Review of tc-2014-88

This is a review of the Cryosphere Discussions manuscript tc-2015-197 *Direct visualization of solute locations in laboratory ice samples* by Theodore Hullar and Cort Anastasio.

General comments

Summary

The paper presents and discusses results from X-ray tomographic imaging of aqueous solutions frozen in small containers in the laboratory. With two solutions, cesium chloride (CsCl) and Rose Bengal solution, three different freezing methods were used: (i) freezing by putting containers in a normal freezer, (ii) unidirectional bottom-up freezing with containers placed on a cold plate and (ii) putting small vials into liquid nitrogene. The frozen samples are imaged my X-ray microtomography, mostly at a voxel size of 16 μm, to obtain 3-d greyscale images of X-ray transmission. After segmentating the greyscale images into different classes that reflect solute and air or gas content, the authors discuss these images qualitatively in terms of distribution of solute inclusions and air bubbles. The authors also perform a quantitative analysis of the distribution and content of solute in liquid like regions (LLRs) versus solute incorporated in the solid ice matrix, as well as some observations on the movement of liquid inclusions. The authors conclude that the work shows that *the structure of laboratory ice samples, including the location of solutes, is sensitive to freezing method, sample container, and solute characteristics, requiring careful experimental design and interpretation of results.* The work is proposed to enhance our understanding of solute segregation in natural snow and ice, as well as of *the air-ice interface and liquid-like regions within the ice matrix.*

I agree with two other referees that the paper is relevant for ´The Cryosphere' and its readership, and also mostly with their comments. I would like to add comments on two major issues on which the paper in my opinion needs improvement. First, I encourage the authors to improve review and referencing of the published background on ice observations and solute redistribution during freezing, to be included in the introduction and discussion of their own observations. Second, I think that there is potential for improvement in the quantitative analysis of the 3-d images, and a critical discussion of the method and results. In my comments I will give literature examples that I hope will help the authors to improve their analysis and presentation.

Main concerns I-III

I. Background - ice, freezing and solute inclusions

1. In the literature on ice physics and chemistry there are several books that include fundamental discussions of ice structure and solute distribution during freezing but none of these is mentioned. I recommend to have a look into the literature (e.g., Shumskii, 1955; Hobbs, 1974; Lock, 1990; Petrenko and Whitworth, 1999; Pruppacher and Klett, 1997), and possibly cite from there.

2. It is well known that during the freezing of saline solutions most solute is rejected into the remaining mother solution and not incorporated into the solid ice matrix (e.g., Hobbs, 1974; Petrenko and Whitworth, 1999). This fact should be more clearly

mentioned in the text. The authors for example write (P16, L13-16) *While the air bubbles remain stationary in the ice matrix, the CsCl moves, consistent with the idea that solutes are present as a concentrated liquid-like solution, which can migrate either along the boundaries between air bubbles and the bulk ice, or possibly by melting into the bulk ice itself.* Such formulation indicates that solute rejection during solidification of water is only an *idea* rather than a fact under most conditions.

3. I am also missing background literature on observations of solute inclusions in ice. For example, already Quincke (1905) has described the morphology and distribution of liquid inclusions of ice grown from saline solutions, and there is much more information in the books on ice physics mentioned above. As an example, Shumskii (1955) describes the solute distribution in ice as (p.180): 'The distance between neighbouring interlayers of inclusions in a crystal decreases with increasing concentration of impurities in the remainder mother solution; often this distance is as much as 35-45 μ with inclusions 8-15 μ thick'. Such information is certainly relevant for the discussion and interpretation of the results in the present paper.

4. An idea of the expected microstructure and potential separation of solute inclusions and air bubbles may be obtained by consulting published work based on thin section analysis of frozen solution or pure water droplets (e.g., Hallett, 1964; Rohatgi and Adams, 1967). For example, a useful information from these studies is the dependence of dendrite or plate spacing on freezing velocity: The faster the freezing, the smaller the spacing of ice plates and solute inclusions, which normally implies smaller dimensions of solute inclusions. For the present study this may affect the detectability of solutes, especially for the samples frozen very rapidly in liquid nitrogene-based freezing.

5. Earlier basic work on solubility of ions in the solid matrix as well as solute partitioning at a freezing interface (e.g., Tiller, 1963; Gross et al., 1975, 1977) should be mentioned and discussed. Such information is particularly important when it comes to the quantitative analysis and discussion - see my comments below.

6. How is the freezing point depression the authors assume for CsCl (2.7 M CsCl at -10 ℃) computed, or on which reference is it based? E.g. according to Pruppacher and Klett (1997) (p. 125, Fig. 4-12) one might expect that a value of 3.1 to 3.3 M is a more realistic value at -10 ℃. While such a change in equilibrium concentration would affect the estimates of the volume of LLR from the greyscale images, it would not affect the solute content within liquid inclusions. However, it would decrease the maxium solute content in voxels in the histogram, and thus may give hints on the proper estimation and possible rescaling of equation (1).

7. X-ray tomography of solutions frozen in the laboratory has been performed earlier Miedaner (2007); Miedaner et al. (2007) and may be compared to the present results.

II. Image segmentation and quantitative analysis of solute content and locations

1. The proposed segmentation approach is based on equation (1) on page 8 assuming 2.7 M equilibrium concentration CsCl at -10 ℃. Please have a closer look in the literature to evaluate the uncertainty of this estimate.

2. The choice of a cutoff at $LLR = 2\%$ to estimate the solute content in liquid like regions seems somewhat arbitrary. As the pure ice histogram in Fig. 2c extends to slightly above $LLR = 4\%$, rather such a cutoff would be more consistent. At least would a $LLR = 4\%$ cutoff define a lower bound of the solute content in liquid inclusions.

3. As the authors correctly point out, the solute content will be underestimated due to the possibility of mixed air and solute pixels, which may then have radio densities between brine and air, and thus be classified as ice. Can this bias be estimated? An approach to place a bound on this bias could be to count the surface voxels of the air bubbles and assume that these contain CsCl brine and air. How would this affect the results in Table 1?

4. In the histogram in Fig. 3 the maximum volume fraction of liquid is roughly 0.9. However, if calibration and equation (1) would be correct I would expect that the maximum value should at least be 1 (due to expected noise even larger), provided that there are at least some liquid inclusions that exceed the volume of a voxel with side length 16μm. While this may not be the case, I would expect that it would very likely be the case for high resolution imaging with 2μm voxel size. How does such a histogram look like, and may it be used to improve the calibration in eq. (1)?

5. According to Table 1 the solute content classified in solute inclusions is 12-35 %, and the remainder is concluded to be incorporated in the ice matrix. How does this compare to expected solubility limits in the solid? E.g., Gross et al. (1975) suggested a solubility limit of 1-2 $\times 10^{-4}$ M for HCl in the solid ice matrix. The result from the authors calculations (65 to 88% of the initial 1 mM CsCl in the ice matrix) would roughly imply a 3-9 times larger solubility of CsCl in ice. Do any studies exist that support such a high solubilty of CsCl in solid ice? If not, then this might be another indication that eq. (1) should be changed by a prefactor that gives larger liquid fractions of at least 1 at the higher end of the histogram. Again, it appears very important to present a similar analysis of high resolution images, that could solve this problem.

6. The inset in Figure 3 compares the histogram envelope around the radiodensity of ice for the Milli-Q and solute samples. It indicates that the ice peak and envelope in the histogram is slightly shifted to the right for the frozen solutions with respect to frozen Milli-Q - which is particularly apparent for the LN2 samples. Such a shift would indeed be consistent with Cs and Cl incorporated in the solid ice matrix, where they act in the same way as strong X-ray absorbers as when in liquid solution. It would be very interesting to evaluate, if it is possible to estimate the solute content in the ice matrix from this shift.

7. A statistical analysis of size distribution of slute inclusions and air bubbles would be very helpful. Such a statistics would also justify to include the results from Rose Bengal solutions, that else is given too little weight in this study.

III. Results and Discussion

1. Every paragraph in the discussion contains a reference to supplementary material, that is the discussion is based very much on the latter (S1-S16). While it is helpful to provide such material, I regard it as inappropriate to build up the discussion of a research paper on that much supplementary information. Some of this information should become part of the paper and the discussion should be rewritten.

Specific comments

P 4, L 23-25 –> *But to our knowledge this method has not been used to investigate the structure and solute locations for laboratory samples prepared under controlled conditions with specific solutes* - I would not call the freezing conditions *controled*, as neither cooling rates or supercooling in the samples were controled or measured.

P 4, L 29 –> *In this work we focus on cesium chloride (CsCl) as our solute. However, because a previous study (Cheng et al., 2010) found different solutes can affect freezing morphology and therefore may influence solute location, we also imaged ice containing the organic compound Rose Bengal.* I suppose that CsCl was choosen because it warrants a high X-ray contrast between ice and solute. Why was Rose Bengal choosen? Also, as the results presented are, except for a histogram in Fig. 3 as well as supplementary material, for the CsCl solutions, I would rather suggest to remove the few Rose Bengal results and notes, and rather present a systematic and quantitative comparison elsewhere.

P 5 L 1 –> *Cheng et al., 2010* - this is a reference to a study based on a rather different method, that yields the surface distribution of solutes/ions. There exist other studies that have shown the influence of solute on freezing pattern, for example the mentioned work by Rohatgi and Adams (1967). I cannot see that the cited paper is an argument to use Rose Bengal as an alternative solution.

P 16 L 13 –> *While the air bubbles remain stationary in the ice matrix, the CsCl moves, consistent with the idea that solutes are present as a concentrated liquid-like solution, which can migrate either along the boundaries between air bubbles and the bulk ice, or possibly by melting into the bulk ice itself* - First, I find it surprising, that the air bubbles remain stationary, because it is well established that air bubbles migrate in a temperature gradient at similar rates as liquid inclusions (Dadic et al., 2010). Second, some refererence on the process of brine pocket migration should be mentioned here, please have a look at Light et al. (2009) and the literature reviewed therein. Third, Light et al. (2009) also found migration for solid crystals, so the movement of solute is no proof for its liquid character.

P 16 L 23 –> *surprisingly* - considering earlier studies on the freezing of saline solutions I would not rate this as surprising.

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