photolysis of frozen and aqueous samples doped with NO$_2$ by given that there is evidence for NO$_2^−$ production in the polar snowpack and no experimental study existed focusing on NO$_2^−$ photolysis in ice. Hydroxyl radicals were measured in a similar fashion as done by Chu and Anastasio (2003). They conducted experiments from 240 to 295 K and illumination wavelengths from 302 to 390 nm to derive a master equation for the $\phi_{\text{OH}}$: $\phi_{\text{NO}_2^- \rightarrow \text{OH}}_{T,L} = \left( y_0 + \frac{a}{1 + \exp\left(\frac{b - c}{\lambda - f}\right)}\right)$, where $y_0 = 0.0204 \pm 0.0010$, $a = 0.0506 \pm 0.0022$, $b = 11.2 \pm 1.2$, $c = 332 \pm 1$, $e = 20.5 \pm 3.2$, $f = 7553 \pm 1204$, uncertainties represent 1 standard error, $T$ is the temperature (K), $R$ is the gas constant (8.314 J mol$^{-1}$ K$^{-1}$), and $\lambda$ is the wavelength (nm). Chu and Anastasio showed that nitrite photolysis accounts for < 1% of the overall rate of OH formation, while HOOH photolysis is the dominant source. Yet, despite NO$_2^−$ small snowpack concentration 10$^{-12}$ to 10$^{-15}$ M, the rate of NO$_2^−$ photolysis is comparable to that of NO$_3^−$, which implies that NO$_2^−$ photolysis could play a significant role in the release and cycling of NO$_x$ in snowpacks.

Cotter et al. (2003) also suggested the release of NO and NO$_2$ by assessing the wavelength (295 ≤ $\lambda$/nm ≤ 385) and temperature (243 ≤ T/K ≤ 253) dependence of their release during the photolysis of
(a) 

(b) 

(c) 

(caption on next page)
Antarctic snow situated in an airtight reaction chamber. The Antarctic snow sample was irradiated by directing light through a Teflon window at one end of the chamber while pure air carried the photoproducts (i.e., NO and NO\textsubscript{2}) to the chemiluminescence analyzer for detection. They showed that NO\textsubscript{2} dominated the production during photolysis, and NO\textsubscript{2} was not detected at \( \lambda > 345 \text{ nm} \). After comparing their laboratory data with the absorption cross section for NO\textsubscript{3}\textsuperscript{−}, they also concluded that NO\textsubscript{3}\textsuperscript{−} was the precursor N-oxide species being photolyzed in the polar snowpack.

Boxe et al. (2003, 2005a,b, 2006) and McCabe et al. (2005) conducted several photochemical temperature-programmed desorption laboratory investigations of spray-frozen nitrate solutions on a temperature controlled coldfinger, where NO and NO\textsubscript{2} were measured by a number of spectroscopic techniques (Fig. 7(a), (b), and (c), Boxe et al. (2003)). During the 302 nm continuous photolysis of KNO\textsubscript{3}-doped spray frozen ice solutions NO and NO\textsubscript{2} were measured by two-photon laser-induced NO\textsubscript{3} fluorescence in the range of \( 238 \leq T/K \leq 273 \) at 0.67 °C min\textsuperscript{−1} heating ramp for [NO\textsubscript{3}\textsuperscript{−}] between 2\( \mu \text{M} \) and 50\( \mu \text{M} \). This study showed that NO\textsubscript{3} accumulated in the deeper layers during photolysis and exhibited sudden bursts/emissions when the ice undergoes a sintering transition (Fig. 8), which coincided with the onset of surface melting at \( T \approx 265 \text{ K} \). It was concluded that doped polycrystalline ice contains operationally distinguishable fluid phases of low dimensionality over various length scales and temperature ranges since the photochemical release of NO\textsubscript{2} was detected far below the KNO\textsubscript{3}/H\textsubscript{2}O eutectic \( (T_{\text{eutectic}} = \sim 270 \text{ K}) \).

Boxe et al. (2005b) conducted another investigation via temperature-programmed NO\textsubscript{2} emissions from the photolysis at 313 nm of spray-frozen NaNO\textsubscript{3} solutions on a temperature controlled coldfinger, which were monitored as a function of nitrate concentration and heating rate at temperature above 243 K. It was shown that NO\textsubscript{2} emissions increase monotonically until \( T \approx 265 \text{ K} \), whereupon NO\textsubscript{2} emissions surged. This surge was observed for [NO\textsubscript{3}\textsuperscript{−}] > 200\( \mu \text{M} \) samples warmed at a heating rate of 0.70 °C min\textsuperscript{−1} under continuous irradiation and also in the dark from samples that had been photolyzed at 243 K. It was also shown that the amounts of NO\textsubscript{2} released in individual thermograms increased less than linearly with [NO\textsubscript{3}\textsuperscript{−}] for the duration of the experiments, revealing the significant loss of photo-generated NO\textsubscript{2}. Specifically, the total amount of NO\textsubscript{2}, \( \sum_{\text{NO}_2} \), released exhibited a square-root temperature dependence upon the initial nitrate concentration, \( \sum_{\text{NO}_2} \propto \text{[NO}_3\text{]}^{1/2} \) at constant heating ramp (Fig. 9). This square-root dependence is consistent with NO\textsubscript{2} hydrolysis: 2NO\textsubscript{2} + H\textsubscript{2}O \rightarrow NO\textsubscript{3} + NO\textsubscript{+} + 2H\textsuperscript{+}, overtaking NO\textsubscript{2} desorption, even below the eutectic point (255 K for aqueous NaNO\textsubscript{3}).

The kinetic evolution of NO and NO\textsubscript{2} was also studied by Boxe et al.
(2006) by laser-induced fluorescence and chemiluminescence during the photolysis of spray-frozen aqueous NaNO3 irradiated at 313 nm. The kinetic behavior of NO and NO2 signals during on-and-off illumination cycles suggest that NO2 is a primary photoproduct evolving from the outermost ice layers and reveals that NO is a secondary species generated deeper in the ice, where it eventually emerges due to its relative inertness and larger diffusivity. Specifically, NO is shown to be more weakly held than NO2 by ice during thermal desorption experiments on pre-irradiated samples. Lastly, this study showed that the experimentally NO/NO2 ratios are up to 10-fold smaller than those determined over sunlit snowpacks, thus implying that the immediate precursors to NO mostly absorb at λ > λmax (NO2 -) ~ 302 nm.

Jacobi et al. (2006) and Jacobi and Hilker (2007) investigated the photochemical transformation of nitrate in artificial snow samples. Jacobi et al. (2006) showed that NO3- photolysis equally is very important in natural snow covers, regarding the formation of OH radicals. They also measured NO2- and NO3- concentrations via ion chromatography, which showed that after a certain photolysis period (≥8 h) their concentrations in the snow remained constant at a level of 10% of the initial nitrogen content. They interpret that this is probably due to a recycling of the anions from nitrogen oxides in the gas phase of the reaction cells, indicating that the chemical reactions occur in or near the surface layer of the snow crystals. Jacobi and Hilker performed photolysis experiments using artificial snow, containing variable initial concentrations of NO3- and NO2-, ranging from 0.7 to 11 μM and 0–12 μM, respectively. They support previous laboratory experiments which show that the formation of NO2 is probably the dominant channel from nitrate photolysis.

Since NO3- is the primary sink for atmospheric NOx, its chemical history provides a key to understanding the global nitrogen budget and the oxidation capacity of the atmosphere over time. Even though ice cores contain chemical concentration and isotopic changes that serve as valuable records of paleoclimate variations, quantitative interpretations of nitrate have proven elusive. Our understanding of variations in ice core nitrate concentrations has been limited by loss processes occurring during depositional and post depositional periods, associated with temperature, accumulation rate, diffusion, photochemistry, and volatilization (Wolff, 1995). McCabe et al. (2005) conducted the first experiments to assess the influence of post depositional photolysis on the isotopic signatures of snowpack NO3-. In particular, they report on the 17O- and 18O-fractionation via a multiple collector mass spectrometer in the 313 nm photolysis of 10 mM aqueous and spray-frozen solutions of KNO3 and NaNO3 (i.e., N2O4, NaNO3−, and NaNO2−). They found that the Fisher KNO3 (i.e., Δ17O = −0.2 ± 0.2‰, mass-dependent NO3-) undergoes mass-dependent O-fractionation, i.e., a process that preserves Δ17O = 0. In contrast, Δ15O in USGS-35 NaNO3 KNO3 (i.e., Δ15O = 21.0 ± 0.4‰, mass-independent NO3-) decreased by 1.6 ± 0.4‰ and 2.0 ± 0.4‰ at 25 °C, 1.2 ± 0.4‰ and 1.3 ± 0.4‰ at −5 °C, and 0.2 ± 0.4‰ and 1.1 ± 0.4‰ at −30 °C, after 12 and 24 h, respectively (Table 1). The observed decreases in Δ15O (for mass-independent nitrate) was attributed to competitive O-isotope exchange of germate OH radicals with H2O (Δ15O = 0) and escape from the solvent cage – in addition to residual O-isotope mixing of the final photoproducts NO, NO2, NO3- with H2O. Given the low NO3- concentrations (e.g., 1–20 μM) and the low temperatures at the polar regions, photochemical processing will not impair the diagnostic value of O-isotopic signatures in tracing the chemical history of nitrate in polar ice.

4. Nitrate and nitrite photochemical links to the production of low-molecular weight (LMW) carbonyl compounds and HONO

LMW carbonyl compounds are formed from the photodissociation of dissolved organic matter (DOM), such as humic substances in the ocean surface water. Nitrate and nitrite photochemistry leads to the formation of condensed-phase OH radicals (r8) (Mark et al., 1996). Grannas et al. (2004) conducted laboratory investigations that focused on the influence of nitrate and nitrite photolysis on the production on LMW carbonyl compounds via the photooxidation of organic compounds. Grannas et al. (2004) found that ice pellets made from melted Arctic and Antarctic snow produced HCHO and CH3CHO when irradiated. This study also showed that their production rates were enhanced by the addition of nitrate to the melted snow samples, which was attributed to the additional amount of OH radicals formed from NO3- photolysis.

Various mechanisms have been proposed for the formation of HONO. If we assume that acid/base equilibria known for the aqueous phase can be applied to snow, it follows that NO3-+, a primary photolytic product from nitrate photolysis, in snow can be protonated to produce HONO at acidic pH (pKα = 2.8) (Riordan et al., 2005), which will be released into the gas phase:

\[ NO_3^- + H^+ \rightarrow HONO(aq) \rightarrow HONO(g) \]

Under more acidic conditions, the nitroacidium ion, HONO+, (pKα = 1.7) (Riordan et al., 2005) may also form via the solvation of nitrosium nitrate (NO+NO3-), which in turn could then react further to form HONO. Nitrite is also formed efficiently via the following reaction: 2NO2 + H2O → NO3- + NO2 + 2H+.1 Jacobi and Hilker (2007) suggested that direct formation of HONO is highly dependent on the pH of the QLL and the HONO transfer rate to the gas phase, with effectively no production at pH ≥ 5 since the pKa of HONO is 2.8 in solution (Riordan et al., 2005). However, they note that due to the small amounts of nitrite and HONO's large Henry's law constant (e.g., 4 × 108 higher than that of NO3- at the same temperature) in the snowpack, the formation of HONO in the QLL is likely a negligible source from nitrate photolysis. Zhou et al. (2001) even suggested that the heterogeneous reaction of NO + NO2 + H2O → 2HONO may also be a significant HONO source. Although the distribution of organics is uncertain within the polar snowpack, NO3- may also react with them to form HONO (Beine et al., 2006; George et al., 2005; Stemmiller et al., 2006). In addition, O- and NO, produced from NO3- photolysis may also participate in the production of HONO in the polar snowpack as shown below in (r20 and r21).

### Table 1

<table>
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<th>Temperature, °C</th>
<th>Irradiation Time (h)</th>
<th>NO3-, mM</th>
<th>Δ18O, ‰</th>
<th>Δ17O, ‰</th>
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</table>

(a) In one case, liquid nitrate was irradiated for 24 h with no helium flow.
(b) Trials with water oxygen isotope composition δ18O = 13.9 ± 0.5‰.
O\textsuperscript{−} + H\textsuperscript{+} → OH \quad r20

NO + OH → HONO \quad r21

Still, this pathway is likely a negligible source to form HONO since snow grain concentrations of both NO and OH will be quite small. Lastly, the formation of HONO has been observed on the walls of an environmental chamber in laboratory experiments, albeit at [HNO\textsubscript{3}-NO\textsubscript{2}] \approx 1.5 ppmv (r22), which could possibly play a potential role in HONO formation at the polar snowpack snow grains (Zhu et al., 1993).

\[
\text{HNO}_3 \overset{\text{surface}}{\longrightarrow} \text{HONO} + \text{O}_2 \quad r22
\]

5. Recent laboratory studies of nitrate photochemistry

5.1. \textit{NOy} measurements

Recent studies complement earlier investigations by showing that nitrate photoproducts are not only released at relevant polar temperatures (Abida and Osthoff, 2011; Abida et al., 2011) but also released down to 70 K (Yabushita et al., 2008; Marcotte et al., 2015). Abida and Osthoff (2011) and Abida et al. (2011) observed the release of nitrogen oxides (primarily NO\textsubscript{2}, with less extent HONO, HONO\textsubscript{2}, HOONO, HO\textsubscript{2}NO\textsubscript{2} via cavity ring-down spectroscopy (CRDS), NO–O\textsubscript{2} chemiluminescence (CL), and chemical ionization mass spectrometry (CIMS) during the photolysis of frozen nitrate solutions photochemistry. Their studies reported the enhanced release of NO\textsubscript{2} as a function of decreasing pH. These findings may improve discrepancies in the upper free Arctic troposphere of NO\textsubscript{2} to NO\textsubscript{2} ratios as models consistently overpredict HNO\textsubscript{3} and NO\textsubscript{2} and tend to underpredict NO\textsubscript{3}.

Barrels-Rausch and Donaldson (2006) used Chemical Ionization Mass Spectrometry (CIMS) to measure HONO (for the first time in a laboratory on ice matrices) and NO\textsubscript{2} fluxes from 193 to 258 K from 250 to 345 nm. They show that NO\textsubscript{2} fluxes are roughly independent of temperature while HONO displays a negative temperature dependence (HONO fluxes increase with decreasing temperature). They also estimate a quantum yield for HONO, which is 10% of the quantum yield for NO\textsubscript{2} – that is, 3.8 ± 0.6) \times 10^{-4}.

Olridge (2009) utilized a photochemical reaction chamber, coupled to a CIMS, to quantify the evolution of NO\textsubscript{2}, Br\textsubscript{2}, Br, and I\textsubscript{2} from sea-ice analogs in the laboratory. They showed that both NO\textsubscript{2} and Br\textsubscript{2} increased as a function of increasing temperature and NO\textsubscript{2} concentration while the concentration of Br\textsuperscript{−} did not affect the amount of NO\textsubscript{2} and Br\textsubscript{2} released. They also showed that increasing acidity increased the amount of Br\textsubscript{2} and NO\textsubscript{2} released from photolyzed ice samples. Olridge’s (2009) study concluded that the majority of the photochemical processes governing Br\textsubscript{2} and NO\textsubscript{2} release occurred in the liquid component of ice as Br\textsuperscript{−} did not impact their releases while they both increased with increasing nitrate concentrations. Olridge (2009) concluded that the lack of dependence of Br\textsubscript{2} and NO\textsubscript{2} release on [Br\textsuperscript{−}] is that it may be readily solvated/dissolved and thus concentrated in liquid pockets. [Br\textsuperscript{−}] and [I\textsubscript{2}] was observed, although much less than Br\textsubscript{2}, imply that OH produced from nitrate photolysis may oxidize I\textsuperscript{−} ice. The smaller amounts of measured Br\textsuperscript{−} and I\textsubscript{2} is likely due to the greater abundance of chloride and bromide relative to iodide, which is only present as an impurity.

Zhu et al. (2010a,b) used 308 nm excimer laser photolysis combined with cavity ring-down spectroscopy to study HNO\textsubscript{3} photodecomposition on ice surfaces at 253 K. They monitored both the ground-state NO\textsubscript{2} and the electronically excited NO\textsubscript{2}, NO\textsubscript{2}*, produced from the HNO\textsubscript{3} photolysis, and showed that NO\textsubscript{2}* + OH is the likely predominant photolysis pathway. The corresponding NO\textsubscript{2}* quantum yield from the HNO\textsubscript{3} photolysis on ice films is 0.60 ± 0.34 at 253 K, whereas the corresponding absorption cross section of HNO\textsubscript{3} on ice films is (1.21 ± 0.31) \times 10^{-18} \text{cm}^{2}/\text{molecule}, which is 50 times greater than its respective solution absorption cross section at 278 K. Morenz et al. (2016) used dual-channel chemiluminescence instrumentation (Air Quality Design Inc.) for the detection of NO and NO\textsubscript{2} and NO\textsubscript{3} (total nitrogen oxides) via the illumination of snow samples as a function of both nitrate and total salt (NaCl and Instant Ocean) concentration. With no salts added, NO and NO\textsubscript{2} and NO\textsubscript{3} increase toward a plateau with increasing [NO\textsubscript{3}–]; conversely, NO and NO\textsubscript{2} and NO\textsubscript{3} decrease with increasing NaCl or Instant Ocean concentration. This behavior may be attributed to the cage effect, which causes photo-excited photoproducts in liquid and ice to lose their excess energy via collisions to other water molecules and often reform the initial compound. Specifically, at low pre-freezing [NaCl] ≤ 25 mM, NO\textsubscript{2} production was enhanced by 42% and by up to 89% at Instant Ocean [Cl–] ≤ 200 mM. This study shows that enhanced NO\textsubscript{2} observed from snow with lower Instant Ocean concentrations, rising to levels similar to that of observed NO, is due to the small amount of Br\textsuperscript{−} present in seawater. The [Br\textsuperscript{−} is approximately 0.15% of [Cl–] in Instant Ocean (Hong et al., 2013). Although bromide’s concentration is small compared to [Cl–], its reaction is much faster with OH than Cl–, thus, selectively promoting Br– activation from frozen salty snow (pH < 5) (Wren et al., 2013; Abbatt et al., 2010).

At temperatures well below the mean lower-limit QL temperature (T ≥ 200 K), Yabushita et al. (2007) observed the release of NO and O(\textsuperscript{3}P), at 100 K via Time-of-Flight Resonance-Enhanced Multiphoton Ionization (TOF-REMPI) (Fig. 10) from 295 to 320 nm photolysis of NO\textsubscript{3}–. Fig. 10a and b shows the REMPI spin spectrum of O(\textsuperscript{3}P) and signal intensity as a function of ice annealing time while Figure c displays typical time-of-flight spectrum of REMPI signals of O(\textsuperscript{3}P) atoms from the photodissociation of NO\textsubscript{3}– on a polycrystalline water ice film at 305 nm. The measurement was undertaken at the substrate temperature of 100 K. The solid lines are fits to the data derived assuming 3 M× Boltzmann distributions, T = 2000 K for the fast component, 500 K for the middle one, and 100 K for the slow one. The inset shows the time-of-flight spectrum of O(\textsuperscript{3}P\textsubscript{x}) atoms from the photodissociation of NO\textsubscript{3}– on water ice films at 305 nm. Assuming a Maxwell-Boltzmann distribution, the translational temperature of T = 500 K is derived from the solid line fit to the data. This was the first study to experimentally detect directly NO and O(\textsuperscript{3}P\textsubscript{x}) atoms from nitrate photolysis. They also conducted sensitivity simulations and incorporated the direct release of O(\textsuperscript{3}P\textsubscript{x}) atoms produced from the photolysis of NO\textsubscript{3}– adsorbed on ice/snow, which produced comparable values when compared to field data at the South Pole. Yabushita et al. (2008) used TOF-REMPI H\textsubscript{2} formation from the photodissociation of ammonium solid water (ASW) films. They deduced that H\textsubscript{2} formation involved two mechanisms: 1) a photolytically-produced H atoms induce abstraction (HAB) of nearby H\textsubscript{2}O H-atoms (H + HOH → H\textsubscript{2} + OH) or H-atom recombination (HR) (H + H → H\textsubscript{2}). Yabushita et al. (2002) used TOF, Infrared Absorption, and Temperature-Programmed Desorption Spectra to investigate the photodissociation dynamics of Cl\textsubscript{2} at 351 nm on water ice films from 80 to 140 K. Overall, laboratory experiments have shown that Cl\textsubscript{2} desorb rapidly from water ice surfaces (Molina et al., 1987). Although the photodissociation mechanism of chlorine is independent of absorbate coverage, states of ice films, and laser intensity, the dissociation quantum yield on an ammonium ice films was much less than on crystalline ice films. This is due to the fact that OH groups on ammonium ice film surfaces interact with Cl\textsubscript{2}. Specifically, the lower production yield for Cl photoproducts (via the Cl\textsubscript{2} surface monolayer on ammonous ice) is due more rapid quenching of photoexcited Cl\textsubscript{2} on ammonous compared to crystalline ice. However, for Cl\textsubscript{2} coverages of more than 1 monolayer, the increased rate of total Cl yield is suppressed for crystalline ice while it is enhanced for ammonous ice. This behavior suggest that the first monolayer Cl\textsubscript{2} covers all/vast majority of OH groups. Yabushita et al. (2002) results indicate that the Cl\textsubscript{2}-oxygen interactions on crystalline ice are much weaker than the hydrogen-bond-like interactions between Cl\textsubscript{2} and OH.

In addition, Marcotte et al. (2015) used nitrate-doped ASW films at
Fig. 10. (a). REMPI excitation spectrum of O ($^{3}P_2$) from the 305 nm photodissociation of NO$_3^-$ on a polycrystalline water ice film. The substrate temperature was 100 K at 2 μs time-of-flight. (b). Time evolution of O($^{3}P_2$) signal intensity after deposition of HNO$_3$ on the ice film at 130 K at 2 μs time-of-flight. During the intercept of measurement, the UV photodissociation beam at 305 nm was blocked. The measured evolution curve is fitted to a single-exponential curve with a rate constant of $(5.3 \pm 0.2) \times 10^{-3}$ s$^{-1}$. (c). Typical time-of-flight spectrum of REMPI signals of O($^{3}P_2$) atoms from the photodissociation of NO$_3^-$ on a polycrystalline water ice film at 305 nm. The measurement was undertaken at the substrate temperature of 100 K. The solid lines are fits to the data derived assuming 3 Mx–Boltzmann distributions, $T = 2000$ K for the fast component, 500 K for the middle one, and 100 K for the slow one. The inset shows time-of-flight spectrum of O($^{3}P_2$) atoms from the photodissociation of NO$_2$ on water ice films at 305 nm. The solid line is a fit to the data derived assuming Maxwell–Boltzmann distribution with $T = 500$ K (Yabushita et al., 2008, Copyright, 2008 Elsevier).
cycryogenic temperatures (70–120 K) to show surface-enhanced nitrate photochemistry by measuring NO₂ via Reflection Absorption Infrared Spectroscopy (RAIRS)-FTIR at λ = 290 nm. This approach provided the first direct evidence that nitrate, absorbed onto the first molecular layer at the ice/snow surface, is photolyzed 3 times more efficiently than in the bulk. Nitrate’s distored intramolecular geometry correlated with this enhancement and showcases the greater chemical heterogeneity in their solution environment at the surface of ice than that in the bulk. Marcotte et al. (2015) used 1st order photo-destruction kinetics to quantify effective photolysis rates for surface and bulk nitrates, which showed that photolysis of surface nitrates was significantly faster than bulk nitrates (e.g., 2.7 ± 0.6 at 70 K). Surprisingly, surface photolysis rates decreased with increasing temperature while bulk photolysis rates showed the opposite trend. At 120 K, surface and bulk photolysis rates are comparable, which may be due to the onset of diffusive uptake kinetics that allows for NO₃⁻ absorbed on ASW films to diffuse into bulk ice regimes (Marcotte et al., 2013). At 70 and 100 K, NO₃⁻ transport kinetics are strongly suppressed, such that the increase in effective photo-destruction rates originates from the enhancement in heterogeneous photolysis of nitrate anions that remain adsorbed onto the top-most molecular layer at the surface of ice – that is, at temperatures < 120 K. In addition, partial solvation of surface adsorbed NO₃⁻ may result in easier release of photoproducts (enhancing photolysis and thus quantum yields) (Richards et al., 2011; Nissenson et al., 2006). The lack of surface nitrate absorption extinction coefficients/absorption cross sections prevented quantification of their quantum yields. The enhanced surface nitrate photochemistry may also be due to greater splitting (at the ASW surface as shown via vibrational spectra) between asymmetric NO₃⁻ vibrational features; this implies that surface nitrate anions may experience greater chemical heterogeneity in their solvation matrix when compared to the bulk. From 70 to 120 K surface and bulk geometrical distortions decreased by 20 and 8 cm⁻¹, respectively. The increased asymmetric NO₃⁻ may also induce an increase in the absorption cross section of the n→π* electronic transition (centered at 302 nm for aqueous nitrate solutions), thus increasing respective surface quantum yields (Hudson et al., 2007; Gvоздиков et al., 2009). The surface of ASW provides a unique model system for the disordered interstitial air-ice interface, where cryogenic temperatures suppress transport kinetics (allowing for the decoupling of bulk and surface processes) and prolongs nitrate residence times at the ice surface. ASW ice models provide a platform to study photochemical behavior at temperatures well below those experimentally-observed for the existence of QLIs. The heterogeneous solvation environment induces significant geometrical distortions for nitrate that (in light of the strongly dipole forbidden character of the n→π* electronic transition), may cause an increase in nitrate’s absorption cross-section at the ice surface. Compared to the bulk the complex coupled interfacial kinetics of HNO₃/NO₃⁻/NO/NO₂/NO₂⁻ desorption, absorption, diffusive uptake, hydrolysis, photolysis, increased quantum yields, diffusion/transport, etc provide a novel perspective of nitrate photochemistry at low temperatures. The bulk environment only experiences diffusion, bulk photolysis and hydrolysis. Marcotte et al. (2015) also used a 1-D kinetic model and showed that a 3 to 6 enhancement in surface nitrate photolysis rates could increase NO₂ emissions (from a 5–8 nm surface layer) by 30–60% and that 25–40% of NO₂ emissions are released from the top-most molecular thin surface layer on ASW films. Enhanced surface photochemistry has also been shown in other mediums, such as deliquesced mixtures of NaCl + NaNO₃ (Wingen et al., 2008), NaBr + NaNO₃ and KBr + NaNO₃ (Richards et al., 2011), NO₂ release via HNO₃ deposited on urban grime (Baereng and Donaldson, 2013), and absorbed nitrate on alumina surfaces (analogs for mineral dust surfaces) (Schuttlefield et al., 2008).

These studies complement the vast amount of photochemistry and astrochemistry investigations done on/in interstellar media (Oberg, 2016) and may also have planetary science implications (e.g., heterogeneous/multiphase modeling on Mars) as well (Boxe and Saiz-Lopez, 2009; Boxe et al., 2012a,b,c).

5.2. Isotopic effects

Nitrate photolysis also induces isotopic effects in the nitrogen and oxygen isotopomers (Frey et al., 2009; Berhanu et al., 2014; Meusinger). McCabe et al. (2005) was the first laboratory study to use Finnigan Mat 251 multiple collector mass spectrometer to show that the photolysis of nitrate induces isotopic effects ice. Since then, Frey et al. (2009) and Berhanu et al. (2014) made advancements by showing perturbations to the isotopic signature of nitrogen and oxygen isotopomers during and after nitrate photolysis. Using an Isotope Ratio Mass Spectrometer (IRMS) (Thermo Finnigan MAT 253), Frey et al. (2009) measured the nitrogen (δ¹⁵N) and triple oxygen (δ¹⁸O and δ³¹O) isotopic composition of NO₃⁻ at Dome C, Antarctica. They showed that post-depositional fractionation in Δ¹⁵O(NO₃⁻) is minor, thus allowing for the reconstruction of past shifts in tropospheric oxidation pathways from ice cores.¹⁸O was depleted in δ¹⁸O by < 40‰, which was attributed to photolysis followed by isotopic exchange with H₂O and OH molecules while in δ¹⁵N enrichment in δ¹⁵N > 200‰ was attributed to ¹⁵N depletions in emissions. Atmospheric nitrate’s δ¹⁸O shows a strong decrease from background levels (4 ± 7‰) to ~35‰ in spring followed by recovery; this phenomenon is consistent with snowpack release of active nitrogen. The Δ¹⁵O signature validates that the spring peak in atmospheric NO₃⁻ is sourced from the stratosphere. Photolysis drives the redistribution of NO₃⁻ from the snowpack photic zone to the overlying atmosphere and a snow surface skin layer, concentrating NO₃⁻ at the surface. Berhanu et al. (2014) used Thermo Finnigan TM MAT 253 Isotope Ratio Mass Spectrometer equipped with a GasBench II™ to quantify an average photolytic isotopic fractionation of ¹⁵N = (−15 ± 1.2)% via broadband Xe lamp photolysis; this result was partially attributed to nitrate’s intense and weak absorption bands at 200 and 302 nm, correspondingly, followed by photodecomposition. Applying a light filter for λ < 302 nm (to approximate the actinic flux spectrum at Dome C), Berhanu et al. (2014) quantified a photolytic isotopic fractionation of ¹⁵N = (−47.9 ± 6.8)% which is in accord with past measurements from ~40 to ~74.3‰. These cross sections can be used in isotopic models to reproduce the stable isotopic composition of nitrate found in Arctic and Antarctic snow profiles.

5.3. Domains of photochemistry

Reported quantum yields for nitrate’s two primary photochemical pathways (i.e., NO₃⁻ + hν → NO₂ + O (Channel 1) and NO₃⁻ + hν → NO⁻ + O(³P) (Channel 2)) aqueous solution span orders of magnitude as discussed in Section 3. These discrepancies have been attributed to differences in experimental methods. Via the 302 nm band illumination of nitrate solutions at 298 K, Channel 1 exhibits an average quantum yield of 1.35 ± 0.3% (Zellner et al., 1999; Zepp et al., 1987; Warnke and Wurzinger, 1988; Chu and Anastasio, 2003; Dubowski et al., 2002; Scharko et al., 2014; Roca et al., 2008; Goldstein and Rabani, 2007). For example, Warnke and Wurzinger (1988) report a quantum yield of 0.11% for the formation of O(³P) via Channel 2, which is an order of magnitude lower than studies that reported a quantum yield of ~1% (Scharko et al., 2014; Roca et al., 2008; Goldstein and Rabani, 2007). The lower value has been used as a basis for excluding Channel 2 from aqueous phase photochemical models (Grannas et al., 2007; Scharko et al., 2014; Shi et al. (2015). Recent work supports comparable quantum yields for Channels 1 and 2 in aqueous solutions at room temperature (Benedict and Anastasio, 2017a) and greater quantum yield for Channel 2 compared to Channel 1 at lower temperatures (Benedict et al., 2017b). Measured quantum yields in ice also exhibit a wide range of values, which is likely due to, again, differences in experimental design used to probe ‘domains of photochemistry’ — i.e., the region around the nitrate chromophore that affect its dissociation (Davis et al., 2008). For instance, the quantum
yield of Channel 1 at −20 °C ranges from 0.0028 (Chu and Anastasio, 2003) to 6 (Zhu et al., 2010a,b).

Meusinger et al. (2014) used an optical detection system consisting of a Maya2000PRO photo-spectrometer (wavelength region 220–400 nm), an optical fibre (solarized, 600 μm diameter), and a cosine corrector (CC-3-UV-T) to quantify quantum yields for the photodecomposition of nitrate from absolute irradiance spectra. Given that the vast amount of photochemical ice studies show that the micro-physical location appears to control how labile nitrate chemical behaves with respect to UV light in snow, Meusinger et al. (2014) quantified quantum yields due to nitrate photodecomposition in the two domains: photolabile nitrate (surface nitrate) and buried nitrate. With what corresponds to day of UV exposure at Antarctica, the quantum yield for loss of nitrate was observed to decrease from 0.44 to 0.003 at 258 K. Meusinger et al. (2014) found that the apparent quantum (for the loss of nitrate) increases with increasing depth z in ice (Fig. 11 (a) and (b) and see Table 2 to contextualize interpretation of this trend), and the apparent quantum yield decreases with photolysis time. They show that the photolabile domain exhibits a quantum yield for nitrate loss between 12 and 44%, and a “buried” domain shows quantum yields between 0.3 and 12%.

To help resolve the uncertainty in measured quantum yields via nitrate photolysis, McFall et al. (2018) measured quantum yields at 263 K, for nitrite formation (i.e., Channel 2) in liquid-like regions (LLRs, (0.65 ± 0.07)% in the ice (0.57 ± 0.05)%, within the solid ice matrix, and in a quasi-liquid layer (QLL, (2.39 ± 0.24)%)) at the air-ice interface. The quantum yield at the ice-air interface is enhanced by a factor of 3.7. These findings also support previous studies that exemplify enhanced nitrate photolysis at ice surfaces.

The great range of reported quantum yields associated with nitrate photolysis in ice makes it one of the largest uncertainties in modeling snowpack NOx emissions. This is primarily due to experimental construction governing ice experiments, which may be focused on a specific ‘domain of photochemistry.’ Modeling non-photolytic (but yet inter-related) chemical reactions in ice is also one of the other primary uncertainties in multi-phase modeling of heterogeneous ice media. Past multi-phase models simplified the parameterization of snow/ice – where ice is often treated as an inert substance coated with a layer of thin liquid water – where all snowpack photochemical processes are assumed to occur. This oversimplified modus operandi enabled such studies to estimate reaction rates in ice based on aqueous phase reactions – mostly, governed by a concentration effect of some degree.

As multiphase modeling explicitly represents the bi-directional physicochemical processing of trace gases in the overlying atmosphere above the snowpack, we restrict this part of the discussion to these studies. Michalowski et al. (2000) was the first study to utilize a multiphase chemical model, Chemical Reactions Modeling System (CREAMS), to simulate Arctic halogen chemistry. The multiphase model contained gas phase and photolysis reactions, and aqueous reactions occurring on aerosols and the QLL of snow. The model simulated mass transfer of species between the gas phase and particles and between the gas phase and the snowpack. Model simulations were parameterized to simulate a 1-week simulation during April at 245 K.

### Table 2

Overview of experiments. The following properties are listed: snow type, starting nitrate mass fraction, average chloride, and sulfate mass fractions (all in ppbw = ng/g), photolysis time, λ, UV filter sigmoidal wavelength, \( \lambda_{\text{light}} \), and gas flow, Q. All experiments were performed at −30 °C. (Meusinger et al., 2014, Copyright, 2014 American Institute of Physics).

<table>
<thead>
<tr>
<th>Exp#</th>
<th>Snow</th>
<th>( w(NO_3^-) )</th>
<th>( w(Cl^-) )</th>
<th>( w(SO_4^{2-}) )</th>
<th>t/h</th>
<th>( \lambda_{\text{light}}/\text{nm} )</th>
<th>Q/(l/min)</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test</td>
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<td>230.6</td>
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<td>...</td>
<td>260</td>
<td>...</td>
<td>1.1</td>
<td>No light, SSA measurement</td>
</tr>
<tr>
<td>1</td>
<td>Dome C (2009)</td>
<td>1434.9</td>
<td>350.0</td>
<td>114.4</td>
<td>139.5</td>
<td>...</td>
<td>2.2</td>
<td>No light</td>
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<td>103.4</td>
<td>89.8</td>
<td>4.6</td>
<td>...</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Dome C (2009)</td>
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<td>436.0</td>
<td>86.3</td>
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<td>...</td>
<td>1.1</td>
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</tr>
<tr>
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<td>Dome C (2009)</td>
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<td>86.1</td>
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<td>88.2</td>
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<td>97.9</td>
<td>76.8</td>
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<td>131.9</td>
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<td>137.8</td>
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<td>...</td>
<td>162.8</td>
<td>...</td>
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<tr>
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<td>164.0</td>
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</table>
within a boundary layer of 400 m. This study simulated NO\textsubscript{x} fluxes from the snowpack, that were consistent with the Arctic observations at that time (10–20 pptv). This indirectly took into account emissions from nitrate photochemistry at the snowpack without explicitly representing nitrate snowpack chemistry in CREAMS. Without the NO\textsubscript{x} flux, the simulated [NO\textsubscript{4}] in the boundary layer would be 100 times lower than observed concentrations. Using an analogous approach to Michalowski et al. (2000), Boxe and Saiz-Lopez (2008) use a multiphase model, CON-AIR (Condensed Phase to Air Transfer Model) and showed that nitrate photochemistry in and on ice and snow surfaces, specifically the QLL, can account for NO\textsubscript{x} volume fluxes (see Fig. 12), concentrations, and [NO]/[NO\textsubscript{2}] measured just above the Arctic and coastal Antarctic snowpack (see Fig. 13). The model incorporates an appropriate actinic solar spectrum, thus properly weighting varying photolysis rates of NO\textsubscript{3}\textsuperscript{−} and NO\textsubscript{2}\textsuperscript{−}.

Thomas et al. (2011) completed a study of ice/snow – air trace gas exchange via a 1-D model with coupled multiphase chemistry in the atmosphere and snowpack. The 1-D snow chemistry model is coupled to the atmospheric boundary layer chemistry – i.e., MISTRA. Similar to Michalowski et al. (2000) and Boxe and Saiz-Lopez (2008), Thomas et al. (2011) includes gas phase chemical reactions both in the snowpack and the atmosphere. They also assume that the physicochemical processing occurs in a liquid-like layer on the grain surface; their model was validated as part of the Greenland, Summit Halogen-HO\textsubscript{x} experiment (GSHOX). Thomas et al. (2011) showed that reactions in the QLL, followed transfer to the interstitial air and venting of the snowpack (by wind-pumping and diffusion), can explain the low levels of NO and NO\textsubscript{2} at Summit, Greenland (see Figs. 14 and 15). Boxe et al. (2012a,b,c) also used a photochemical box model to assess the impact of Butkovskaya et al. (2005, 2007) laboratory-derived pressure/temperature dependent rate constant of the second branching channel of the HO\textsubscript{2} + NO reaction: HO\textsubscript{2} + NO \rightarrow HNO\textsubscript{3} on NO\textsubscript{x} (amongst other trace gases). Their simulations illustrated a decrease in NO and NO\textsubscript{2}, which is consistent with the expected decrease in their respective species lifetimes as a
result of increased sequestration into HNO₃.

Hamer et al. (2014) used steady-state photochemical box models to investigate the production of HCHO in the South Pole snowpack. They investigated two chemical sources of HCHO within the snowpack: 1) HCHO production from the processing of methyl hydroperoxide (CH₃OOH) via photoxidation and acid catalyzed rearrangement; and 2) oxidation of organic matter. Model result inconsistencies with field measurements of HCHO were resolved by incorporating new measurements of the molecular dynamics of the OH photofragment from H₂O₂ and NO₃⁻ photolysis. These findings also show that OH produced in the outermost layers contribute to gas phase and surface layer chemistry. Realistic treatments of the ice grain size, H₂O₂, and NO₃⁻ distribution within ice grains, diffusion of gas phase species within solid ice, and observed OM particle size distributions also helped in simulating HCHO fluxes consistent with observations. Hamer and Shallcross (2007) also used a photochemical box model that incorporated methyl hydroperoxide measurements to better understand their influence on high ozone events at the South Pole boundary layer; utilizing standard chemistry, which included nitrate photochemistry in ice/snow, they were able to produce model simulations that were comparable to field observations. Hamer et al. (2008) also used a photochemical box model to assess the impact of O(3P) emissions via nitrate photolysis from ice surfaces on NO₂ photochemistry at the South Pole. Their study suggests that the O(3P) emissions could account for a portion of the observed ozone production at the South Pole and may explain observed upward fluxes of ozone identified at the South Pole.

Davis et al. (2004) used a photochemical box model to understand why South Pole NOx levels are so much greater when compared to other polar sites and what processes govern the large day-to-day NO concentration shifts there. These model simulations reveal that the uniqueness of the summertime environment controls this phenomenon – that is, the presence of the large plateau region just east of the South Pole (which defines one of the world’s largest air drainage fields, nearly 1000 km across and ~3 km in height), South Pole summertime temperatures rarely exceed ~25°C (leading to frequent strong near-surface temperatures inversions), and non-stop photochemical reactions within and above the snowpack (due to 24 h continuous sunlight). The latter component is distinctive to the South Pole and causes enhanced NOx levels, which lead to longer lifetimes – thus producing non-linear increases in NOx. Finally, NOx is rapidly recycled to the very fast dry deposition of HNO₃ and HONO₂.

The assumption that chemical reactivity, based on aqueous phase kinetics, in ice/snow (or at ice-air interfaces) can be accurately constrained in a multi-phase model is not well supported (Bartels-Rausch et al., 2014; Domine et al., 2013; Kahan et al., 2014). Each scenario has to be treated on a case-by-case analyses as physicochemical processes vary depending on the specific phase/media and experimental approach. As an example, select aromatic pollutants that cannot photolyze in water can photolyze in the ice while some aromatic reactions are enhanced in the ice compared to solution (Kahan and Donaldson, 2007, 2010; Malley and Kahan, 2014; Statitch et al., 2016). The oxidation of aromatics via OH occurs readily at liquid surfaces but does not oxidize aromatics (at all) on ice surfaces while ozonation of aromatics occur faster on ice surfaces compared to liquid surfaces (Kahan and Donaldson, 2007, 2008; Ray et al., 2013, 2014). Krausko et al. (2014), investigated the role that NaCl plays in suppressing reactivity of other species from experiments that showed that the photolysis rate of the aromatic dye harmine was greater on frozen freshwater surfaces than in aqueous solution; yet, the addition of NaCl resulted in comparable photolytic rate constants in ice and aqueous solution.

Attaining additional/well-needed rate constants (both photolytic and chemical) is crucial. To optimally do so, it is also vital that the polar science community build upon ongoing efforts to understand the ‘nature’ of nitrate (within the context of the multi-component solute

Fig. 13. Calculated summertime gas phase NO and NO₂ concentration profiles as a function of height above the snowpack (Boxe and Saiz-Lopez, 2008, Copyright, 2008 European Geosciences Union).

Fig. 14. Modeled NO mixing ratios in the atmosphere (A) and interstitial air (B). Modeled mixing ratios in the atmosphere at an altitude of 1.5 m above the snowpack are compared with measurements in (C). Predicted interstitial air mixing ratios 10 cm below the snow surface are shown in (D) (Thomas et al., 2011, Copyright, 2011 European Geosciences Union).
system of the polar snowpack). For instance, one can quantify the fractional component of select ice media (based on solute concentration and temperature); yet, this does not provide any insight into the composition of such surfaces (Cho et al., 2002; Kuo et al., 2011). In addition, solutes accumulate in the internal water-vein system at triple junctions (three-grain intersections) and nodes (four-grain intersections) (Mulvaney et al., 1988; Nye, 1989; Fukazawa et al., 1998). Mulvaney et al. (1988) observed sulfuric acid ions at −20°C via Scanning Electron Microscopy (SEM) at grain boundaries/triple junctions in Antarctic ice; they concluded that at least 40% of sulfuric acid is contained in triple junctions. Nye (1989) provided quantitative constraints on the geometry of water veins and nodes in polycrystalline ice. Using Raman Spectroscopy, to study ice from −35 to −8°C, Fukazawa et al. (1998) showed spectral peaks indicative of the presence of both sulfuric and nitric acid at triple junctions.

In a one-/multi-component system(s) – e.g., HNO3/NO3− what does the nature of the ice system look like? Krepelova et al. (2010) used X-ray photoelectron spectroscopy (XPS) and near edge X-ray absorption fine structure (NEXAFS) spectroscopy at the Advanced Light Source (ALS) to study the HNO3 adsorption on ice surfaces at 230 K. They concluded that the O K-edge NEXAFS (under low nitrate coverage) is comprised of a linear combination of 80% clean ice spectrum and 20% HNO3 solution spectrum, which indicates that 20% of water molecules of the ice surface (several top nanometers) hydrates NO3− ions. Several additional studies have also supported Krepelova et al. (2010)’s findings (Krausko et al., 2014; Blackford et al., 2007; Tokumasu et al., 2016; Doppenschmidt and Butt, 2000). Environmental SEM has been used to observe NaCl or NaCl2H2O crystals above sodium chlorides eutectic temperature (−21.1°C) at −6°C (Lange and Forker, 1956). Environmental SEM has also been used to observe uranyl salt in water veins in ice (Krausko et al., 2014). SEM was used to study the composition of sintered NaCl solutions above and below the NaCl’s eutectic temperature (Blackford et al., 2007); clean water ice and isolated liquid patches were observed above its eutectic temperature, and webs of solid salt were observed below NaCl’s eutectic. Isolated clumps/islands of solid salts were observed below NaCl’s eutectic temperature via Atomic Force Microscopy (AFM) and X-ray Fluorescence (XRF) (Doppenschmidt and Butt, 2000; Krepelova et al., 2010).

Raman spectroscopy’s versatility has catalyzed its popularity for use in investigating the structure and composition of solid and liquid media. Specifically, it can: 1) be used to study liquids and solids; 2) operate at atmospheric pressures; 3) result in the likelihood of less frequent beam damage (when compared to electron/x-ray microscopy); 4) can study composition of particulate matter; 5) identify the composition of micro-inclusions in sea-ice; and 6) distinguish between liquid and solid water ice (Kahan et al., 2007). Recently, it has been used to investigate the speciation of nitrate at the ice surface and in bulk ice (Morenz and Donaldson, 2017; Eichler et al., 2017; Wren and Donaldson, 2011). Kahan et al. (2007) used glancing-angle Raman spectra coupled to glancing-angle Laser-Induced Fluorescence (LIF) to study the OH-stretch region of the air-ice interface, the air-water interface, and bulk ice. They quantified the depth of sensitivity for this technique to be 50 monolayers of water (15 nm) via Raman spectra of dodecane. They probed perturbations to the water OH-stretch band via NaCl, HCl, or HNO3 adsorption on ice surfaces. They found that NaCl decreases the presence of hydrogen bonding while HCl and HNO3 adsorption on ice surfaces increases the occurrence of hydrogen bonds. The increase in hydrogen bonding may be due to dissociation of acids to produce hydronium ions, which participate in hydrogen bonding with water molecules at the ice-air interface. Wren and Donaldson (2011) used glancing-angle Raman spectroscopy and showed that nitrate is excluded to the ice-air interface but not as much as predicted when using equilibrium thermodynamic analyses. They also cautioned that it is also likely that during the freezing process, nitrate may also segregate within liquid pockets and grain boundaries in the ice bulk. Morenz and Donaldson (2017) showed, using Raman spectroscopy, that nitrate concentrations are enhanced on surface ice and varies depending on the amount and type of salt added. Eichler et al. (2017) used an optical microscope and Raman spectroscopy to detect over 5000 μ-inclusions in laboratory ice.

6. Conclusions and future directions

The movement of traces gases in the polar cryosphere is pivotal to polar tropospheric chemistry and dynamics, since it affects its composition and oxidizing capacity. Paying special attention to nitrate photochemistry in the polar regions, we have covered the span of the serendipitous discovery of ice photochemistry, via the first findings in the Arctic snowpack. We then delved into the abundance of initial field, laboratory, and snow chamber studies done to further understand the impact of nitrate ice/snow photochemistry on overlying boundary layer chemistry and climate. Finally, we conclude by discussing recent
laboratory advancements and how they contextualize multi-phase modeling efforts aimed at simulating field, laboratory, and snow-chamber observations.

What does the future hold for nitrate photochemistry in ice media?

1) Firstly, a central and virtual data portal/website would be useful to the polar science community as it could make all relevant ice-related data (e.g., photolytic rate constants, kinetic rate constants, fraction of clean ice vs hydrated solutions at a select ice surface (and as a function of solute content), experimental technique, etc.) available at a central location. This would aid in streamlining the access of data due to increased transparency.

2) Future of nitrate photochemistry experiments in ice/snow should involve multi-component photochemical analyses of ice matrices given the Arctic and Antarctic snowpack over their respective pH range and at actual concentrations. The pH of the sea-ice/snowpack at the Arctic (Curit et al., 2005) and Antarctic (Ali et al., 2010) range from 4.5 to 6 and to 6.5, respectively. Caritat et al.119 showed that the Arctic snowpack is primarily comprised of eight ions: 1) Cl$^-$ (3 μM–12 mM); 2) NO$_3^-$ (1–14 μM); 3) SO$_4^{2-}$ (2 μM–0.23 mM); 4) Ca$^{2+}$ (0.5 μM–0.2 mM); 5) K$^+$ (1.25 μM–0.2 mM); 6) Mg$^2+$ (0.3 μM–0.9 mM); 7) Na$^+$ (1 μM–11.6 mM); and 8) S (2 μM–0.3 mM). Ali et al.210 showed that the major ions in the Antarctic snowpack are: 1) Cl$^-$ (30 μM–0.1 mM); 2) NO$_3^-$ (2 μM); 3) SO$_4^{2-}$ (5 μM–3 μM); 4) Ca$^{2+}$ (2.5 μM); 5) K$^+$ (5 μM); 6) Mg$^2+$ (0.2 μM–2 μM); and 7) Na$^+$ (0.3 μM–1 μM).

3) The polar regions also encompass a wide temperature regime (∼220–273 K at the Arctic and ∼183–270 K at Antarctica). Future studies should aim to couple 2) and 3) – that is, quantify the dependence of products, photolysis rates, kinetic rates, the nature of ice surface and bulk, via photolytic nitrate experiments as a function of solute/relevant solute concentrations.

4) Investigations should also aim to normalize experimental and field data and multi-phase modeling constructs by assessing and improving upon experimental parameters that add uncertainty/error to empirical data. For instance, Constantin et al. (2018) revisited QLL thickness measurements for pure water ice films via AFM. They produce AFM force curves over pure water ice as a function of temperature and different AFM tips. They were able to attain accurate control over temperature and humidity via a mini-environmental chamber; this allowed the first force curve measurements at the air-ice interface of thin pure water ice films without AFM tip jump-in. Previous AFM studies were plagued by AFM tips repeatedly dipping the surface of ice samples. Their measurements imply that previous AFM measurements overestimated QLL thicknesses as they quantify (between 7 and −2°C) QLL thickness of ~1 nm. Improvements in the modeling treatment/particle-size measurement of surface photochemistry, but especially bulk photochemical and physicochemical processes. More frequent field campaigns, including more winter campaigns are also recommended to measure well-needed data needed for model parameterizations. Polar field sites should transition toward more sustainable forms of energy (e.g., Geo-Summit as noted in Grannas et al. (2007)) to minimize anthropogenic influence. As noted in Boxe (2005a,b), low-to-mid-latitude snow-covered regions contain [NO$_3^-$] ~ fractions to several mM; therefore, seasonal impacts may not negligible/significant to overlying boundary layer chemistry/air quality. Hence, additional lower-latitude investigations of snow-covered regions could aid in refining the seasonal influence of photoproduct fluxes from snow-covered lower-latitude regions due to nitrate photodecomposition.

5) Conduct experiments at appropriate light fluxes using an Earth-defined solar simulator.

6) Extensive sensitivity simulations are also needed to assess the impact of empirical data uncertainties.

7) Improvements and utilization of non-evasive laboratory-based instruments (ellipsometry, Raman Spectrometry, etc.) and potential remote sensing techniques that can quantify structure and physicochemical properties, relevant to multi-phase modeling.

It has been quantitatively shown that the exchange of trace gases between the snowpack and overlying atmosphere is dominated by photochemical processes. We suggest that field, laboratory, and multi-phase modeling studies will provide sound platforms for future work in both the Antarctic and Arctic regions – to shed light into un-answered queries and invigorate new insights pertaining to snow/ice photochemistry. Moreover, we envision these pivotal investigations on nitrate photochemistry in ice and snow will cultivate cross-disciplinary research into planetary science.

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