

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 #3

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Bartels-Rausch et al. present an original piece of research, investigating the phase changes in the NaCl-water binary system by measuring NEXAFS spectra across the chlorine K-edge when varying the temperature- and relative humidity conditions the particles are exposed to. The assignment of the three basic spectra types recorded for anhydrous NaCl particles, aqueous NaCl solution droplets, and the first-time measurement for hydrohalite, are convincing. I do not have any major concerns regarding the scientific content and quality of the manuscript, but I would strongly encourage the authors to improve to some extent the way of presentation of the data, and thereby better “guide the reader” through the various parts of the article.

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Major comment:

All the while reading the section “NEXAFS of brine, halite, and hydrohalite”, I kept wondering how exactly the experiment was carried out, i.e., what was the actual trajectory in the T-RH space, how exactly was the freezing of the NaCl solution droplets induced, how did you move along the ice/NaCl(aq) equilibrium line, how was hydrohalite without ice (Fig. 3F) formed? All these experimental details are only provided in later parts of the article (e.g. line 348ff, line 442ff). I see some good reason for the chosen manuscript structure, i.e., that you first want to describe the NEXAFS spectra, discuss some technical aspects like spectra quality and reproducibility, compare your measurements with literature spectra - and then later discuss the exact formation conditions for hydrohalite and the atmospheric implications based on the T-RH trajectory. But having a better general idea of the experimental procedure before reading the section with the NEXAFS spectra would be in my opinion a clear improvement regarding the clarity of presentation. One suggestion would be the following:

On line 84, you introduce the NaCl-water phase diagram, but describe it with some “hypothetical” trajectory, starting from a sample below 251.9 K and then increasing the temperature. But why not discuss the phase diagram with a “proper” trajectory from your experiments, which could be schematically depicted in Fig. 2 – meaning you start with an aqueous NaCl solution droplet, induce some supercooling to nucleate ice, and then move along the liquidus curve towards the eutectic and below, to investigate at which point hydrohalite precipitates. This is also the trajectory during which most of the spectra shown in Fig. 3 (B – E) were recorded (apart from the anhydrous NaCl, A, and the “ice-free” hydrohalite, F. At the end of the introduction or at the beginning of the “NEXAFS of brine, halite, and hydrohalite” section, you should then include a paragraph and inform the reader about the general structure of the manuscript, i.e., that you want to disentangle the detailed description of the NEXAFS spectra of the three species (shown first) from the detailed analysis of the phase changes when moving in the T-RH space (shown later). Please also number all section and subsection headings

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correctly.

Additional comments:

1) Regarding line 88 and 112: Isn't 251.9 K the ice-hydrohalite eutectic, and shouldn't ice and $\text{NaCl}\cdot 2\text{H}_2\text{O}$ be the energetically favored phases below that temperature?

2) Line 279/280: "249 K in the presence of ice and at 244 K in the absence of ice": When reading this sentence for the first time, I was also wondering whether spectra 3E and 3F were from the same trajectory and asked myself how the experimental procedure could have been – it is only explained much later (line 441ff). You should include here at least a short description of how the particles from spectrum F were generated.

3) Line 337: Here starts the detailed discussion of the phase behavior of the particles in the T-RH space. I would also appreciate an introductory paragraph describing how this section is structured and what different aspects are discussed. Otherwise, the reader may quickly lose track of things. For example, the heading "Liquid below eutectic and nucleation" in line 347 comprises a very long section that could be divided into various subsections. In the headings, you could also be more specific what you mean by "nucleation", nucleation of ice or the precipitation of hydrohalite.

4) Line 353: Can you please quantify "modest" supersaturation – did you need to reach the homogeneous freezing limit for aqueous solution droplets (Koop et al., 2000b) or did the surface catalyze heterogeneous ice nucleation?

5) Line 442, regarding the trajectory when recording spectrum 3F: Could you please elaborate a bit more on the idea and temporal order behind this trajectory (Fig. 4C), I did not quite understand how the procedure was – did you again try to cool a NaCl droplet along the liquidus curve but without inducing sufficient supersaturation to nucleate ice? And then at about 244 K reduced the RH to 59% to induce the crystallization of hydrohalite? And then increased RH back to 73%?

Technical corrections:

- 1) Doesn't the title sound a bit awkward? Maybe better: "Investigation of interfacial supercooling ..." or "... NaCl solutions studied by X-ray absorption spectroscopy"
- 2) Line 86: "shows a part of the phase diagram"
- 3) Line 109: "in equilibrium with ice"
- 4) Line 115 – 117: Very long sentence, please split into two.
- 5) Line 138: "nitrate and chloride form solvation cells"
- 6) Line 173: "and with a pass energy"
- 7) Line 186: "take-off angle of detected electrons (?)"
- 8) Line 220: photon energy in eV
- 9) Line 240: Br- (superscript is missing)
- 10) Line 338: "the hydrohalite"
- 11) Line 353: maybe better "supersaturation"
- 12) Line 355: maybe: "and is thus a sole function"
- 13) Line 411/412: This is a pretty nested sentence, please re-phrase.
- 14) Line 416: "in larger patches/inclusions"
- 15) Line 444/445: The sentence seems incomplete, it also misses the point at the end.
- 16) Line 450: Fig. 3A
- 17) Line 462: check super- and subscripts

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

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