

Referee #1

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 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.

We thank Subha Chakraborty for the detailed comment and for the kind acknowledgement of our work in the field.

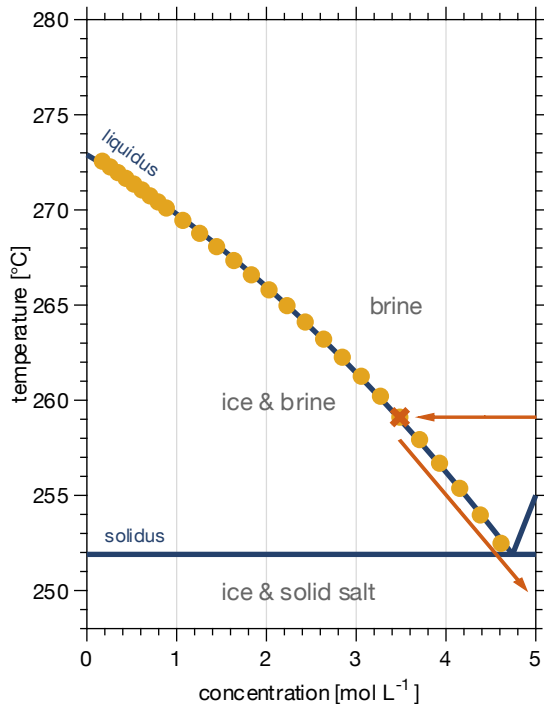
Some suggestions and corrections:

1. Fig. 3: the unit in the horizontal axis should read [eV], not [hv].

Thanks, done.

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.

Figure 2 is certainly redundant; we agree with the referee. We added this purely to remind the reader and to initiate the introduction of Fig. 4 – the phase diagram in the relative humidity space – with this more common representation of the phase diagram. We will add a description of a typical experiment to introduce the concept of sample handling and preparation earlier based on the suggestion of another referee. And yes, you spotted our deviation in Fig. 2 from the classical phase diagrams in wt-%. The “Handbook” lists the freezing point depression data both in molarity and in molality and we preferred to use molarity for reasons of consistency as concentrations throughout the text are given in molarity.



“The focus of this work was to experimentally observe phase changes of sodium chloride below the eutectic temperature. A typical experimental procedure started with a dry sample of anhydrous sodium chloride (halite, NaCl) which was exposed to increasing gas-phase water at constant temperature of 259 K. By absorbing water from the surrounding air, a phase transition from the solid salt to a liquid solution (deliquescence) took place. Upon increasing the gas-phase water dosing further (Fig. 2, red arrow) ice crystallised and a two-phase system of ice and brine occurred (Fig. 2, red cross). After probing the sample at this position in the phase diagram (see below), temperature was lowered and the dosing of the water-vapor adopted to move along the liquidus line to below the eutectic temperature to perform additional measurements. During this cooling period, salt concentration and volume of the brine changes. Such changes with varying relative humidity (hygroscopic growth) have long been discussed for aerosol in the troposphere.”

To limit the number of units in this work we prefer to keep the units in Fig. 2 as they are. To give the reader better access to the data, we added a table to Appendix B listing the freezing point depression, molarity, and molality as given in the “Handbook” (Rumble, 2019):

mass fraction [%]	molal concentration [mol kg ⁻¹]	molar concentration [mol l ⁻¹]	freezing point depression [K]
0.1	0.017	0.017	0.06
0.2	0.034	0.034	0.12
0.3	0.051	0.051	0.18
0.4	0.069	0.069	0.24
0.5	0.086	0.086	0.3
1	0.173	0.172	0.59
1.5	0.261	0.259	0.89
2	0.349	0.346	1.19

2.5	0.439	0.435	1.49
3	0.529	0.523	1.79
3.5	0.621	0.613	2.1
4	0.713	0.703	2.41
4.5	0.806	0.793	2.73
5	0.901	0.885	3.05
6	1.092	1.069	3.7
7	1.288	1.256	4.38
8	1.488	1.445	5.08
9	1.692	1.637	5.81
10	1.901	1.832	6.56
11	2.115	2.029	7.35
12	2.333	2.229	8.18
13	2.557	2.432	9.04
14	2.785	2.637	9.94
15	3.02	2.845	10.89
16	3.259	3.056	11.89
17	3.505	3.27	12.94
18	3.756	3.486	14.04
19	4.014	3.706	15.22
20	4.278	3.928	16.46
21	4.548	4.153	17.78
22	4.826	4.382	19.18
23	5.111	4.613	20.67

3. Do you have an estimate of the cross-sectional area from which the spectra are being collected?

Thank you very much for this question. Indeed, an interesting parameter to include to facilitate comparison with previous studies. In our set-up this area is determined by the area from which electrons will reach the analyser, and not from the area that is exposed to X-ray. On first approximation, this electron acceptance area is given by the diameter of the analyser's sample orifice which is 500 μm in this work.

«The distance of the sample to the electron analyser inlet (working distance) was 1 mm. The electron analyser was operated with an electron sampling aperture with a diameter of 500 μm , which results in sampling roughly an area with a diameter of 500 μm of the sample from which the emitted electrons reach the detector.»

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 subtlety 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)?

Thank you for asking for clarification of the issue of the location of the brine within the frozen samples. Before answering the question, let me summarize that the X-ray absorption spectra that we present (Figure 3) probe exclusively chlorine. We (and others) have shown, that these spectra are sensitive to phase changes. In other words, the spectra intensities reflect the chlorine present in the samples and are insensitive to the fraction of ice. Sampling a larger area and thus more chlorine in the sample would indeed change the intensity of the observed spectra. Please note that the spectra in Fig. 3 are normalised to focus on and to compare their shape and any intensity information is lost. We can modify our set-up and work with either a 500 μm or 300 μm orifice, but we have not done this in this work.

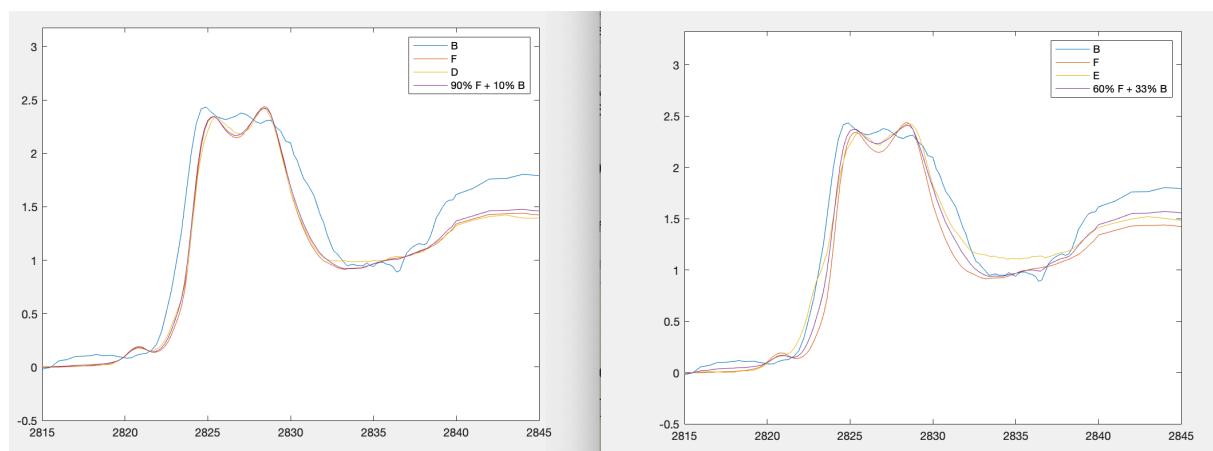
Concerning the location of the hydrohalites (and brine). We agree with the referee that based on previous studies and on thermodynamic considerations a fractionation of brine and ice phases or hydrohalite and ice is very likely. The brine/hydrohalite can be present in channels, patches, micropockets. In this work, we focused on phase changes and the goal was to report the significant and large differences in the spectra of hydrohalite and brine. More subtle changes of X-ray absorption spectra are known and have been reported with concentration of solutions, for example for chloride containing solutions. Investigating these, or differences of the X-ray absorption spectra for brine/hydrohalite at different locations, was beyond the scope of this work and would require different approaches such as a liquid-jet set-up. We happily include the suggested references and also address the question of the sample area when discussing the patches and nanopockets:

«Support for large patches at the interface when solutions are frozen comes from a number of studies {Malley, 2018; Krausko, 2014; Tokumasu, 2016; Lieb-Lappen, 2017}. Low temperature scanning electron microscopy work suggested the ice surface of frozen 0.05 mol l⁻¹ sodium chloride – water mixtures being covered by μm sized brine features (Blackford, 2007; Blackford et al., 2007). Malley et al. (2018) used Raman microscopy of sodium chloride solutions between 0.02 – 0.6 mol l⁻¹ initial concentration to identify micrometre-sized, partially connected patches of liquid covering 11 % to 85 % of the ice surface at temperatures above the eutectic. Despite the impact of freezing temperature and rate -- that differs among the individual studies -- on the distribution of impurities (Bartels-Rausch et al., 2014; Hullar and Anastasio, 2016), these results clearly show the tendency of μm sized features dominating at the air-ice interface. In the dominant presence of nano-inclusions, we would also expect the deliquescence to occur at a lower temperature. This was not observed in our experiments, suggesting the absence of nano-inclusions in the experiments presented here in the interfacial region. Please note, that the NEXAFS spectroscopy presented here probes an area at the interface of the sample with a diameter of about 500 μm . As the spectroscopy is selective to chlorine, we have no information about the fraction of brine versus ice in the probed part of the sample.»

How certain are we that spectrum 3D is not in fact a combination of brine and solid chloride phase? Well, we can't exclude the presence of small amounts of brine in neither sample (D and E) based on the X-ray absorption spectra. In the manuscript, we tried to argue for the

existence of hydrohalite as main phase rather than the absence of brine. We will carefully reword the manuscript to make this clearer. Thank you for pinpointing this shortcoming. Further, we will add a paragraph explicitly mentioning the possibility of small amounts of liquid. This is fully consistent with the current argumentation and conclusion as one might expect micropockets to show a size distribution resulting in a small fraction of pockets being small enough to stabilize liquid at a given temperature.

Indeed, spectra D and E show a small increase in intensity starting at 2823 eV which could be consistent with a contribution of liquid brine as spectrum B (brine) shows such a feature, but not spectrum F (hydrohalite). The spectrum shown in 3F was derived in absence of ice and at a partial pressure of water where brine -even at very high concentration- is not stable. The following graph shows results from a linear combination of spectrum F and spectrum B and a comparisons of the resulting spectrum to spectrum D (left graph) and E (right graph).



A linear combination of 10% B (brine) and 90% F (hydrohalite) reproduces the spectrum D indeed quite well. This clearly illustrates that we cannot rule out small amounts of brine in that sample. For spectrum E the situation is different. If we attempt to match the intensity of the features at 2825 eV and 2829 eV, a combination of 60% F and 33% E gives best results. However, this linear combination does neither match spectrum E at 2823 eV, nor at around 2835 eV. We assign this mainly to an insufficient quality of spectrum B (as detailed in the manuscript) and therefore prefer not to present this analysis in the manuscript. However, we will mention the possibility of small amounts of liquid brine and that the spectra do not rule this option out. Thank you for pointing this out and apologies for appearing so black and white.

We will update the discussion of the manuscript to make this clearer:

«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. Secondly, ...»

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?

Because beamtime is rare and thus expensive, we have not recorded a Cl K-edge NEXAFS on a NaCl free surface. One would probably sample traces of chlorine impurities, but I question those being intense enough to give a relevant and significant signal. Note that this study was done with molar quantities of chloride.

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 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?

Well, we started in all experiments with dry NaCl as water was pumped away in all samples when introducing the sample into the experimental set-up. Water was then dosed from the gas-phase forming brine and ice once the RH was sufficient high. The sample in our set-up is mounted vertically, which limits the possibility to sample liquids. In this work, the trick was to stabilize the liquid brine with the ice matrix by probing brine-ice binary mixtures. The only spectrum we have is that of brine at 259 K, the equilibrium concentration of which is 3.5 mol l⁻¹. To make this clearer, we have added a paragraph to the introduction when discussion the phase diagram there and modified Figure 2:

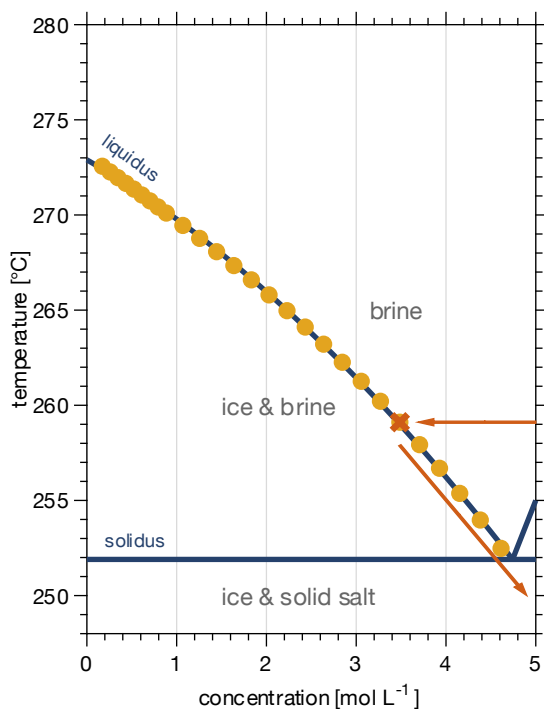


Figure 2: Phase diagram of the NaCl-water binary system. The data show the freezing point depression of sodium-chloride solutions (yellow filled circles) and give the concentration of an aqueous sodium chloride solution in equilibrium with ice in the temperature range of 273 K to

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).

«The focus of this work was to experimentally observe phase changes of sodium chloride below the eutectic temperature. A typical experimental procedure started with a dry sample of anhydrous sodium chloride (halite, NaCl) which was exposed to increasing gas-phase water at constant temperature of 259 K. By absorbing water from the surrounding air, a phase transition from the solid salt to a liquid solution (deliquescence) took place. Upon increasing the gas-phase water dosing further (Fig. 2, red arrow) ice crystallised and a two-phase system of ice and brine occurred (Fig. 2, red cross). After probing the sample at this position in the phase diagram (see below), temperature was lowered and the dosing of the water-vapor adopted to move along the liquidus line to below the eutectic temperature to perform additional measurements. During this cooling period, salt concentration and volume of the brine changes. Such changes with varying relative humidity (hygroscopic growth) have long been discussed for aerosol in the troposphere.»

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),305iA~ 310,(2020)).What do the authors believe that may lead to the large hysteresis?

We like to stress that nucleation is a stochastic process and therefore variation in the freezing point are expected. Further, freezing rate and amount of salt will play a role: Here we come back to the location of the brine. Depending on the concentration the size of brine batches varies and thus the formation of nano-pockets with lower freezing points due to surface curvature of the pockets is more or less likely. We address this now in an expanded paragraph and hope this is clearer:

This difference in crystallization temperature may reflect the stochastic character of freezing, as already noted by Koop et al. (2000a) when discussing the scatter in their data. The precise crystallization temperature is also influenced by freezing rate, concentration, and the availability of surfaces (Bartels-Rausch et al., 2014). 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.

We judge the concentration of humic acid used in Chakraborty too high to explain the hysteresis in the data by contamination. We have added this study when discussing the impact of organics on freezing:

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 their presence impacts the microphysics and thus reactivity of salt particles towards ozone (Edebali et al., 2019). Further, {Chakraborty, 2020} has shown a depression in hydrohalite precipitation temperature in humic acid – sodium chloride mixtures.