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Interactive comment on "The Morphology of Ice and Liquid Brine in the Environmental SEM: A Study of the Freezing Methods" *by* L'ubica Vetráková et al.

Anonymous Referee #1

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– General comments –

This paper presents a logical series of well-designed experiments which address a significant concern when studying the behavior of solute-containing ice samples prepared in a laboratory. Additionally, the results suggest additional experimental methods, and can be applied to behavior of natural systems in the cryosphere. The work is of high quality and is well presented, both in written form and visually. The use of Supplemental materials is particularly thorough and commendable. The work is publishable in its current form. However, I believe it can be improved either by clarifying or elaborating some specific points, listed below.

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Discussion paper

– Specific comments –

Line 113: The molar concentration of typical seawater is at the upper end of the experimental range of concentrations used here, and the authors do an excellent job discussing relevant concentration ranges in Line 583 ff. I believe it would aid the reader to have this concentration information presented earlier in the work, but this may be a matter of personal preference.

Lines 120-137: Did the authors have any suspicions or intentions on how each freezing method would cause the solutes to be organized in the sample? If so, it would be helpful to include that information here, even if (actually, especially if) those expectations were later found to be untrue.

Lines 138-141: While it makes sense to protect the surface from sublimating, how can the experimental procedure ensure the sublimation reveals only the original ice surface? Is it possible the ice surface is also sublimated to a certain degree, as subsequent experiments suggest? If so, what impact would this have?

Line 218: It is interesting that the surface became flooded with brine over the course of the procedure. How long did this take? Do you have a hypothesis what physical process would explain this?

Line 322-323: It may be useful to discuss the uncertainties this introduces into the analysis.

Line 315 ff: The idea of surface coverage is an interesting one. I think I understand the limitations of the technique, and I agree it is unfortunate the depth of the brine layer cannot be determined. However, is it worth including even some rough calculations of the total CsCl mass present in the sample, and determining if the freezing method assumptions are supportable? For example, you could calculate the surface area of the brine layer and assume it is present to a depth of 1,500 nm (the ESEM interrogation depth); does that volume account for all the CsCl, or just a tiny fraction of it?

As the authors (and some of the cited literature) suggest, assumptions about where freezing methods place solutes can be very speculative; any opportunity to constrain this information would be welcome.

Line 329: I'm not convinced the seeded sample would grow from the exposed surface downwards. Why wouldn't crystallization be favored at the basal surface, where presumably maximum heat transfer was happening and the droplet temperature was slightly lower?

Line 341-343: Was the droplet used here the same droplet presented in Figure 2b? If it is or if it isn't, I would clarify this point in the text. If it is a different droplet, what was the surface brine coverage for the droplet in 2b? This comparison might give the reader some idea of the variability in the system. Section 3.3.2 discusses surface coverage for the 0.05 M sample; while I understand it represents additional work, it may be worth at least tabulating surface coverage for all 9 samples presented in Figure 2 as a Supplemental figure.

Line 356-359: This, to me, is an interesting and important finding. As a suggestion, would it make sense to include the relative brine volume versus temperature (based on the phase diagram) as a second line on Figure 4, or add an additional scale on the right hand side indicating relative brine volume? This would allow a more direct comparison between brine surface area and brine volume.

Line 381-383: I'm a bit confused by the assertion that the brine volume has increased dramatically. You have previously stated the experimental method cannot evaluate brine volume, only surface area coverage. What data supports the idea that the brine volume has increased dramatically? Is it possible the brine volume is unchanged, and the brine has simply spread laterally? I would suggest addressing this uncertainty in the paper.

Line 432ff: While reading the first paragraph of this section, the question that came to mind was, "Would ice sublimation also explain the apparent motion of grain boundaries,

as the surface ice erodes?" a possibility I'm glad to see discussed in lines 486-490. I would suggest considering rewording some of the introductory statements of this section to acknowledge the motion is apparent, and may be an experimental artifact, not "true" motion. Do you have a sense how quickly sublimation occurs off the ice surface? The fact that the surface coverage of CsCl stays the same suggests sublimation is not happening on a timescale relevant for the apparent boundary movement, but an explicit reference to the amount of time required for sublimation (perhaps in section 3.4) would be welcome. It may be possible to combine the apparent lateral motion of the grain boundaries with a known sublimation rate to estimate the angle of the grain boundaries relative to the ice surface. If all the calculated angles are shallow, which would be geometrically unlikely, the finding would support the idea that the grain boundaries are actually moving and not just appearing to move.

Line 441: If it's easy to do, I would suggest adding text to the movie (Figure S1) including a timescale, or a caption stating the overall elapsed time in the movie. Otherwise the timescale is indirectly available in the caption for Figure 6.

Line 512: This line seems to suggest the method of freezing a droplet using a seed crystal should exclude impurities to the surface of the droplet during freezing. However, Line 329 suggests the opposite, that the droplet would crystallize from the surface downward. I suggest reconciling these two statements (or clarifying them if I have misunderstood either), or discussing it as an uncertainty.

Figures 744-749: This is a useful finding. It is worth noting that in at least one other related work, the same investigator suggested crushing an ice sample would preferentially expose impurities because the ice would cleave "along defect sites such as veins and pockets" (Kahan et al., 2010). If the research presented here can be used to address this issue as well, and it appears to me it could, I would suggest the text be modified accordingly.

– Technical corrections –

Line 266: Figure 21a should read Figure 2a. Line 373: Suggest that “expected” is a better word choice here than “expectable”. Line 672: I think “special” should be replaced by “spatial”. Line 729: I think that “expected” is a better word choice here than “expectable”. Line 744: “Figure 2-7” should be “Figures 2-7”. Line 769: I believe the correct temperature here should be -16 °C, not 16 °C.

– References –

Kahan, T. F., Zhao, R., Jumaa, K. B., and Donaldson, D. J.: Anthracene photolysis in aqueous solution and ice: Photon flux dependence and comparison of kinetics in bulk ice and at the air-ice interface, Environ Sci Technol, 44, 1302-1306, 10.1021/es9031612, 2010.

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