Bartels-Rausch et al present an elegant laboratory NEXAFS experiment investigating the presence of hydrohalite at the air-ice interface (top ~6 nm) below the eutectic temperature, through aqueous NaCl experiments from 240 – 259 K. Notably, this work presents the first NEXAFS spectrum of hydrohalite through the advantage of probing the chlorine K-edge, in comparison to their previous work examining the oxygen NEXAFS spectra. Overall, the manuscript is well-written and has good motivation, particularly to air-snow interactions. Here, I present suggestions to improve the clarity of the manuscript and relevance to other previous work that further shows the utility of the current work.

We thank the referee for the kind judgement.

Introduction: When discussing the links to air-snow reactions on Lines 34-49 and 67- 82, it would be helpful to briefly discuss all of the reaction pathways shown in Figure 1. Regardless of the depth of discussion, references need to be provided in the figure caption, or at least in the main text, for the reactions shown in Figure 1. The authors discuss gas-phase OH reacting with chloride, but don't discuss aqueous OH reacting with chloride at the ice surface (Halfacre et al. 2019, Atmos. Chem. Phys.), which would seem to be of relevance. Of particular relevance, and not currently cited in this manuscript, is the work by Wren et al (2013, Atmos. Chem. Phys.) and Custard et al. (2017, ACS Earth & Space Chem.) that showed reduced snow/ice Cl2 production, in the lab and field, respectively, at temperatures below the eutectic, which was attributed this to the presence of hydrohalite, thereby directly connecting to this present lab study. Similarly, the lack of observed Cl2 at lower temperatures by Sjostedt and Abbatt (2008, Environ. Res. Lett.) was attributed to the presence of either halite or hydrohalite. Also, Lopez-Hilfiker et al. 2012 (Atmos. Chem. Phys.) also invoked the presence of hydrohalite to explain the relative production of ClNO2 vs Br2 in N2O5 reactions on saline ice.

Apologies for our obviously too limited literature search. As excuse we might only say that we had expanded this discussion rather late in the writing process and maybe therefore not with the care necessarily. Thank you for pointing us to this reference, we will be happy to include a discussion on this work in a revised manuscript.

"In the cryosphere, where the snowpack is strongly impacting the chemistry in the overlaying atmosphere (Dominé and Shepson, 2002; Thomas et al., 2019), halogen compounds are also found within the snow. Sea-salt components, a source of halogens in snow in costal snowpack, might originate from migration from underlying sea-ice or from deposition of wind-transported sea-spray aerosol (Dominé et al., 2004). One characteristic of the cryosphere are its subfreezing temperatures and the consequent precipitation of chemical constituents at specific temperatures, their eutectic temperature, as also observed in sea-ice (Petrich and Eicken, 2009). It is known that the precipitations or phase changes of the reactants critically impact the reactivity (Bartels-Rausch et al., 2014; Kahan et al., 2014). Reduced chlorine production in frozen systems was observed by Wren et al. (2013) and by Sjostedt and Abbatt (2008), at temperatures below the eutectic temperature of sodium chloride in laboratory experiments that was attributed to the precipitation of sodium chloride. In an arctic field study, Custard et al. (2017) observed reduced Cl2 production when temperatures dropped below the eutectic temperature of sodium chloride and suggested limited availability of chloride as consequence of the precipitation in this surface snow. Further, Lopez-Hilfiker and Thornton (2012) proposed the precipitation of sodium chloride to

explain the changes in the production yield of ClNO2 from the reaction of N2O5 with saline frozen systems with temperature. More generally, it is not only the chlorine chemistry that responds to the phase of sodium chloride present in frozen systems both in the laboratory and in the environment. Oldridge and Abbatt (2011) showed that the rate of the heterogeneous reaction of ozone with bromide in sodium chloride -- water mixtures is strongly reduced once the salt precipitates below 252 K. The author explained this with the reduction in liquid volume that serves as reaction medium for the bromide in the sample due to the precipitation of sodium chloride."

Figure 5: Are optical images available for D-F as well? It would be particularly useful to refer to this, for example on Line 366 when the optical image is being described for D, for example. Also, please define the letters in the caption of Fig 5 so that reader is not required to refer back to Fig 3. In addition, consider changing the font on the letters and making them bold so that they are easier to discern; in particular, B is difficult to distinguish from B'.

Unfortunately, no. This are all the pictures that we have. We will clearly state this in the caption in a revised manuscript and also apply the editing suggestions. Thank you.

"Figure 5: Optical microscopy pictures of the frozen samples. Each picture shows a 1 mm wide section of the sample holder with the sample. The letters refer to the samples in Figs. 3 and 4: A Solid NaCl at 248 K and 44 % relative humidity. B Ice with brine at 88 % RH and 259 K. Picture B' shows the deliquesced sample prior to freezing. C Sample below the eutectic temperature at 248-249 K in presence of ice. F Sample in absence of ice at a relative humidity lower than 73 % and at 244 K. Pictures of samples D and E were not taken."

Additional Comments: - Fix section numbering throughout (all start with 1)
Well, thanks. I must confess that I did not manage to get the numbering right. I have no idea what "Word" is doing here. I must leaf this to the editorial office to change in the final version.

- Lines 37-38, 41, 44-45, 80-82: Please add references to these sentences.
Done, thanks.

«Taken the abundance of chloride in the form of sea-salt over wide areas of the globe, the atmospheric chemistry of chlorine has long raised interest in a number of multiphase reactions that liberate chloride into chlorine species in the gas phase (Simpson et al., 2007; Finlayson-Pitts, 2010).

Common to all of these reactions is the generation of chlorine gases that either react with OH radicals or photolyze at wavelengths available in the troposphere to generate reactive chlorine (Fig. 1 and Finlayson-Pitts (2010)).

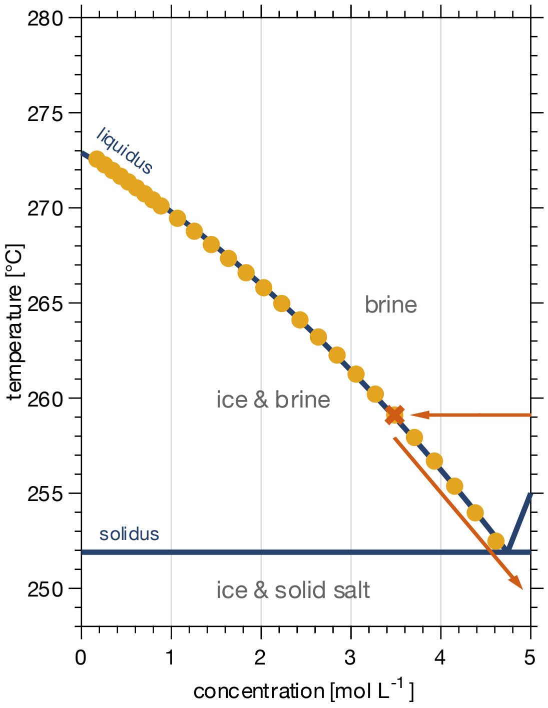
Its importance arises from its atmospheric abundance but also because its eutectic temperature of 252 K falls into typical springtime Arctic temperatures – a region and time period when atmospheric halogen chemistry is most active. For example, at the Arctic coast near Utqiagvik (Alaska) temperatures between 247 K and 259 K have been reported (Custard et al., 2017). Another region of Earth's cryosphere, where temperatures drop below the 252 K is the troposphere (Thomas et al., 2019). Wang et al. (2015) has proposed a significant role of heterogeneous halogen chemistry on the ozone budget there. More recently, Murphy et al. (2019) has shown that the amount of sea-salt aerosol lifted to the upper troposphere is *small, casting some doubt on the environmental relevance of sea-salt as source of reactive halogens.»*

- Lines 57-65: This paragraph about bromine chemistry detracts from the focus of the current study and is suggested to be removed. Instead, it would be better to discuss the reaction mechanisms pertinent to chlorine chemistry shown in Figure 1.

We will expand the discussion on the mechanism shown in Figure 1. This more detailed discussion of chlorine chemistry will then shift the focus away from bromine to chlorine. With all respect, we'd like to keep a somehow shortened mention of the bromine chemistry for two reasons. First, the findings in this work are not restricted to chlorine, but valid for any salt (at different temperatures compared to those found here for chlorine). Second, that chemistry at the interface differs from that in the bulk has, our judgement, been shown most elegantly for bromide. Therefore, we feel that this information is crucial to motivate investigation of the phase changes at an interface.

- Figure 2: Please add the year to both Rumble citations in the caption and fix the spelling of "aqueous" in multiple locations the figure.

Done, thanks.



«Figure 2: Phase diagram of the NaCl-water binary system. The data show the freezing point depression of sodium-chloride solutions (yellow filled circles) and give the concentration of an aqueous sodium chloride solution in equilibrium with ice in the temperature range of 273 K to 254 K (Rumble, 2019). The dark blue lines indicate the phase boundaries (Koop et al., 2000b; Rumble, 2019), that is it denotes the so-called liquidus and solidus line, respectively, and thus

shows the temperature and concentration range where ice and aqueous sodium chloride solution co-exist. The eutectic temperature of sodium chloride – water binaries is 251.9 K (Koop et al., 2000a). Also shown is a typical experimental procedure (red arrows and cross).»

- Line 228: Fix typo "disused".
Done, thanks.

- Figure 4: Consider making the phase labeling on plot A more similar to Fig 2. For example, the labeling of the "ice melting" line was confusing at first given the locations of the individual words surrounding the line in the figure.
Done, thanks. We have updated Figure 2, where the phases are now no longer labelled near the lines.

- Lines 348-359: Consider moving this paragraph to the methods section, as it de- scribes how the experiment was conducted, rather than the results of the experiment.
Yes, we will better separate the experimental description from discussing the results. Based on the suggestions by referee 3 we will slightly re-structure the manuscript to better link results in Figure 3 to the conditions of the individual measurements and also omit repetitions of the experimental procedures.

We have expanded this section by adding more observables

«In a typical experiment, anhydrous salt was exposed to increased relative humidity at a fixed temperature of 259 K. Once the relative humidity reached 72 %, the sample started to dissolve by water up-take from the gas-phase and an aqueous solution was formed (brine). This phase change was evident by the sample becoming shiny and then forming transparent spheres as observed by an endoscope digital camera (Fig. 5B'). Then, the relative humidity was further increased to cross the ice stability line until ice nucleation occurred at a modest supersaturation of typically 90 % to 95 % relative humidity at 259 K. Ice nucleation was evident by a sharp pressure drop from the pressure dosed to the cell to the water vapor pressure of ice at that temperature, for example 88 % relative humidity at 259 K. In some experiments, temperature was lowered 1 K to 2 K as well to trigger ice nucleation. Please note, that temperature was always well above the homogenous freezing temperature, which was found at 210 K to 230 K at relative humidities of 60 % to 90 % (Koop et al., 2000a).»

and by moving the more general description to the experimental part:

«Water vapour was dosed to the flow-through cell via a 0.8 mm i.d. steel capillary from the vapour above liquid water (Fluka Trace Select 142100-12-F) in a vacuum-sealed, temperature-controlled glass reservoir. Before dosing, the water was degassed by 4 freeze-pump-thaw cycles. The the water dosing and thus the partial pressure or relative humidity that the sample is exposed to was varied by setting the temperature of the reservoir to change -the flux of water vapour into the experimental cell.»

- Line 370: Please provide the temperature here in parentheses for clarity (rather than just simply 11 K below the eutectic) to aid the reader in referring to Fig 4 and quickly finding the proper star marker.
Done, thanks.

- Line 371: Where is this "11.4 K below the eutectic" data shown? This sentence seems like it is discussing the current work, but Fig 3 only shows 10 K and 12 K below the eutectic.

«Consistent with that, the chloride has a local environment indistinguishable from that of the hydrohalite 11.4 K below the eutectic temperature and in the presence of ice in the current study (Fig. 3D)».

Corrected, thanks. The temperature given in Figure 3 were wrong. Apologies. We have also added the partial pressure of water for each NEXAFS spectrum to the caption.

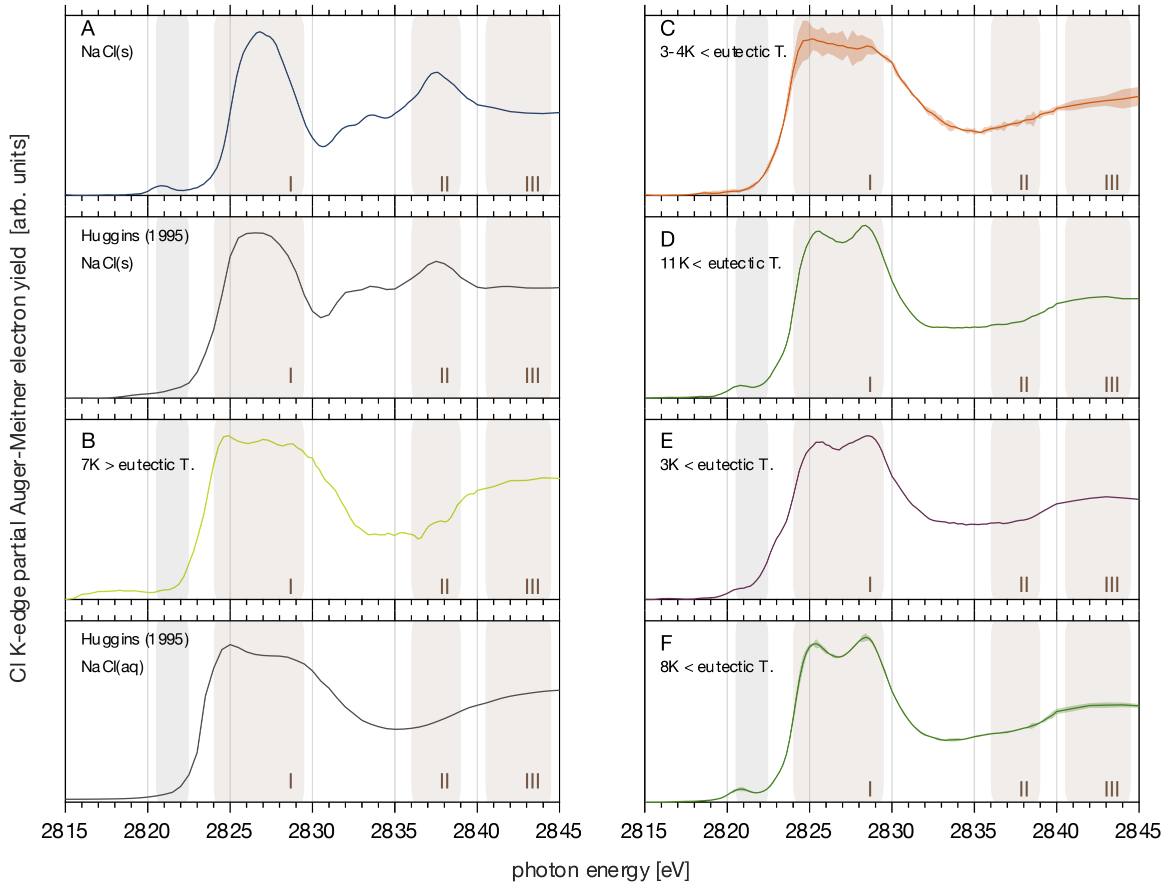


Figure 3: Partial electron yield chlorine K-edge NEXAFS spectra of the sodium chloride -- water binary system: A Solid NaCl at 248 K and 44 % relative humidity (0.34 mbar water vapour pressure). B Aqueous NaCl solution in equilibrium with ice at 88 % RH (1.82 mbar) and 259 K. C An averaged spectrum at the thermodynamic ice stability line at 248 K to 249 K and 78 % (0.60 mbar) to 80 % RH (0.71 mbar). D An individual spectrum upon further cooling to 241 K and 74 % RH 0.29 mbar). E An individual spectrum upon heating back to 249 K in the ice stability domain at 79 % RH (0.69 mbar). F The averaged spectrum at 244 K and a RH of 59 % (0.32 mbar) and 73 % (0.40 mbar), lower than the ice stability domain. See Fig. 4 for precise measurement settings. The shaded area in the colour of the graph in C and F denote the standard deviation of 3 and 2 repeated NEXAFS acquisitions. Also shown are NEXAFS spectra of NaCl salt and aqueous solutions for comparison that were detected in fluorescence mode and not in partial electron yield (Huggins and Huffman, 1995). The brownish shaded area (I-III) highlights regions in the NEXAFS spectra discussed in the text. The grey shaded area at 2821 eV highlights the photon energy region where carbon-chlorine bonds from carbon contamination might show an absorption feature (see text for details).

- Lines 378-383: Is it possible that the hydrohalite may form within the bulk prior to the surface, explaining the higher temperature observed by Malley et al (2018) compared to this work?

Good point, thanks. We will add this to the manuscript.

"It appears thus that the precise occurrence of crystallisation is governed by stochastics at the surface as has been shown for freezing of bulk samples (Alpert and Knopf, 2016). Because of the good agreement between the precipitation temperatures observed in this study and in (Koop et al., 2000a), we believe that the deviation from (Malley et al., 2018)'s results does not indicate differences in the freezing behaviour at the surface vs. in the bulk."

- Line 387: For clarity, I suggest adding "at 5 K below the eutectic temperature" after "spectrum" in this sentence.

Done, thanks.

- Line 392: Change "snow" to "ice" here, since authentic snow was not studied in this work.

Done, thanks.

- Lines 394-426: This is a very long paragraph. Please consider breaking up.

Done, thanks. We also added some guiding sentences for the reader.

For samples that were cooled to temperatures that triggered efflorescence, the chlorine NEXAFS spectra show that the hydrohalite is the dominating phase at the interface of frozen sodium chloride – water binary mixtures. Cho et al. (2002) have shown that when frozen aqueous solutions were warmed, a liquid fraction was observed below the eutectic temperatures. In their experiments, ice was frozen in NMR tubes lowering the temperature to 228 K in 15 min. which is significantly colder than the efflorescence temperatures observed here and by Koop et al. (2000a). After 10 minutes, the samples were warmed and NMR signals were recorded. Interestingly, Cho et al. (2002) have observed the liquid fraction only in experiments where the sodium chloride concentration in the initial aqueous solution was below 0.01 mol l-1. If the initial aqueous solution had a concentration of 0.5 mol l-1 no indication of liquid features below the eutectic were found. Tasaki et al. (2010) has shown a similar concentration dependence for sodium bromide solutions using X-ray absorption reporting solvated bromide in the bulk of the samples below the eutectic temperature only for concentrations below 50 mmol l-1.

We will now detail the concentration of brine in the study presented here to elaborate if differences in concentration might explain the differences the observed liquid content of sub-eutectic samples. The experiments described here started with an aqueous solution that was formed in-situ and was kept in equilibrium with a vapour pressure of roughly 1.9 mbar. The chloride concentration in such solutions is close to the concentration in a solution at 1.8 mbar and at 259 K, where ice nucleation occurred and where the freezing point depression data *give a concentration of 3.5 mol l-1. This concentration can be directly compared to the concentration in the initial solutions of Cho et al. (2002), which ranged from below 0.01 mol l-1 to 0.5 mol l-1. This back-of-the-envelope calculation thus suggests that the concentration of the solutions from which ice nucleated in the experiments reported here exceeded those described by Cho et al. (2002) for which no liquid fraction was observed.*

Next, we discuss how higher concentrations of initial solution might impact the location of brine in the frozen matrix. The concentration of the initial solution from which ice precipitated, determines the ice to brine ratio after ice formation. This is because the volume of the brine relative to that of ice is given by the water to sodium chloride ratio in the initial solution. The concentration of the brine is a sole function of temperature, and not of the initial concentration of the solution.

- Lines 428 – 439: This paragraph overall should be revised to make it clearer and easier to read and relate the previous work to the current results. In particular, the goal of this paragraph could be clarified at the beginning of the paragraph to help guide the reader, as I had to read the beginning sentences multiple times to understand them in the context of the current work.

Done, thanks.

The previous argumentation is based on the features in the NEXAFS spectrum of sodium chloride – ice mixtures shown in Fig. 3 D and E being dominated by the NEXAFS spectrum of hydrohalite shown in Fig. 3F. In particular the spectrum in Fig. 3E, acquired 3 K below the eutectic temperature, shows a shoulder starting at 2823 eV. Such a feature is absent in the spectrum of the hydrohalite (Fig. 3 F), but the spectrum of brine (Fig. 3 B) shows an increase in absorption starting at this X-ray energy. We can thus not exclude the presence of brine in the samples where the hydrohalite dominates the NEXAFS. Taken the spectra quality and the small difference in the shape of the liquid and of the hydrohalite spectrum, it is beyond the scope of this work to elaborate whether the NEXAFS spectrum in Fig. 3E might be understood by deconvoluting it in its hydrohalite and brine components and by this reveal a fraction of the chloride being embedded in a brine-like hydrogen bonding network. Two reasons might explain the presence of liquid in these samples at sub-eutectic temperatures. First, one might expect a certain distribution in the size of micropockets and a small fraction of the pockets might thus be small enough to stabilize liquid at these temperatures. This explanation is consistent with the sample at warmer temperatures showing a more intense shoulder at 2823 eV. Secondly, some of the chloride might form solvation shells with water molecules from the ice matrix as proposed for trace gases adsorbed to ice {Krepelova; Bartels-Rausch, 2019}. In particular, we have recently reported chloride forming solvation shells in the interfacial region of ice upon adsorption of HCl at 253 K (Kong et al., 2017). The surface concentration as derived from XPS suggested that it was done in the stability domain of ice, i.e., the concentration of HCl was too low to melt the ice. Oxygen K-edge NEXAFS spectra showed that a substantial fraction of the water molecules at the air-ice interface is arranged in a hydrogen-bonding structure like that of liquid water.We like to note, that Krepelova et al. (2010a)'s oxygen K-edge spectra of sodium chloride -- ice did not reveal water molecules being coordinated like in the liquid. Taken together the signal from the hydrohalite by far exceeds the signal from a chloride in brine or in an liquid-like environment at the molecular level.

- Lines 444-445: This sentence appears to be missing its end.
We have rewritten this paragraph.

«Such a trajectory, that is the temperature and water vapor pressure the sample experienced, is shown in Fig. 4C (green solid line). In this set of experiments, water was evaporated by decreasing the relative humidity to about 70 % at 252 K from a brine sample in absence of ice, followed by lowering the temperature to 247 K at constant partial pressure of water (so that the relative humidity increased to about 80 %).»

- Line 450: I believe the authors mean to refer to Fig 3A here.
Corrected, thanks.

- Line 475: Please provide an estimate or approximate range here in parentheses to provide improved understanding of what "the upper few nanometre" mean.
Done, thanks.

- Line 447: I suggest changing "identical" to "similar" here, as the sea salt aerosol in the environment are more complex than simple NaCl-H2O systems. Of particular relevance is that sea spray aerosol particles can have thick organic coatings (e.g., Kirpes et al. 2019, ACS Central Science).
Agree. We will change this and mention organic coatings, thanks.

Introduction: "An advantage of this experimental approach with environmental relevance is that the relative humidity precisely matches that in the atmosphere in contact and in thermodynamic equilibrium with ice clouds or snow cover, because the relative humidity is a sole function of temperature in presence of ice. Therefore, the chemical concentration of such particles exactly matches those of same composition in snow or in the atmosphere under environmental conditions."

Line 447: « The sample was always in equilibrium with gas-phase water which makes cooling conditions identical and concentration of brine similar to that of aerosol particles embedded in snow or in the troposphere.»

«From temperature and relative humidity alone, nucleation or efflorescence cannot be predicted at the interface as in the bulk. We suggest that further studies focus on samples with more complex chemical composition to enhance our knowledge of environmental multiphase chemistry. For example, organic compounds are a common constituent of sea-salt aerosol (O'Dowd et al., 2004) { Kirpes, 2019} and recently we have shown how there presence impacts the microphysics and thus reactivity of salt particles towards ozone (Edebeli et al., 2019).»

- Lines 489 – 490: It would be useful to add discussion about the temperature ranges that are important to consider here (that would matter) when considering the polar environment that is being discussed in which temperature swings regularly occur with changing weather.

A more detailed discussion referring to temperature ranges would be helpful to bring the gap to observations, based on the temperature and RH- dependent results of the current work.

Good point, thanks. We will extend the paragraph in the introduction on typical temperature ranges in Polar environments:

"Its importance arises from its atmospheric abundance but also because its eutectic temperature of 252 K falls into typical springtime Arctic temperatures – a region and time period when atmospheric halogen chemistry is most active. For example, at the Arctic coast near Utqiagvik (Alaska) temperatures between 247 K and 259 K have been reported (Custard et al., 2017). Another region of Earth's cryosphere, where temperatures drop below the 252 K is the troposphere (Thomas et al., 2019). Wang et al. (2015) has proposed a significant role of heterogeneous halogen chemistry on the ozone budget there. More recently, Murphy et al. (2019) has shown that the amount of sea-salt aerosol lifted to the upper troposphere is small, casting some doubt on the environmental relevance of sea-salt as source of reactive halogens. "

And come back to this in the Summary

"Multiphase reactions may proceed at accelerated rates in these highly concentrated brines at temperatures ~10 degrees below the eutectic compared to reactions on solid hydrohalite. This temperature range of ~240 K is frequently observed in polar coastal sites during spring and also in the free troposphere."

- Lines 495-496: This discussion of micro-pockets is confusing when comparing to text on Line 424. Please clarify.

We will reword to make this clearer :

«We suggest that the brine observed by Cho et al. (2002) is a consequence of the presence of very small pockets holding the brine. Because pockets only tend to be small enough to establish a significant depression in freezing point when solutions with low concentration are freezing, and because aerosol at typical relative humidity that prevail in cold parts of the atmosphere are highly concentrated; we suggest that such micro-pockets at the air-ice interface are of small relevance to the environment.»

- Lines 500-501: Would the concentration effect discussed on page 17 have an impact here?

Yes, this might well be; depending on the source and location of the sodium chloride in sea ice (from ocean water with lower salinity, or from deposited aerosol in snow on sea-ice). We prefer not to go into detail here.

- Lines 503-504: Perhaps this would also have an impact on brine migration upward through the snow (i.e. Domine et al. 2004, Atmos. Chem. Phys.)?

Interesting aspect, thanks.

«For modern Earth, precipitation of brine constituents in sea ice is relevant for ion mobility and might result in ion fractionation during wash out events (Maus et al., 2008; Obbard et al., 2009; Maus et al., 2011) and possibly brine migration upwards through the snow {Domine, 2004}.»

- Lines 506-510: It would be useful to add discussion here about where in the atmo- sphere this might matter (using the temperature and RH knowledge from this work). Also, would the history of the production of sea spray aerosol as droplets (and therefore not starting at 0% RH) matter in terms of halite vs hydrohalite based on the results presented herein? Also, might the presence of organics coating the sea salt aerosol have an impact?

Thank you for pointing to the atmospheric relevance. It does certainly matter in arctic spring, when snowpack chemistry is most active. We will add a paragraph in the discussion to elaborate this and other regions in more detail.

«Precipitation of sodium chloride in sea spray aerosol in the troposphere, not embedded in snow or sea ice, is further of ongoing interest. Again, the arctic coastal areas are of high relevance here, because temperature and relative humidity frequently favour precipitation of hydrohalite. Other studies have focus on the temperature range of 230 K to 260 K at a relative humidity of 30 % to 70 % (see Fig. 4 and references therein) to explore the precipitation in the dryer free troposphere. focus is placed on whether anhydrous sodium chloride (halite) or hydrohalite precipitates. In regions of the phase diagram, where the hydrohalite is the thermodynamic stable form, precipitation of the halite was observed with impacts on stability of the solid phase upon warming and or humidification, since the deliquesce relative humidity of the two compounds differs by 6 percentage points (Wagner et al., 2012; Wise et al., 2012; Peckhaus et al., 2016).»

The history of the droplets certainly matters. We believe that this is a strength of the current study. Indeed, the sample was exposed to UHV (0 % RH) prior to adding gas-phase water. The important point is that at the time we started to cool and approach the nucleation temperature the salt had formed a brine solution in equilibrium with the water vapor at RH identical to that above ice. The nucleation experiments thus started with samples that were liquid and identical in concentration to those found in/on snow.

Organic coatings might indeed impact the surface tension and thus the freezing properties in nano pockets or even act as antifreeze proteins. This is an interesting point, worth further studies which we will happily suggest in a revised version.