

## ***Interactive comment on “Interfacial supercooling and the precipitation of hydrohalite in frozen NaCl solutions by X-ray absorption spectroscopy” by Thorsten Bartels-Rausch et al.***

### **Anonymous Referee #2**

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Bartels-Rausch et al present an elegant laboratory NEXAFS experiment investigating the presence of hydrohalite at the air-ice interface (top  $\sim 6$  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.

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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 Cl<sub>2</sub> 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 Cl<sub>2</sub> 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 ClNO<sub>2</sub> vs Br<sub>2</sub> in N<sub>2</sub>O<sub>5</sub> reactions on saline ice.

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'.

Additional Comments: - Fix section numbering throughout (all start with 1)

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

- 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.

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- Figure 2: Please add the year to both Rumble citations in the caption and fix the spelling of “aqueous” in multiple locations the figure.
- Line 228: Fix typo “disused”.
- 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.
- Lines 348-359: Consider moving this paragraph to the methods section, as it describes how the experiment was conducted, rather than the results of the experiment.
- 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.
- 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.
- 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?
- Line 387: For clarity, I suggest adding “at 5 K below the eutectic temperature” after “spectrum” in this sentence.
- Line 392: Change “snow” to “ice” here, since authentic snow was not studied in this work.
- Lines 394-426: This is a very long paragraph. Please consider breaking up.
- 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

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reader, as I had to read the beginning sentences multiple times to understand them in the context of the current work.

- Lines 444-445: This sentence appears to be missing its end.
- Line 450: I believe the authors mean to refer to Fig 3A here.
- Line 475: Please provide an estimate or approximate range here in parentheses to provide improved understanding of what “the upper few nanometre” mean.
- Line 447: I suggest changing “identical” to “similar” here, as the sea salt aerosol in the environment are more complex than simple NaCl-H<sub>2</sub>O systems. Of particular relevance is that sea spray aerosol particles can have thick organic coatings (e.g., Kirpes et al. 2019, ACS Central Science).
- 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.
- Lines 495-496: This discussion of micro-pockets is confusing when comparing to text on Line 424. Please clarify.
- Lines 500-501: Would the concentration effect discussed on page 17 have an impact 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.)?
- Lines 506-510: It would be useful to add discussion here about where in the atmosphere 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 there-

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fore 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?

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Interactive comment on The Cryosphere Discuss., <https://doi.org/10.5194/tc-2020-253>, 2020.

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