

Response to Referee #1:

The authors thank the referee for his or her comments.

P19281 L5: Period added

P19281 L24: Added approx. depth in nm for comparison

P19282 L7: Added dash

P19282 L12: The referee is concerned that (a) the presence of harmine at the ice surface might inhibit HCl uptake, and (b) that the harmine may itself act as a buffer, and influence the local surface pH.

A very small concentration of harmine was used in these experiments (1×10^{-7} M). If every harmine molecule in the solution was present at the interface, the organic would form a loose monolayer there – such monolayers have not been found to be effective at blocking interfacial transport at the liquid surface. We note that in our previous study using acridine as a dye (Wren and Donaldson, *J. Phys. Chem. C.*, 116, 10171 – 10180, 2012), deposition of HCl(g) to a frozen freshwater surface led to a sudden increase in the acridine fluorescence decay rate, indicating that the dye was sensing the deposition of acid. In that study measurements of final bulk pH indicated that the same amount of HCl had been delivered to liquid and frozen (pure water) samples, indicating that the dye was not preventing HCl uptake in the frozen case. In the present study we also find that final bulk pH is similar for frozen salt water and frozen freshwater experiments, again indicating that there is not a difference in harmine's blocking ability towards HCl between the two cases. In the experiments on frozen salt water or seawater, harmine is clearly sensitive to a change in pH due to deposition of HCl/NH₃.

Since the harmine concentration is low, we do not expect it to have a large influence on the surface acidic properties (although we cannot say definitely that there is no effect). We note that acridine and harmine have pKa's which differ by > 3 , yet both dyes respond similarly when liquid and frozen freshwater samples are exposed to HCl(g) (also see Wren and Donaldson, *J. Phys. Chem. C.*, 116, 10171 – 10180, 2012). We also note that the harmine 290/320 ratio follows the same trend as a function of initial pH (Figure 1b) on both the frozen freshwater and frozen salt water surface. If harmine had a strong influence on surface acidic properties at the surface one might not expect to see such good agreement (given that the surfaces present very different solvation environments).

P19282 L17: A liquid core waveguide was used for its suitable optical transmission properties (we have been using these for several years in our LIF experiments).

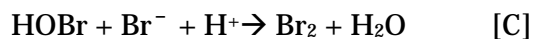
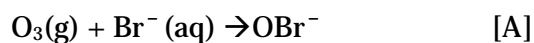
P19282 L20: The floor of the chamber was made from copper (and was covered by a thin stainless steel plate during experiments). The temperature of the coolant was controlled such that the temperature of the samples (as measured in a few experiments using a thermocouple) was ~ 263 K. We have added some text to Section 2.2 to clarify this. We also note that the temperature was the same for all experiments.

P19283 L21: The surface area of the samples was added to the text in Section 2.3.

P19284 L 20-22: The text has been changed to make it clear what is meant by 5 – 10% uptake (5-10% of the total HCl was estimated to be taken up the ice surface).

P19285 L 20-24: The referee is concerned about the minor differences in harmine's excitation spectra measured at the frozen salt water and frozen freshwater surface. Figure 1a is meant to illustrate that the (rough) locations of the absorption maxima are the same for both environments. Some differences in the relative intensities may be due to a small difference in the initial pH. It should be recognized that the overall fluorescence signal from the frozen surface is quite noisy. Second, the initial pH of the solutions was not exactly the same (simply strongly basic or near-neutral). The good agreement between the salt water and freshwater data shown in Figure 1b also supports the conclusion that the spectral features are not strongly influenced by the different environments. Some text was changed in Section 3.2 to clarify this.

P19290 L 20-23: The heterogeneous ozonation of bromide is expected to proceed as follows (based on its aqueous phase mechanism):



Where both reactions B and C depend explicitly on the presence of acid; reaction C is the same as R1 in the text. Some text has been added to Section 1 (where R1 is first introduced) to make this clear.

P19291 L3: We have changed the wording in the text to indicate that the results of our study are 'consistent with' the results of Dieckmann et al. and Morin et al. The Morin et al. study, shows that precipitation of ikaite does not lead to a decrease in the total alkalinity in the brine below seawater values. Their model is an equilibrium chemical thermodynamic model which is parameterized for the Na-K-Mg-Ca-Fe(II)-Fe(III)-H-Cl-Br-SO₄-NO₃-OH-CO₃-O₂-CH₄-H₂O system and takes into account the equilibrium between atmospheric CO₂ and carbonate species in seawater. Those results suggest that the solution's buffering capacity is maintained in this system during freezing. The Dieckmann et al., field studies indicate that ikaite is indeed the dominant form to precipitate. Thus it is a logical conclusion that frozen seawater will have a maintained buffering capacity (which is what we observe).