Chapter 9

Conclusions

During the winter, approximately 50% of the northern hemisphere's surface is covered by snow/ice. Therefore, it is important to address phenomena, such as nitrate photochemistry, that is occurring in snow/ice. The photochemistry of nitrate is both relevant at mid- and high-latitude regions.

At the beginning of my thesis research, the hypothesis that photochemical reactions in ice occur in macroscopic liquid-like domains, which are nominally known as quasi-liquid layers remained to be confirmed. Furthermore, there was much speculation that nitrate photolysis could alter ice core records of trace species, which would affect the elucidation of past atmospheric conditions. In addition, nitrate photolysis, which leads to NO_x and $^{\cdot}OH$ production in interstitial air of snowpacks, can impact the overlying boundary layer and thus influence tropospheric chemistry. Nitrate photochemistry is also likely to be important in the production of NO_x in the upper troposphere, since HNO_3 and NO_y appear to be rapidly removed in the presence of cirrus clouds. Coupled with the *in situ* production of nitrite from nitrate photolysis, acidic snow/ice environments may release HONO (i.e., pronated nitrite) to the overlying boundary layer, which would lead to $^{\cdot}OH$ production via the gas-phase photolysis of HONO.

Over the course of my thesis research, I was able to address many of the issues described above. In the first experimental project, we determined that the quantum yield, ϕ, of nitrite formation increases monotonically with temperature over the range of 248 to 298 K during the photolysis of 10 mM $NaNO_3$-doped liquid and ice matrices at $\lambda \sim 302$ nm. Based on these results, it was inferred that nitrate photodecomposition occurs in a liquidlike media at all temperatures. This is primarily based on the fact that the detection of nitrite as a product is only possible after the photofragments (NO_2^- + O) escape the solvent cage, and the fact that the diffusivity of ice, D_{ice}, is approximately 6 orders of magnitude smaller than supercooled water, D_{aq}, at the same temperatures. In addition, considering that the quantum yields, ϕ, of nitrite formation were larger than quantum yields calculated from linear ϕ vs $D_{aq}T^{1/2}$ extrapolation of aqueous phase data indicate that the QLL is, to some extent, analogous to supercooled water. Similar to the photochemical properties of nitrate in the aqueous phase, the addition of formate, an efficient $^{\cdot}OH$ scavenger, enhanced nitrite concentrations in the ice phase, confirming even further that nitrate photolysis in ice occurs in macroscopic liquidlike domains, such as the QLL and subeutectic channels.

In the second research project, we measured NO and NO_2 by way of temperature-programmed desorption two-photon laser-induced fluorescence during the photolysis of KNO_3-doped ($2\ \mu M \leq [NO_3^-]_o \leq 50$ mM) , spray-frozen ice layers at $\lambda \sim 302$ nm, between 238 and 273 K. The KNO_3-doped ice layers were ramped at a 0.67 $^oC\ min^{-1}$ heating ramp. This study revealed that NO_x accumulated at lower temperatures in the deeper layers bursts when the solid undergoes a sintering transition, following the onset of major increase in surface melting at about 263 K. In addition, the detection of NO and NO_2 well below the eutectic temperature of KNO_3/H_2O ($T_{eutectic} = 270.27$ K) suggest that doped polycrystalline ice contains not only a QLL, but also subsurface subeutectic solutions.

In a joint research effort with Prof. Mark Thiemens at UCSD, we determined the ^{17}O- and ^{18}O-fractionation in the 313 nm photolysis of 10 mM aqueous solutions of normal Fisher KNO3 (e.g., $\Delta^{17}O = -0.2 \pm 0.2$ ‰) and ^{17}O-enriched USGS-35 $NaNO_3$ ($\Delta^{17}O = 21.0 \pm 0.4$ ‰) between 243 and 298 K. We determined that normal Fisher KNO_3

preserves $\Delta^{17}O = 0$ (or undergoes mass-dependent O-fractionation) during its photolysis over 12 to 48 hrs. Therefore, nitrate photochemistry should have little influence on the atmospheric mass-independent isotopic composition preserved in snow. In addition, considering the minute quantum yield (~ 0.2 %) of NO_3^- photodecomposition into (NO_2 + $^{\cdot}OH$) is due to extensive cage recombination of the primary photoproducts rather than to intramolecular processes, the small dilution effect of $\Delta^{17}O$ in USGS-35 $NaNO_3$ with temperature and irradiation time indicates that competitive O-isotope exchange of geminate $^{\cdot}OH$ with H_2O ($\Delta^{17}O = 0$) and escape from the solvent cage. This observed decrease in $\Delta^{17}O$ also indicates the occurrence of residual O-isotope mixing of the photoproducts NO, NO_2, NO_2^- with H_2O.

In another cooperative research project, this time with Prof. Ronald Cohen at UC-Berkeley, we measured the temperature-programmed desorption of NO_2, due to the photolysis of $NaNO_3$-doped water ice irradiated at $\lambda \sim 302$ nm over 243 to 278 K using laser-induced fluorescence as a function of nitrate concentration ($2\ \mu M \leq [NO_3^-]_o \leq 50$ mM) and heating ramps ($\partial H = 0.70$, 0.30, and 0.10 $^oC\ min^{-1}$). We observed that the number of sintering transition temperatures increased with decreasing ramp rate, ∂H for $[NO_3^-]_o > 200\ \mu M$; one transition temperature is apparent at ~ 266 K (at $\partial H = 0.70\ ^oC\ min^{-1}$), while an additional transition temperature arises at ~ 250 K. Moreover, we showed that total NO_2 released under continuous photolysis does scales nonlinearly with the duration of the experiment (e.g., with ∂H^{-1}) and was found to vary as $\propto ([NO_3^-]_o)^{1/2}$. These findings demonstrate the occurrence of significant *in situ* losses of NO_2 produced in the initial photolytic event, prior to desorption.

Additional experiments at UC-Berkeley confirmed that NO is a secondary photoproduct from nitrate photolysis since its desorption rates were much lower than NO_2 desorption rates, throughout. Still, desorption rates for NO increase at ~ 253 K, whereas desorption rates for NO_2 exhibit a more dramatic increase at ~ 263 K. Given the relative differences in Henry's Law constants for NO and NO_2 and their temperature dependencies, there appears to be a preferential retention of NO_2 compared NO in the quasi liquid channels within the micrograined ice aggregates.

In order to verify some of the evolving ideas regarding the quasi liquid domains in polycrystalline ice, we measured the *in situ* acidity changes that occur during the freezing of various dilute electrolyte solutions (e.g., KNO_3, $NaNO_2$, NaCl, Na_2SO_4, NH_4OH, and NH_4Cl) using ^{19}F NMR as a function of freezing rates (*F.R.* = 1.0, 2.0, and 10 $^{o}C\ min^{-1}$) between 200 and 298 K. The apparent pH of the QLL domains was determined by using an indirect pH probe based on the temperature dependence of ^{19}F NMR chemical shifts of 3-fluorobenzoic acid. We determined that the nominal pH of the QLL domains either increase or decrease upon freezing, depending on the type of electrolyte dissolved in liquid water and the imposed freezing rate. For example, the freezing of NH_4OH or Na_2SO_4 solutions produce QLL domains that are more acidic (i.e., result in lower pH values), while NaCl, $NaNO_2$ or KNO_3 solutions produce QLL domains that are substantially more basic after freezing (i.e., the pH increases).

With these conclusions in context, further relevant knowledge can be attained for the science community by studying even more critically 'these' subset areas of ice photochemistry, which I have addressed in my thesis. For instance, in the study pertaining to the isotope fractionation in the photochemistry of nitrate in water and ice, 10 mM mass-dependent NO_3^- (Fisher KNO_3) and 10 mM mass-independent NO_3^- (USGS-35 $NaNO_3$) was utilized, while nitrate concentrations in remote snow-covered regions range from ~ 1 to 20 μM. Although no deviation in the initial value of $\Delta^{17}O$ is expected for both mass-dependent and mass-independent NO_3^- in the photolysis of μM NO_3^- in water and ice, due to the factor 500 to 10000 less NO_3^- concentration found in remote snow-covered areas, it is still necessary to show for completeness that the photolysis of μM nitrate in water and ice will not have an effect on the isotopic composition of the residual nitrate. A more sensitive mulitiple mass spectrometer is needed to measure the inevitabley smaller amount of $\delta^{17}O$ and $\delta^{18}O$ from the resulting O_2 introduced in the multiple mass spectrometer.

Secondly, it important to further investigate the effects of variable heat ramp rates (e.g., $\partial H > 0.70$ °C min^{-1} and $\partial H < 0.10$ °C min^{-1}) on the release of NO_2 in real-time during the photolysis of nitrate concentrations between 2 μM and 50 mM. These studies would reveal if the total photodesorbed NO_2 released 'still' scales nonlinearly with faster and slower heating rates than already utilized; these findings would also verify definitively the 'rational' for the observed total photodesorbed NO_2. If the 'rational' is verified, it would further confirm the existence of the QLL and that nitrate photochemistry occurs in this environment. A more sensitive technique for detecting NO is needed to properly address its real-time release out of ice during the irradiation of μM and mM NO_3^- at variable heating rates. This would also yield pertinent information relating to effect on variable nitrate concentration on NO release during nitrate irradiation. Desorption (without light/irradiation) experiments after the photolysis (over variable and specified time increments) of μM and mM NO_3^- would also yield qualitative information pertaining to the % desorption vs. % photodesorption contributing to NO_x release out of ice during μM and mM NO_3^- trials. Studying the release in real-time of both NO and NO_2 during the photolysis μM and mM nitrate+formate-doped ice matrices (w/ formate in excess concentrations compared to nitrate) at variable heating rates would also further confirm the existence of the QLL and that environment where photochemistry occurs in ice media is fluid-like by showing enhanced releases of NO and and reduced releases of NO_2 out of ice. Reduced emissions of NO_2 are expected with the addition of formate since it would scavenge OH (reducing NO_2 production by reacting with produced NO_2 via the reaction: $O_2^- + NO_2 \rightarrow NO_2^- + O_2$ and by lessening the reaction: $NO_2^- + {}^{\cdot}OH \rightarrow NO_2 + OH^-$), while enhanced emissions of NO are expected from greater NO_2^- concentrations through the secondary photolysis of NO_2^-. These findings would give further confirmation that nitrate photochemistry in ice occurs mainly in the QLL. Overall, these studies would bridge further the gap between field observations measuring NO and NO_2 made at high and mid-latitude snow-covered regions, where μM and mM (measured at mid-latitudes) NO_3^- concentrations have been measured.

Thirdly, further studies are needed to assess pH changes that occur during the freezing of electrolyte-doped solutions. For example, alternate cooling/freezing rates (than ones used in this thesis) could yield pertinent information, while also doping aqueous solutions with additional electrolytes (e.g., NH_4Cl, HCl, H_2SO_4, etc.). In addition, flouroacetic acid can also be used as a probe via ^{19}F NMR to show coincidence with findings illustrated in this thesis. Aqueous solutions doped with a mixture of solutes should also be investigated to quantify pH changes that may occur during the cooling process of such environments. These findings would have direct relevance to snowpack regions that may release gases at a particular pH or pH region, such as $HONO_{(g)}$. More importantly, it appears that certain impurities will induce interfacial subeutectic regions far below their respective eutectic temperatures (e.g., $T_{eutectic}$ (KNO_3) = −2.88 °C, $T_{eutectic}$ ($NaNO_3$) = −11.29 °C, $T_{eutectic}$ (NaCl) = −20.67 °C, and $T_{eutectic}$ (NH_4Cl) = −9.47 °C), which is based on the fact that ^{19}F NMR signals for these species have been detected at temperatures between ~ −25 °C to ~ −40 °C. Impurities, such as H_2SO_4 and NH_4OH ($T_{eutectic}$ (H_2SO_4) = −73 °C and $T_{eutectic}$ (NH_4OH) = −84 °C) will induce such interfacial subeutectic fluid phases at even lower temperature, leading to ice environments conducive for ion mobility, which in turn, depending on the pH and solute-makeup, will lead to pH increases or decreases in the remaining liquidus environment.

Lastly, an in-depth laboratory analysis investigating the production of aldehydes over the snowpack is needed. Since nitrate photolysis leads to production of $^{\cdot}OH$, one pathway to study this phenomenon is to study ice matrices doped with both NO_3^- and humic or organic substances, where $^{\cdot}OH$ would oxidize such substances, leading to the release of aldehydes, such as formaldehyde out of ice.