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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.

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The work from T. Bartels-Rausch et.al. titled, "Interfacial supercooling and the precipitation of hydrohalite in frozen NaCl solutions by X-ray absorption spectroscopy" demonstrates the first known NEXAFS studies of the interfacial phase transition properties of NaCl-H2O system at sub-freezing temperatures. The group has previously published significant original research and review articles on cryogenic atmospheric chemistry, including X-ray spectroscopy at the air-ice interface. This work adds to their NEXAFS research at the air-ice interface by showing the spectra of hydrohalites. The manuscript demonstrates a technique to identify phase transitions in frozen NaCl solution and a

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method to observe chemistry in the first few nm of the surface. The manuscript, in my opinion, is well-communicated except for a few things, which I believe can be omitted for brevity and another couple of things requiring clarifications.

Some suggestions and corrections: 1. Fig. 3: the unit in the horizontal axis should read [eV], not [hν]. 2. The phase diagram of NaCl-H2O binary system is redundant as it has been investigated for years. However, the representation used in this manuscript is different from the conventional representation in terms of wt% or molal concentration. Here the authors used a molar concentration representation which must have taken into account volume contraction of the solution. However, it is difficult to find these in the articles they cited for reference. Koop 2000b has not directly shown the data shown in FIG. 2 of the manuscript. The CRC handbook 100th edition released only very recently. Although not a big concern, but I would suggest providing the molal labels in the x-axis as well along with the molar labels which are easier to trace for using the phase diagram. 3. Do you have an estimate of the cross-sectional area from which the spectra are being collected? Several groups showed physically separated ice and brine channels in frozen solutions in sub-100 μm scales (ACS Earth Space Chem. 2018, 2, 702−710, Langmuir 2014, 30, 5441−5447, Langmuir 2016, 32, 527−533, Cold Regions Science and Technology 138 (2017) 24–35). Does an average spectrum from a large area covering pure ice and brine have any effect on the intensity (and shape) of the spectra? 4. In the same line of thoughts, when hydrohalites are formed, they also cover a fraction of the ice surface (ACS Earth Space Chem. 2018, 2). Does it have an effect on the shape and subtility of the spectra? This might have direct implication on assigning the correct spectrum of the hydrohalite from FIG. 3D. How do you confirm that the spectrum in FIG. 3D is entirely from hydrohalite, and not from a mixture of liquid and solid phase co-existing as proposed by Cho et al. (J. Phys. Chem. B, Vol. 106, No. 43, 2002)? 5. In absence of NaCl, what would the spectra look like in the 2825 – 2830 eV ranges at different temperatures, knowing that these are the chlorine K-edge NEXAFS spectra? 6. In all cases, the authors started from a nearly 0.5 M.L-1 pre-frozen concentrations. Do the authors have any liquid spectra of

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3.5 M.L-1 or higher concentrations along the liquidus line to check if the spectrum at a particular temperature down to Eutectic point is represented by brine at equilibrium at the given temperature? 7. Finally, the authors showed that down to 12 oC below Eutectic point, formation of hydrohalites are kinetically hindered. While Koop et al (J. Geophys. Res. 2000, 105, 26393) showed this is indeed possible down to 240 K, some other groups showed much lower hysteresis in their experiments (Phys. Chem. Chem. Phys., 2020,22, 17791-17797, ACS Earth Space Chem. 2018, 2). On the other hand, some results suggest that a little bit of contamination (surfactant-type) may also depress the formation of hydrohalite quite significantly (ACS Earth and Space Chemistry, 4 (2), 305ïĂ■310, (2020)). What do the authors believe that may lead to the large hysteresis?

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