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How does deposition of gas phase species affect pH at frozen salty interfaces?

S. N. Wren[1] **and D. J. Donaldson**[1,2]

[1]Department of Chemistry, University of Toronto, Toronto, ON, M5S 3H6, Canada
[2]Department of Physical and Environmental Sciences, University of Toronto at Scarborough, Toronto, ON, M1C 1A4, Canada

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Correspondence to: D. J. Donaldson (jdonalds@chem.utoronto.ca)

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Abstract

Chemical processes occurring on snow and ice surfaces play an important role in controlling the oxidative capacity of the overlying atmosphere. However, efforts to gain a better, mechanistic understanding of such processes are impeded by our poor understanding of the chemical nature of the air-ice interface. Here we use a surface-sensitive spectroscopic technique to investigate how the nature of the ice, whether frozen freshwater, salt water or seawater, influences pH changes at the surface. Deposition of HCl(g) leads to a very different pH response at the frozen freshwater surface than at the frozen salt water surface indicating that these two surfaces present different chemical environments. Importantly, the sea ice surface is buffered against pH changes arising from deposition of gas phase species. These results have important implications for understanding pH-sensitive processes occurring at the air-ice boundary, such as bromine activation.

1 Introduction

Natural ice and snow were once considered to be chemically inert, but a growing body of evidence shows that air-ice chemical interactions can significantly influence the composition of the overlying atmosphere (Domine and Shepson, 2002; Grannas et al., 2007; Abbatt et al., 2012). For example, the photolysis of snowpack nitrate has been shown to lead to upward fluxes of NO_x ($= NO + NO_2$) and HONO (Grannas et al., 2007; Honrath et al., 2002; Dibb et al., 2002; Zhou et al., 2001) and heterogeneous reactions occurring on sea ice surfaces are thought to be responsible for the activation and release of reactive halogen species to the gas phase (Simpson et al., 2007; Abbatt et al., 2012). Although the importance of snow and ice as (photo)chemical reactors is now recognized, a molecular-level understanding of chemical reactions occurring on these substrates is still lacking. This is due, in part, to an inadequate characterization of the surfaces on which air-ice chemical processes occur. As a result, and in lieu of a better option, aqueous-phase physical-chemical mechanisms are often used to interpret or model heterogeneous chemistry occurring on snow and ice substrates (Bock and Jacobi, 2010).

Accordingly, in keeping with the pH-sensitivity of their liquid phase counterparts, many reactions occurring on ice are thought to be pH-sensitive. For example, a key reaction for bromide activation is the heterogeneous oxidation of sea salt bromide by hypobromous acid:

$$\mathrm{HOBr} + \mathrm{Br}^- + \mathrm{H}^+ \rightarrow \mathrm{Br}_2 + \mathrm{H}_2\mathrm{O} \tag{R1}$$

This reaction, which consumes one reactive bromine species but produces two (leading to the "bromine explosion") is acid-catalyzed in the aqueous phase (Fickert et al., 1999). Based on this pH-dependence, it has been thought (Fan and Jacob, 1992; Morin et al., 2008) that the medium on which bromine explosion chemistry occurs should achieve a low enough pH for this reaction to proceed at an appreciable rate. Similarly, the photolytic release of HONO from the snowpack (via R2 or R3 followed by R4) is thought to be proton mediated:

$$\mathrm{NO}_3^- + h\nu \rightarrow \mathrm{NO}_2^- + \mathrm{O}(^3\mathrm{P}) \tag{R2}$$

$$\mathrm{NO}_3^- + \mathrm{O}(^3\mathrm{P}) \rightarrow \mathrm{NO}_2{}^- + \mathrm{O}_2 \tag{R3}$$

$$\mathrm{NO}_2^- + \mathrm{H}^+ \rightarrow \mathrm{HONO} \tag{R4}$$

However, some recent kinetic and photochemical measurements indicate that reactions occurring at the air-ice interface are not well represented by parameters measured at the air-aqueous interface (Kahan et al., 2010b, c; Kahan and Donaldson, 2010). A better understanding of the pH-sensitivities of ice surface processes such as bromine activation and snowpack HONO production is needed. Clearly, this in turn requires a better knowledge of the local pH where the key reactions occur. This is difficult to obtain experimentally because surface pH measurement techniques are lacking, and the bulk pH measured upon melting of a sample may not be the same as that present at the air-ice interface.

Our ability to measure, predict, or even define, properties such as pH at the ice surface is complicated by the presence of a disordered interfacial layer there. At temperatures as low as ∼ 240 K, a relatively pure ice surface is covered by what is commonly referred to as the quasi-liquid layer (QLL): a disordered layer some tens of nanometres thick that has properties intermediate to that of liquid water and bulk ice (Kahan et al., 2007; Wei et al., 2002; Li and Somorjai, 2007). The surface of snow grains within a relatively "clean" snowpack may be covered by such a genuine QLL. The thickness of the liquid-like region is temperature dependent and also increases with increasing concentration of impurities, such as salts or acids, (Cho et al., 2002; Doppenschmidt and Butt, 2000; McNeill et al., 2006), until the system enters a regime in which a liquid brine layer coexists with pure ice, in accordance with multi-component phase equilibria (Kuo et al., 2011; Koop et al., 2000). Trace acids (e.g., HNO_3, HCl or H_2SO_4) in the atmosphere can be deposited to the snowpack or sea ice surface, potentially altering the local pH there. Currently it is not known how the nature of the interfacial layer (QLL vs. brine layer) affects the surface pH following deposition of trace atmospheric acids.

Critically, it is also not known how or whether the uptake of trace acids affects local pH at sea ice surfaces. Seawater with pH ∼ 8.3 is naturally buffered against pH changes by the carbonate system (i.e., dissolved CO_2, HCO_3^-, and CO_3^{2-} in equilibrium with atmospheric CO_2). It is important to determine whether this buffering is maintained at the frozen surface since seawater is generally thought to be too alkaline to activate bromine via the acid-catalyzed mechanism shown above (R1). Sander et al. (2006) first proposed that the precipitation of carbonate during the freezing of seawater could lead to a reduced buffering capacity in the brine, allowing the pH to drop following acid deposition thereby triggering "bromine explosion" chemistry. However, Morin et al. (2008), using improved thermodynamic parameters, showed that the identity of the calcium carbonate polymorph influences the total alkalinity (and thus the pH) of the brine. In their model, when calcite ($CaCO_3$) precipitates at ∼ 271 K the total alkalinity of the brine drops, significantly reducing the buffering potential, and allowing acid deposition to lower the pH. However, if ikaite ($CaCO_3 \cdot 6H_2O$) is the form to precipitate (at ∼ 268 K), the total alkalinity of the brine does not drop below its initial value. Recent field studies in both the Arctic (Dieckmann et al., 2010) and Antarctic (Dieckmann et al., 2008) have shown that it is ikaite, and not calcite, that precipitates in freezing seawater brine.

In the present study, we use glancing-angle laser-induced fluorescence (LIF) (Wren and Donaldson, 2012) to address two questions concerning pH at the air-ice interface First, does the nature of the interfacial layer (QLL vs. brine layer) affect pH changes at the surface caused by the deposition of gas phase acid? Wren and Donaldson (2012) showed clear evidence for different pH behaviour following acid deposition at the frozen vs. liquid freshwater surfaces. And second, is there a change in the buffering capacity of seawater at the air-ice interface upon freezing? Answering these questions will provide further insights into the environmental air-ice interface and help to constrain models of chemical reactions there.

2 Experimental methods

2.1 Experiment overview

Three types of frozen surface were investigated in this study: frozen freshwater (i.e., deionized water), frozen salt water (0.5 M NaCl in deionized water) and frozen “0.5 M” artificial seawater (“Instant Ocean®” dissolved in deionized water). Glancing-angle laser-induced fluorescence (LIF) was used in conjunction with a surface-active fluorescent pH indicator to study pH at these frozen surfaces. Surface-selectivity is achieved through the use of a laser beam which impinges the sample surface at a very shallow, glancing angle (> 85° from the surface normal). This technique, which has been used extensively for the study of atmospheric interfaces (Clifford and Donaldson, 2007; Clifford et al., 2007; Mmereki and Donaldson, 2002; Kahan et al., 2010a), has been shown to be sensitive to the upper ~ 50 monolayers of an aqueous surface (Kahan et al., 2007). In the present experiments, we also expect to be probing a narrow interfacial region because (a) of the known aqueous phase surface activity of the pH indicator

(Clifford and Donaldson, 2007); (b) of the fact that this class of compounds is thought to be excluded to and self-aggregate at the air-ice interface (following exclusion during freezing or deposition from the gas phase) (Heger et al., 2005; Liyana-Arachchi et al., 2011; Kahan and Donaldson, 2007) and (c) we are investigating changes due to deposition of gas phase species to the surface. Here we used harmine (7-methoxy-1-methyl-9H-pyrido[3,4-b]indole) – a surface-active fluorescent dye whose absorption and fluorescence properties depend on pH (Dias et al., 1996; Balon et al., 1993) as the pH indicator. This technique was first developed for the frozen freshwater surface and has been described in greater detail in Wren and Donaldson (2012). In the present study we extend this method to the study of frozen salt water and frozen sea water surfaces. Harmine is particularly suited to this application since its fluorescence is not readily quenched in the higher ionic strength environments presented by the salt solutions.

2.2 Apparatus

The experimental apparatus consisted of a Teflon reaction chamber outfitted with 2″ diameter quartz windows to allow the laser beam to enter and exit. Side ports allowed gases to be introduced and ventilated from the chamber. A liquid light guide was suspended from the top of the chamber and samples were placed on a piece of stainless steel shimstock resting on its floor below the liquid light guide. The chamber temperature was held at 263 K via coolant flowing through a copper coil beneath the chamber.

Fluorescence at the sample surface was induced using the frequency-doubled output of an optical parametric oscillator (OPO) (10 Hz, ∼ 0.4 mJ per pulse) pumped by the frequency-triplet output of a Nd : YAG laser. The laser beam impinged the surface at > 85° from the surface normal. Fluorescence was collected by the liquid light guide and imaged onto the entrance slit of a 1/4 m monochromator. The emission was detected and amplified by a photomultiplier tube and then read out by a digital oscilloscope averaging the fluorescence decay profile over 64 laser shots. A LabView program running on a PC sampled a 5 ns time slice from the fluorescence decay.

Glancing-angle harmine excitation spectra were acquired by monitoring fluorescence at ~430 nm (near the cation emission maximum) while scanning the excitation wavelength in 5 nm steps from 260 nm–355 nm. The excitation spectra were normalized to 1 at an excitation wavelength of 320 nm. Figure 1a shows examples of spectra acquired in this way. During experiments where the pH was monitored during deposition of gas-phase species, the ratio of the fluorescence intensities measured following excitation at 290 nm and 320 nm (the harmine 290/320 ratio) was recorded (vide infra).

2.3 Sample preparation

A stock 2.5×10^{-5} M harmine solution was prepared volumetrically by dissolving harmine (Aldrich, 98 %) in 18 mΩ deionized water. Experimental solutions containing 1.0×10^{-7} M harmine were prepared fresh daily by diluting the stock solution in deionized water (the freshwater samples), 0.5 M NaCl (the salt water samples) or "0.5 M" Instant Ocean® (the seawater samples). The 0.5 M NaCl solution was prepared volumetrically by dissolving sodium chloride crystals (ACP Chemicals, min 99.0 %) in 18 mΩ deionized water (100 ml). The "0.5 M" seawater solution was prepared volumetrically by dissolving the same mass of Instant Ocean® (Spectrum Brands) in 18 mΩ deionized water (100 ml). The composition of the artificial sea salt as reported by Langer et al. (Langer et al., 1997) is predominantly: chloride (47.53 wt%), sodium (26.45 wt%), sulfate (6.41 wt%), magnesium (3.19 wt%), calcium (1.00 wt%), potassium (0.952 wt%), bicarbonate (0.356 wt%) and bromide (0.16 wt%). Samples were prepared by spreading 4 ml of solution onto a stainless steel plate resting on the chamber floor. Prior to sample introduction, the chamber was purged with a dry N_2 flow at 0.5 SLPM (Linde, Grade 4.8). Ice samples were frozen from the bottom-up under the dry N_2 flow with the floor of the chamber cooled to 263 K.

2.4 Bulk pH measurements

The bulk pH of the experimental solutions was measured using a commercial pH electrode (Orion Model 520 A) which was calibrated daily using a three-point calibration (pH 4.01, 7.00, 10.00). For simplicity, in the text we use the term “initial pH” to refer to the bulk, pre-freezing, solution pH. The freshwater and salt water solutions were initially slightly acidic (pH ∼ 5.9), as governed by equilibrium with atmospheric CO_2 while the seawater solution had an initial pH of ∼ 8.1. Initial sample pH was occasionally adjusted using NaOH(aq) (prepared from ACP Chemicals, min 97.0 %) or HCl(aq) (prepared from Fisher Scientific, 36.5–38.0 %). In some cases the final pH of the melted samples was also measured using the commercial pH electrode. To do this, the frozen sample was removed from the chamber immediately after the experiment, separated from the stainless steel shimstock, and allowed to melt in a covered beaker. The final bulk pH was obtained in order to gain a rough sense of the total acid or base uptake.

2.5 Introduction of HCl(g) or NH_3(g)

pH decreases at the frozen freshwater vs. frozen salt water surface were studied following the deposition of gas phase HCl to the surface. In these experiments, the initial sample pH was adjusted to be > 9. Samples were frozen and then glancing-angle LIF was used to obtain the harmine 290/320 ratio. A stable 290/320 ratio was obtained under a 0.5 SLPM N_2(g) flow. This ratio was then followed as a function of time under a 0.5 SLPM flow of 100 ppmv HCl(g) in N_2(g). The same conditions were used in our previous study (Wren and Donaldson, 2012), where we calculated ∼ 5–10 % uptake of HCl by the frozen samples.

A similar approach was used to investigate pH increases at the frozen salt water vs. frozen seawater surface. In those experiments, the initial salt water pH was adjusted to bring it close to the seawater pH (∼ 8.1) and the artificial seawater pH was not adjusted (pH ∼ 8.1). Gas phase ammonia was delivered to the chamber by passing a 50 SCCM flow of dry N_2(g) through a round-bottom flask containing a 12.75 wt% NH_3(aq) solution kept at 253 K. Because the solution froze, we cannot properly calculate an ammonia partial pressure from the parameters of Clegg and Brimblecombe (1989). Had the solution remained liquid, the ammonia partial pressure is estimated to be ~ 70 Pa

3 Results and discussion

3.1 Harmine as a pH indicator at the frozen salt water surface

In the ground state, the pyridinic nitrogen on neutral harmine can accept a proton to form a cation (with reported $\mathrm{p}K_a \sim 7.7$ at 298 K, Balon et al., 1993). Both the neutral and cationic forms absorb in the UV with absorption maxima at ~ 300 nm and ~ 320 nm for the neutral and cationic forms, respectively. Following excitation in the UV, the harmine cation fluoresces strongly at ~ 400 nm while neutral harmine fluoresces more weakly at ~ 350 nm. Previously (Wren and Donaldson, 2012), we showed that for the frozen freshwater surface, the shape of harmine's excitation spectrum (i.e., the spectrum obtained by monitoring harmine fluorescence at ~ 430 nm while scanning the excitation wavelength over the neutral and cationic absorptions) reflects the relative abundances of the two species. This is illustrated in Fig. 1a, which shows harmine excitation spectra acquired at the frozen freshwater surface: as the initial solution pH is increased from neutral (dashed red line) to strongly basic (solid red line), the peak maximum shifts from ~ 320 nm to ~ 290 nm. In this study we used harmine to study frozen salt water/sea water surfaces for the first time. Also shown on Fig. 1a are harmine excitation spectra acquired at the frozen salt water surface for near-neutral (dashed green line) and strongly basic (solid green line) initial pH's. Figure 1a illustrates that harmine's spectral features are not influenced by the different environments presented by the frozen salt water vs. frozen fresh water surfaces (e.g., by higher ionic strength or greater liquid layer fraction at the air-ice interface).

Previously (Wren and Donaldson, 2012) we reported that the ratio of harmine's fluorescence intensity following excitation at 290 nm to that following excitation at 320 nm (hereinafter the harmine 290/320 ratio) provides a useful parameter for studying pH at the frozen freshwater surface. The harmine 290/320 ratios are plotted as a function of pre-freezing pH for frozen freshwater and frozen salt water samples in Fig. 1b. The pre-freezing pH of each sample was adjusted with either HCl(aq) or NaOH(aq) as required. Figure 1b shows that the harmine 290/320 ratio obtained at the ice surface using glancing-angle LIF (a) increases monotonically with an increase in pH for pre-freezing pH values > 8.5; and (b) is the same at the frozen freshwater vs. frozen salt water surface. The good agreement gives us confidence that harmine can be similarly used to study pH changes at the frozen salt water surface.

As reported in Wren and Donaldson (2012), and illustrated by the red symbols in Fig. 2, the freezing of freshwater samples is accompanied by a marked decrease in the harmine fluorescence intensity (by ∼ 50 % or more). We have noted such fluorescence quenching previously, for other probe compounds present at frozen interfaces (Wren and Donaldson, 2012). However, as illustrated by the blue and green symbols in Fig. 2, freezing salt water and seawater samples does not result in a decrease in overall fluorescence intensity. Indeed, a slight increase in harmine fluorescence intensity (∼ 10 %) is observed upon freezing. The lack of quenching on the frozen salt water surface is suggestive of a more liquid-like environment there, in accord with thermodynamic models (Koop et al., 2000).

3.2 pH changes at the frozen freshwater vs. frozen salt water surface

First we report on changes in surface pH due to the deposition of gas-phase HCl to frozen freshwater vs. frozen salt water surfaces. Figure 3 shows the harmine 290/320 ratio as a function of time relative to the introduction of HCl(g). The results obtained at the frozen freshwater surface are shown as red circles and at the frozen salt water surface as green triangles. The initial pH of both samples was > 9 and the final melted pH of the samples was < 3. Although a similar amount of HCl(g) was delivered to each sample in a *bulk* sense, the pH response at the *surface*, as inferred from the harmine 290/320 ratio, was very different.

The red symbols in Fig. 3 show that deposition of HCl(g) to the frozen freshwater surface results in a very slow (or no) decrease in the harmine 290/320 ratio, which we interpret as a very slow decrease in the surface pH. The same result – obtained using acridine as a pH indicator – is reported in Wren and Donaldson (2012) where the possible reasons are discussed in detail. In the case of HCl(g) deposition to frozen freshwater, the high harmine 290/320 ratio measured at the end of the experiment is not consistent with the low pH measured upon melting the sample. Since (a) the solubility of HCl in single crystal ice is low (Hanson and Mauersberger, 1990) and (b) the diffusion of HCl within single crystal ice has been shown to be very slow (Thibert and Domine, 1997), it is unlikely that the deposited HCl is incorporated into the bulk ice matrix. We have previously suggested (Wren and Donaldson, 2012) that the deposited HCl may migrate away from the ice surface along grain boundaries in the ice. Migration of HCl along grain boundaries has also been inferred in other studies (Wolff et al., 1989; Molina et al., 1987). Another possibility may be that HCl remains in a molecular form at the surface. A few groups have shown that molecular and ionic HCl can coexist on ice surfaces at very low temperatures (< 150 K) (Delzeit et al., 1993; Kang et al., 2000; Park and Kang, 2005; Parent and Laffon, 2005). However, it is not well known how the decreased water availability in the QLL may affect dissolution and dissociation of HCl there.

In contrast to the frozen freshwater result, the green symbols in Fig. 3 illustrate that when HCl(g) is deposited to the frozen salt water surface the harmine 290/320 ratio decreases much more rapidly, indicating a lowering in surface pH (cf. Fig. 1b). This is consistent with acid dissolution at a liquid brine surface, which is expected thermodynamically to be present for the frozen salt solution and which is also inferred from the fluorescence intensity results presented above.

Several studies point to the presence of brine layers at the surface of frozen salt solutions. Koop et al. (2000) showed that frozen NaCl and NaBr mixtures would be partially liquid down to ~ 230 K. Cho et al. (2002) used NMR line widths to show that a liquid brine coexists with solid ice for salt solutions at sub-eutectic temperatures. They found that the system could be well described using an equilibrium thermodynamic approach. Using their formulation for the liquid brine fraction, which is based on freezing-point depression, we estimate a total liquid brine fraction on the order of ~10 % for a 0.5 M NaCl solution at 263 K. For a ~4 ml sample, with surface area ~6 cm^2, this translates to a maximum brine thickness of roughly 60 µm, assuming all the liquid is present exclusively at the air-ice interface (although the samples in this study did not have the visual appearance of being "wet"). Noting that this represents an extreme upper limit to the brine layer thickness, the fact that the frozen salt water surface responds to the deposition of HCl(g) as if it were a liquid is not necessarily surprising. By contrast, a pure ice surface near the freezing temperature, is thought to be covered by a QLL which is much thinner (10 s of nm) (Li and Somorjai, 2007). As noted above, the properties of this interface are often quite different from those of a true liquid surface.

Recently, Kahan et al. (2010a) studied the kinetics of harmine photolysis at the frozen freshwater surface vs. frozen salt water surface and found that at pre-freezing salt concentrations greater than 0.1 M, the photolysis kinetics were well described by the aqueous-surface kinetics but at the "pure" ice surface the photolysis rate was significantly enhanced over its liquid value. Such a rate enhancement has also been observed for other aromatics (Kahan and Donaldson, 2007). The authors concluded that by increasing the salt concentration, the brine fraction at the surface was increased until the frozen salt water surface behaved like a true liquid solution. Together with the present results, these results indicate that (a) the frozen freshwater and frozen salt water surfaces are fundamentally different and that (b) the frozen salt water surface provides a chemical environment much like that of a liquid surface, consistent with its greater predicted liquid fraction.

3.3 pH changes at the frozen salt water vs. frozen seawater surface

Now we address the question of whether the frozen seawater surface is buffered against pH changes. Because the sensitivity of harmine towards pH changes is greatest in the pH 8–10 region (as shown in Fig. 1b), in these experiments we monitored increases in surface pH due to the deposition of gas-phase NH_3(g). The initial pH of the salt water solution was adjusted using NaOH(aq) to bring it close to the initial pH of the artificial seawater (~ 8.1). The experimental approach was the same as that described above except that in this case NH_3(g) was introduced to the chamber. The experiment was also performed on room temperature liquid salt water and seawater samples; as expected, buffering by liquid seawater was observed in these experiments.

Figure 4 shows the harmine 290/320 ratio measured at the frozen salt water surface (green symbols) and at the frozen seawater surface (blue symbols), as a function of time relative to the introduction of NH_3(g). First, it should be noted that the harmine 290/320 ratio measured at the frozen seawater surface prior to NH_3(g) deposition is consistent with a surface pH ~ 8.1 (i.e., unchanged with respect to the pre-freezing pH). This result is consistent with a previous study in which we demonstrated that freezing of water samples doped with trace amounts of acid or base leaves the surface pH largely unchanged with respect to the pre-freezing pH (Wren and Donaldson, 2012). However, since harmine's usefulness as a pH indicator is limited to the pH 8–10 region, a large acidification of the surface upon freezing would be impossible to detect.

Deposition of NH_3(g) to the frozen salt water surface gives rise to an increase in the harmine 290/320 ratio, indicative of an increase in surface pH. This result is expected given the observations reported above which indicated that the frozen salt water surface is covered by a brine layer which behaves much like a liquid surface. The final melted pH of the salt water sample was > 10 and the high final 290/320 ratio reflects this strongly basic pH. However, under the same experimental conditions, the harmine 290/320 ratio increases much more slowly, if at all, at the frozen seawater surface. The molality of the salt in the seawater solution was the same as that of the salt water solution and thus at the experimental temperature of 263 K, the liquid layer fractions of the two substrates should have been very similar. As with freezing NaCl solutions, there was no decrease in fluorescence intensity on freezing of seawater (see Fig. 2), consistent with our interpretation of a more liquid-like layer on both higher ionic strength substrates. The difference in the pH response is therefore not explained by a difference in liquid layer fraction as it was for the freshwater ice. Rather, the results suggest that the frozen seawater surface is resistant to pH changes, likely due to the brine present at the interface maintaining its buffering capacity.

4 Atmospheric implications

Due to the high salinity of seawater (ca. 30 ‰ ≈ 30 g of salt per kg of solution), at temperatures above the eutectic, the frozen surfaces on which halide activation chemistry is expected to occur (sea ice, frost flowers, saline snow etc.) are thought to be wetted by a liquid brine layer (Abbatt et al., 2012). Depending on the processes that accompany freezing, brine salinities may exceed 100 ‰ (e.g. on frost flowers) (Alvarez-Aviles et al., 2008). On the other hand, the surface of snow grains within a relatively “clean” snowpack may be covered by a more genuine QLL. The present work has shown that deposition of trace atmospheric acids to different frozen substrates may affect the surface pH quite differently.

Of particular interest to the air-ice community is the question of the pH at surfaces important for bromine activation. As mentioned in the introduction, a key reaction for bromine activation (R1), is acid-catalyzed in the aqueous phase (Fickert et al., 1999). Based on this requirement for hydronium ions (i.e., a low pH), it has been thought (Fan and Jacob, 1992; Morin et al., 2008) that the medium on which bromine explosion chemistry occurs must have a low pH for this reaction to proceed at an appreciable rate. Despite this expectation, a few laboratory studies have shown that the heterogeneous ozonation of frozen seawater (Oum et al., 1998) or frozen saltwater solutions (Oldridge and Abbatt, 2011; Wren et al., 2010) still leads to bromine production at ambient (neutral) pH.

The various surfaces which have been proposed for bromine activation chemistry – first-year sea ice, brines on sea ice, frost flowers, saline snow and sea-salt aerosol – derive their salinity from seawater, which is naturally alkaline. The results presented above indicate that the frozen seawater surface (a) likely maintains its slightly basic pH and (b) is resistant to changes in surface pH due to deposition of gas phase species. These results strongly suggest that the buffering capacity at the sea-ice interface is maintained upon freezing. This observed buffering at the frozen sea water surface supports field studies which show that ikaite is the dominant form of carbonate to precipitate from freezing seawater (Dieckmann et al., 2008, 2010) and also a modelling study which shows that precipitation of ikaite does not lead to a reduction in total alkalinity (Morin et al., 2008). Given that brine alkalinity may not be reduced upon freezing, the "low pH requirement" of bromine activation may be overstated.

Indeed, as mentioned briefly above, laboratory studies of bromide activation on frozen surfaces (by oxidants HOBr, OH and O_3) indicate that although the chemistry is accelerated at low pH, it is still operative at neutral or even basic pH values. For example, Adams et al. (2002) studied the uptake and reaction of HOBr on frozen NaCl/NaBr and found that the product yields were independent of pre-freezing pH between pH 4–10. Sjostedt and Abbatt (2008) studied the heterogeneous oxidation of frozen salt solutions by OH(g) and found that halogens were released from neutral samples, although to a lesser extent than from acidic samples. Finally, Oldridge and Abbatt (2011) and Wren et al. (2010) have also observed evidence for bromine release due to the heterogeneous ozonation of frozen salt solutions at ambient pH. Thus, there is a growing consensus that low pH may not be a strong criterion for halogen activation (Abbatt et al., 2012). Gaining a better understanding of surface parameters such as pH will help to elucidate the mechanism and the important substrate characteristics of bromine activation.

5 Conclusions

In summary, we studied pH changes at frozen freshwater, frozen salt water and frozen seawater surfaces using a surface-sensitive spectroscopic approach. At the frozen salt water surface, changes in surface pH due to the deposition of either HCl(g) or NH_3(g) could be rationalized on the basis of a brine layer at the air-ice interface which behaved like a true liquid layer. Changes in pH at the frozen freshwater surface were distinctly different, indicating that when a “true QLL” exists, it may not be appropriate to describe it as a cold, liquid layer. In the cryosphere, impurity levels and temperature (two factors which should affect the liquid-layer fraction) can vary widely, so care should be taken in ascribing a universal surface pH. We also show, for the first time experimentally, that the frozen seawater surface is buffered against pH changes. This work has significant implications for understanding and interpreting pH-dependent processes occurring on ice surfaces, such as “bromine explosion” chemistry.

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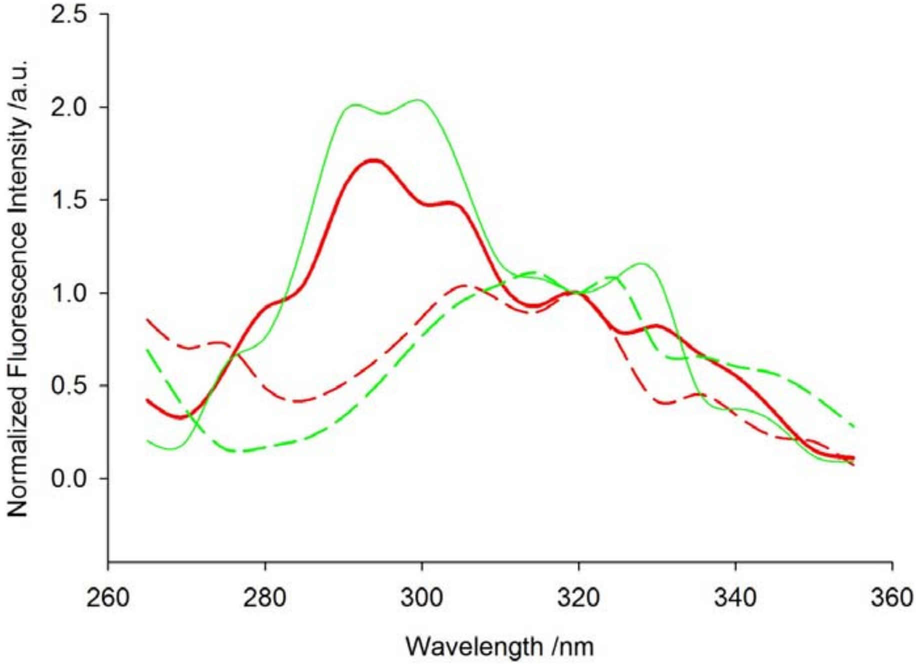

Fig. 1a. Harmine excitation spectra acquired at the frozen freshwater surface (red traces) and at the frozen salt water (0.5 M NaCl) surface (green traces) for strongly basic pre-freezing pH ∼ 9.8 (solid traces) and near-neutral pre-freezing pH (dashed traces). Spectra were collected by scanning the excitation wavelength in 5 nm steps while monitoring harmine fluorescence at ∼ 430 nm.

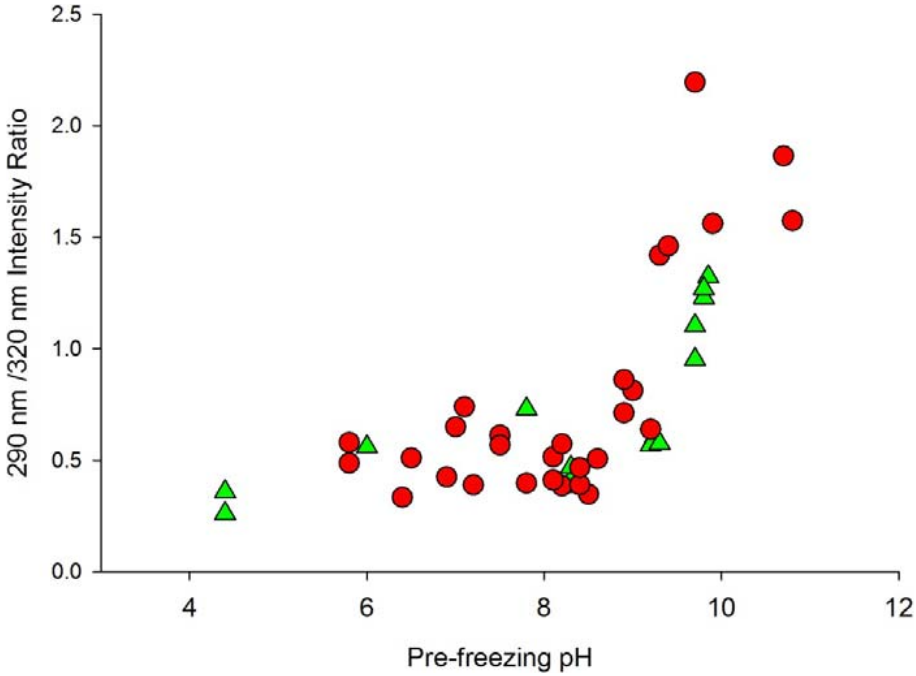

Fig. 1b. The harmine 290/320 intensity ratio measured at the frozen freshwater surface (red circles) and at the frozen salt water (0.5 M NaCl) surface (green triangles) as a function of pre-freezing pH. Initial pre-freezing pH was adjusted with NaOH(aq) or HCl(aq) and measured with a commercial pH electrode.

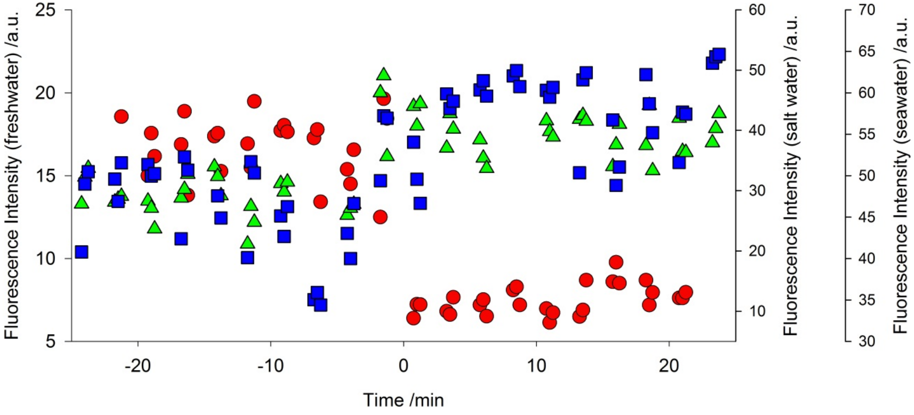

Fig. 2. Harmine fluorescence intensity (in arbitrary units) measured at 430 nm following excitation at 320 nm plotted as a function of time relative to the freezing of freshwater sample (red circles, left axis); salt water (0.5 M NaCl) sample (green triangles, inner right axis) and artificial seawater sample (blue squares, outer right axis).

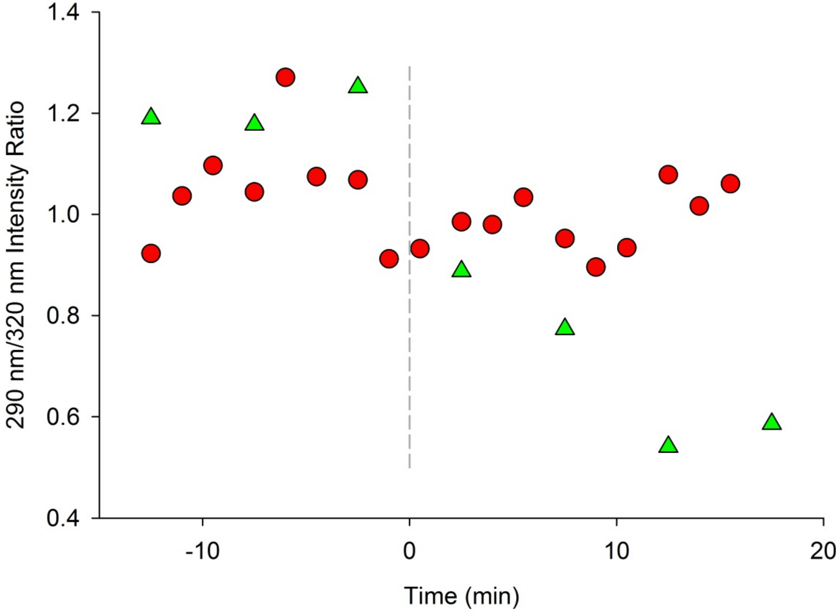

Fig. 3. The harmine 290/320 intensity ratio measured at the frozen freshwater surface (red circles) and at the frozen salt water (0.5 M NaCl) surface (green triangles) as a function of time. The dashed line indicates the time ($t = 0$) at which a 0.5 SLPM flow of 100 ppm of HCl in N_2 was introduction to the chamber. The pre-freezing pH of the samples was adjusted with NaOH(aq) to a pH ~ 9.8. The final melted pH of the freshwater sample was ~ 3 and the final melted pH of the salt water sample was pH ~ 2.5.

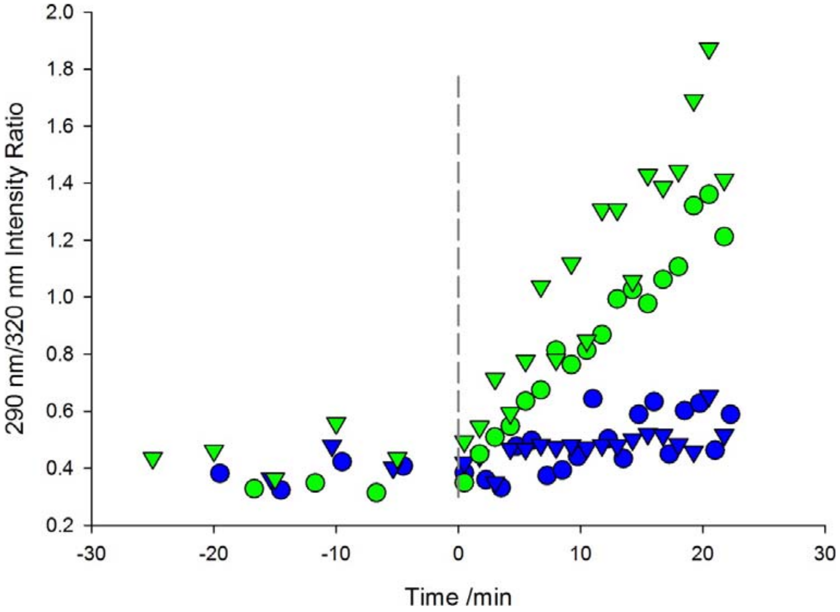

Fig. 4. The harmine 290/320 intensity ratio measured at the frozen salt water surface (green symbols) and at the frozen artificial seawater (blue symbols) surface as a function of time. The dashed line indicates the time ($t = 0$) at which a 50 sccm flow of N_2 passing over a 12.75 wt% $NH_4OH(aq)$ solution held at 253 K was introduced to the chamber. The pre-freezing pH of the salt water samples was adjusted with NaOH(aq) to a pH ~ 8.1, to be the same as the equilibrium pre-freezing pH of the seawater samples. The final melted pH of the salt water samples was > 10 while the final melted pH of the seawater samples was < 10. The different shapes of the symbols represent two separate trials.