

Interactive comment on “Direct visualization of solute locations in laboratory ice samples” by T. Hullar and C. Anastasio

Anonymous Referee #2

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I found this paper interesting and easy to read, and agree with the authors that it is important that the effect of sample preparation method is considered when interpreting the results of analyses on laboratory samples. This article is relevant to The Cryosphere and its readership, demonstrating the results of a laboratory study on experimentally grown ice.

I would recommend that this article be published, after minor revision. I found several areas where I would have appreciated more information and/or discussion on both the choice of sample preparation methods, and the discussion of results. I have split my recommendations into General comments/Specific comments and Typographical comments.

General comments

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Introduction/Methods

From the introduction as it is written, it is unclear to me why these three sample preparation methods have been chosen. The authors suggest that their results are relevant to solute positions in snowpack, but the sample preparation procedures here - freezing directly from a liquid solution to a (presumably crystalline) solid - do not seem to be immediately comparable with snowpack formation. Additional discussion of snowpack formation mechanisms, and/or justification of these sample preparation methods, would improve the paper, clarifying the reasoning behind these experiments. (Have these sample preparation methods been used in previous experimental studies? Does the resultant structure represent snowpack well?)

Why were CsCl and Rose Bengal chosen? Are these solutes present in real snowpack? If not, what is the reasoning behind using them, are they expected to behave like the real solutes? (And what is the evidence (with references) for this?)

The samples frozen are of different sizes (Table 1). Is it possible to compare samples of different volume? Will the greater volume of the Freezer and LN2 samples not also affect the freezing behaviour?

If I understand correctly, you make the assumption with your calibration curve that the effect of CsCl on the radiodensity of water and ice is the same. And so all results based on this method are dependent on this assumption. What is the support behind this assumption? (Page 7).

Discussion

Were there any measurements of the grain size/shape of the ice in these samples? And the position of the pores/solutes with respect to grain boundaries? Might the grain size (likely controlled by the freezing temperature and subsequent annealing) play a role in the position/size of solute pockets?

The experiments are carried out with a high concentration of solutes (with respect to

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inland snows). Additional discussion as to the impact of this higher concentration on the results would be enlightening – will a lower concentration have similar results?

I find the result that solutes are often associated with air bubbles in the Freezer samples, but less so for Freeze Chamber samples, very interesting – do you have any ideas of potential mechanisms which would be working differently in the two situations?

Specific comments

Page 3 Line 27. Define PAH at the first usage.

Page 4 Line 4. “the cage effect at a given temperature”. It is unclear what the cage effect is, an extra sentence explaining this would be helpful.

Line 9. Not clear what is meant by “compartments”

Page 5 Line 4. You have given example of qualitative results, (visual), is there an equivalent example for quantitative?

Line 17. What is the (potential) effect of the elevated concentration of solutes?

Page 6 Line 4 Did you consider the effect of the annealing time? “At least 1 hour” – were some samples annealed for much longer? What effect might this have/did this have on the solute/pore distribution?

Line 5 - You specify the thickness of polypropylene vial walls, you should also specify the glass wall thickness. Is this the same thickness? If it isn't, any thermal consideration as to the differences between the samples frozen in glass and plastic is not only due to the difference in thermal conductivity between glass and plastic, but also the thickness. Any difference between glass and plastic vials (even though there likely will be) cannot be evidenced by these experiments if the thickness is not the same.

Line 28 “small amounts of sample” – can you quantify this?

Line 29 “very little sample in contact with air.” – similarly, is this quantifiable?

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Page 7 Line 25 – the process of solute rejection on freezing has been seen in several systems, including papers earlier than the referenced Cho paper. I would suggest further literature should be included here (and possibly in other places) to avoid over-reliance on this one article.

E.g. starting points for the sea ice system: Lake and Lewis 1970 *JGeophysRes* 75 3
Wettlaufer et al *J. Fluid Mech.* (1997), vol. 344, pp. 291-316. Other systems (metals):
Worster *J:Fluid Mech.* (1992), vol. 237, p p . 649-669

Page 8 Line 2 – what is the temperature effect on the solubility of CsCl? I would anticipate the solubility to decrease with a decrease in temperature – so the value you quote here at 20C would not be appropriate at -10C. A difference in solubility will change the calculated masses.

A quick literature search provided me with this, but there are probably other options in the literature: Jiang et al, 2003 *Indian Journal of Chemical Technology* Vol. 10, 391-395

Line 5 – are there no other effects on the radiodensity than the concentration of solute? What about temperature?

Line 14 – reminder of the value used for pure ice radiodensity would be helpful here.

Line 18-21 I find this sentence complicated to understand – is there a better way of presenting the four domains – in particular the distinction between 2-10% and 10% LLRs is not clear to me without rereading several times.

Page 9 Line 2 – can you put a number on the amount of solute “lost” in this process? Quantitative idea of the effect that the threshold has?

Line 4 – why only carry out this calculation for some samples? Why not all?

Line 14-16 – The different thermal conductivities between water and glass has no impact here – even if you had two materials with the same thermal conductivities, the sample would still freeze from the outside in. Suggest suppressing the reference to

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thermal conductivity.

Suppl Fig 1 - The directionality of bubbles in your Supplementary Figure 1 also seems to support freezing from the exterior of the sample – e.g. Carte 1961 talks about direction of bubble formation in a temperature gradient (Proc Phys Soc 77, <http://iopscience.iop.org/article/10.1088/0370-1328/77/3/327/pdf>), I'm sure there are other references as well.

Line 21 can you quantify the size of the bubbles in the two figures?

Fig 2c – adding a vertical line and label at the central point of the air peak would make the histogram easier to interpret, with an equivalent label for the pure ice peak at $V_{LLR}/V_{VOXEL} = 0$.

Page 10 Line 2 – this would read better if the sentence was inverted to mention log scale before the “clearly...” comment. E.g. “Taking into account the log scale... the volume is clearly less...”

Line 12 – What are you basing the expectations of freezing speed/direction of heat removal/position of solute inclusions on? Need a reference (or more explanation of the reasoning).

Line 21 – can you find a more technical term than “blow up”? –e.g. magnification/detail...

Line 22 – do you have a mechanism/an idea for the link between solute pocket position and bubbles?

Line 24 – The use of the word “identically” here is disingenuous, the samples are not produced identically (I agree the solutions may have been). But as the aim of the paper is to demonstrate the differences when samples are produced using non-identical methods, it would bring this message home more convincingly if you avoid referring to differently frozen samples as “identically” produced. (There is another place this happens later on as well – Page 14, Line 25).

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Line 29 – “blow up” – as above.

Page 11 Line 1 – “surprisingly different” – are these morphologies repeatable? To me it is not that “surprising” that a difference in freezing front gives a difference in solute distribution – maybe a different word than “surprisingly” could be used – I agree that it is interesting that this happens and that you have been able to observe it. Also, you are comparing samples of different size, this will cool/freeze differently regardless of environment.

Line 10 – Why would a freezing front process only affect the solutes and not air bubbles? I would be interested in an expansion on a theory for the mechanism for this.

Line 23 – “No air bubbles...” I don't agree there is nothing in FigS6 – I see one inclusion/something in Fig S6.

Fig 3g – (g) label appears twice. Labelling of individual curves is unclear.

Line 28 – how does histogram show that voxels contain concentrated solutes?

Page 12 Line 5 – If the effect is barely visible, does that necessarily mean it is not there/definitely not important?

Line 12 – where are the concentrated solutes in Figure 3f? It is not clear in either Fig 3f or FigS9 where these are – there seem to be only air bubbles.

Line 17-19 – this sentence is poorly worded (“much different than ...”) . Can you expand on the reasons why the ice matrix would be modified? There needs to be a reference for this.

Line 24 – precipitates in LLRs? – but these LLRs are not visible in Figure 3f or Supplementary Figure 6? So how could there be precipitates within them?

Line 25 – it would improve the flow of this section if the discussion about the histogram was combined with earlier discussion (Page 11, line 7-8) as the earlier part seems truncated and unfinished.

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Page 13 Line 22/ Fig S10 – do you only have replicates for the freeze chamber? It would be interesting to have the equivalent histograms for each method.

Line 24 – You cannot say that the “two variables [freezing method and solute] are the primary factors influencing ice morphology” as you only change these variables in your experiments, so of course they are the two primary influencing factors here.

Page 14 Line 1 – what are the errors on the VLLR/VVOXEL = 2-10% for the two methods? These would be useful to determine whether the factor of 2 difference is reliable – as a difference between 0.003 and 0.006 doesn't seem large (but may still be significant).

Line 24 – If I understand correctly, LLRs are present when there is solute extruded from the crystallising ice – so why do you have LLRs in this (pure ice) sample?

Line 25 – use of “identical” confusing again.

Line 29 – “while the reason for this morphology is unclear...” the morphology of bubbles, and the effect of a temperature gradient, has been studied previously – e.g. Proceedings of the Physical Society, Volume 77, Number 3 <http://iopscience.iop.org/article/10.1088/0370-1328/77/3/327/pdf>.

Page 15 Line 15- Where are the “elongated solute inclusions” in Figure S14. They seem no more or less elongated than the air bubbles.

Figure 5 – is this a vertical slice? Specify this in the caption. Also - “along the direction of the temperature gradient” – specify which direction – i.e. from colder to warmer.

Page 16 Line 16 – a reference for “melting into the bulk ice” is required (e.g. Movement of brine pockets by salt diffusion - Notz D and Worster MG (2009) Desalination processes of sea ice revisited. J. Geophys. Res. Ocean., 114(5), C05006 (doi:10.1029/2008JC004885))

Line 20 – what is the concentration of solutes in clean polar samples? This should be

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mentioned in the introduction as well.

Line 21 – “significant impacts” - I think significant should only be used in statistical context, so here “important” or similar would be more appropriate. There should also be more discussion on how this assumption that a lower concentration will have the same effect was made.

Page 17 Line 3 – this sentence (“Cesium chloride...”) starts abruptly, would be improved with an introductory couple of words.

Line 14-15 “Our work here can help guide further investigations to understand the driving forces shaping snow and ice structures in the natural world, as well as the rate of chemical reactions in snow and ice.” – it is not clear to me how this work helps to understand the driving forces etc, nor how there is any (direct) impact on studies into the rate of chemical reactions.

Line 16-19 “At the same time, our results suggest subtle changes in the preparation of laboratory ice samples can have significant impacts on the location of solutes in samples, requiring careful and consistent sample preparation to ensure meaningful results.” - this part is the important conclusion from this work.

I would therefore suggest removing/reducing/rephrasing the first half of this paragraph, and expanding on the second half.

Supplementary info

It would be more coherent if there was only one format for videos and one for images in the supplementary information.

It would be useful to have brief captions/explanations of supplementary images and videos in the supplementary information, to avoid having to search through the main text for the information.

The colours marked “orange” in the text do not appear orange in the videos (at least

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on my screens), they are yellow.

Typographical errors

Pg 3 Line 6 “to form hydroxyl radicals” Pg 5 Line7 – missing word? “was produced from...” Pg 5 Line 10 - repetition of “its” Pg 8 Line 17 “VVOXEL” should be in capitals Pg 11 (22-23) “Results for a 1.0mM CsCl sample.. are shown in Fig. 3e”

Figure 4 – the blue arrows are not visible when printed in black and white.

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