Review of manuscript tc-2019-13

by Sönke Maus

This is a review of the manuscript *The Morphology of Ice and Liquid Brine in the Environmental SEM: A Study of the Freezing Methods* by L'ubica Vetrakova et al.

Below I cite from the Cryosphere Discussions manuscript tc-2019-13 in *italic font*.

I Summary

The paper presents an analysis of images of ice samples with an environmental scanning electron microscope (SEM). All samples stem from laboratory freezing experiments of CsCl solutions, with different CsCl concentrations and different freezing conditions. The article is well written and structured into the sections 1.Introduction, 2. Methods, 3. Results and discussion, 4. Relevance to previous observations. Based on the results and discussion the authors conclude: *The findings thus quantify the amounts of brine exposed to incoming radiation, available for the gas exchange, and influencing other mechanical and optical properties of ice. The results have straightforward implications for artificially prepared and naturally occurring salty ices.*

I find the manuscript interesting, well written and to some degree worth publishing, as there is limited information available about the distribution of solute in ice formed in the environment, especially with the noted spatial resolution of 5 μm. However regarding the relevance for ice in the environment (section 4.) and the *straightforward implications for naturally occurring salty ices* proposed by the authors, I strongly disagree. While the paper puts many observations in the light of possible processes and phenomena described in the literature, the discussion is very vague. Some quantitative results are given but not compared to theories. It is neither clearly presented which of the observed ice-brine pattern are created by the method, and which relate to the freezing process. The following aspects illustrate my major concerns/ the weaknesses in the study:

I. While the authors apply different freezing methods, it is not clear to which degree these resemble natural freezing conditions. For (I), freezing of a filtered (0.45 μm) solution, in a silicon sample holder rather high supercoolings were likely to exist followed by unidirectional freezing. This may resemble nucleation in the atmosphere, yet filtering, silicon holder and unidirectionality introduce considerable differences. Method (III) and (IV), freezing within liquid nitrogene, is easy to perform but may lead to rather artificial freezing conditions. Hence only (II) seeding a slightly supercooled droplet with ice crystals resembles natural conditions. In general, the freezing of solutions is a morphological stability problem for which the pattern depends on temperature and solute gradients (that may be derived based on the degree of supercooling) and the solidification velocity. None of these boundary conditions is documented or monitored.

II. The technique only yields information about the distribution and pattern of ice and solute at the sample surface. For these brine films the thickness remains undetermined. The brine film coverage on the surface may not only depend on its (unknown) thickness, but also on processes in the interior of the samples. E.g. noting that brine will be expelled from the interior, the surface to volume ratio or specific surface area of samples can be expected to be a highly relevant parameter. However, sample size has not been varied during the experiments. Another important property that affects expulsion of brine is the bulk density of an ice-brine aggregate. Some results obtained here (e.g., line 339-346) should be discussed in terms of the non-linear behaviour of the expansion coefficient of an ice brine-mixture that may take positive or negative values depending on solute concentration and temperature (e.g. Timco and Frederking, 1996). Overall, the discussion of brine coverage is incomplete and speculative - see specific notes below.

III. For all samples the author create (line 138) a thin layer of ice from condensed moisture on the samples surface, to protect the surface from sublimation. It should be tested how this thin layer of ice might affect the surface brine pattern: could the layer be porous and imply suction of brine into it? Does the creation of the layer change the surface temperature? May it lead to dissolution of ice in surface brine? How is the time determined at which the thin layer has sublimated? The behaviour of this layer needs to be described better, possibly through time-series of images showing its sublimation. In general, on the one hand there appear surface features that change during the imaging due to sublimation (grain boundaries), while others do not change (humps). On the other hand, the humps form during sublimation, while the grain boundaries have formed earlier, during freezing. It should be distinguished better which morphological parameters are forming during the freezing process and which during sample preparation and observation.

IV. Also the described dynamics of ice surfaces (3.5) appears to be related to sublimation during imaging and it is not clear for which process in natural ice the experiment with the present scales (time, sample size) is relevant. The description of these results and its discussion remain qualitative. Grain boundary migration in a temperature gradient is discussed, but no estimates of actual temperature gradients and migration velocities are given. It is also mentioned that tilting of grain boundaries with respect to the plane of sublimation might create an apparent rate of grain boundary migration, but no tests were made to verify this. The author's conclusions are vague: *We are, however, uncertain if the reason for these unusual dynamics of the frozen surface consists in one of the previously described conditions, both of them, or a completely different process.*

I would like to recommend the manuscript for publication, after these points have been adressed. The paper may also be improved by focusing on facts and validation of theories, rather than discussing a wide range of natural systems for which it does not provide new evident insight.

II Specific comments

1. Introduction

L29 *straightforward implications* –> I would hardly call the results/conclusions as straightforward

L103–104 *and the location of sea water brine on sea ice can be inferred* –> sea ice is a rather different system, involving natural convection, unidirectional growth, a freeboard, the presence of snow, etc....

L138–141 –> This process of thin layer application and sublimation needs to be better shown/validated (VI. above)

2. Methods

L146– (2.2.) –> Here I would expect information about image resolution (mentioned later as 0.5 μm in the results section.

L163–168 *We estimate that the surface of a frozen sample is up to 2 ℃ warmer compared to that of the sample holder...*–> The crystallization temperature you observe is -25℃ which, allowing for some uncertainty, is within the eutectic temperature range you mention from other sources for aqueous CsCl solutions. There is thus no need to assume a warmer surface. Why is it assumed/likely then?

L170– (2.3.) –> The manual threshold segmentation process needs to be described better. What is the uncertainty in brine coverage related to segmentation uncertainty?

3. Results and discussion

L236– (table 1) –> These results are interesting. To understand their relevance for natural freezing processes they need however to be related to an estimate of freezing rates. Please consider model and other observation approaches to obtain such an estimate. Also, I suggest that for the freezing method IV, capsules in liquid nitrogen, the pattern shown in Figure 9 should be given here - see next note on L274–277. It would be further helpful to provide a table comparing the basic information for all methods (directionality, temperature difference, sample size, surface of observations).

L258–265 –> Crystal orientation is not retrieved by the imaging and its discussion is confusing. Supercooling and freezing rate alone explain different crystal sizes.

L274–277 *Therefore, based on analysing the crystal sizes, we can infer that the spontaneous freezing of the non-seeded droplet supercooled to about -16 ℃ occurred at the highest freezing rates experimentally attempted in this.*–> Based on the facets in Figure 9, I would rather suggest that freezing in LN2 with method IV was faster than in method I. Next, the freezing rate of droplets sprayed onto LN2 may have been be largest overall, with the difference that this interface has not become morphologically unstable. Such a planar growth can be expected based on morphological stability theory for high growth rates (e.g., Sekerka, 1973; Coriell et al., 1994).

L309– (table 2) –> I would skip one decimal, if the image resolution is roughly 0.5 μmİt would be interesting to see statistics for higher temperature - this is discussed in detail for the brine surface coverage. Also, and estimate of salt content based on the surface grooves should be presented, to illustrate if pattern in the interior need to be different to reflect the nominal salt content.

L356-359 –>*Even though it is not possible to evaluate the volume from the microscopic images, we documented well that the brine surface coverage had risen four times during the warming, becoming much larger than the coverage implied by the phase diagram.*–> During cooling the coverage changed from 80 to 40%, consistent with the phase diagram. This indicates that thickness changes are sometimes involved and sometimes not. and should be discussed.

L379-381 –>*The results of this temperature cycling experiment indicate that, as the ice from the surface was required to melt during the heating in order to double the volume of the brine, a formerly inaccessible portion of the brine (restrained due to being trapped below the surface layer of the ice) surfaced.*–> The results can also be interpreted in terms of a thinning of the brine layer.

L395-397 –>*It cannot be excluded that the sample surface was several degrees warmer than the holder due to the effects of the electron beam; purging relatively warm gas through the specimen chamber.*–> Could you please present some numerical estimates?

L405-409 –>*Thus, the temperature increase with the subsequent spread of the brine on the surface may lead to the surface darkening, resulting in higher solar radiation absorption and further increase of the temperature.*–> The effect of a brine film on sea ice albedo has to my knowledge not been discussed yet - rather the number and size of inclusions in the bulk ice are relevant.

L432–434 (and whole 3.5.) –>*The dynamics of the frozen samples' surfaces could be observed even at -23 °C . The CsCl brine-filled grain boundaries were not static: their positions changed swiftly in time. Interestingly, the positions of the humps on the ice surface did not change accordingly.* –> The two explanations (i) migration of grain boundaries in a temperature gradient and (ii) exposure of inclined grain boundaries during surface sublimation are not so expected and their discussion is lengthy. Could they be validated by some data and estimates (possible temperature gradients, sublimation rates, internal sample observations, etc...)?.

L526-528 –> 10 μm indicates rather fast freezing - see note on freezing rates above.

4. Relevance to previous observations

L578–591 –> It is corrrect that the range 0.005 to 0.5M solute concentration is found in nature. However, the classification into relevant salinity regimes and processes in nature sounds a bit artificial: sea ice can have 0.05 M solute content (brackish ice, Baltic Sea ice), and for salt concentration near roads I would expect a large range depending on environmental conditions. Surface snow on sea ice may be much more saline than 0.005 M, and a range of 0.01 to 0.1 M is more representative.

L592-595 –> *The principal finding presented within our study is embodied in the very strong sensitivity of the ice-brine morphology and brine distribution to the freezing method (Figure 2, 3). Even for identical solution concentrations, the method and direction of freezing strongly modify the appearance of the ice surface morphology.*–> These principal findings are not new.

L601-610 –> It is not clear that natural convection played a role for solute redistribution within the different freezing experiments, as freezing was either fast or upwards. The comparison to sea ice formation and desalination is thus not useful here. While directionality is important, it is not due to natural convection.

L662–664 –>*Apparently, the amount of the brine on the ice surface was not sufficient to fill the groove around all the ice grains due to low brine concentration and/or the freezing method concentrating the brine towards the interior of the ice matrix*–> As mentioned, directionality, local brine expulsion and bulk ice-brine density changes are relevant here and this statement needs to be validated.

L678 –>*frozen aqueous solution (without added salt)*–> Do you mean frozen (almost pure) water?.

L710–712 –>*The present study suggests that the remaining solute is likely to be found in not only the puddles of the highly concentrated solution but also, the veins or grain boundary grooves threading the crystals.*–> This is not a new observation. To produce something new you should at least give some estimates of the solute contained in the veins/grain boundaries, based on your observations.

5. Conclusion

L759 –>*amount of brine*–> You have not determined the amount, just the surface coverage.

L766–767–>*The presented micrographs clarified the possible porosity and pore microstructure of sea ice.*–> The relevance of the freezing conditions/sample sizes for sea ice has not been demonstrated. Regarding microstructure of sea ice there are textbooks that 'clarify' this much better (e.g., Weeks, 2010; Shokr and Sinha, 2015).

L768–770–>*From the ice crystal sizes we infer the actual 769 freezing rates*–> In fact no freezing rates are inferred. Also, freezing rates are very likely largest for the LN2 freezing (III and IV) - see discussion above.

References

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