

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

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The authors present an experimental study investigating the location of impurities in ice samples produced in the laboratory from aqueous solutions applying different freezing procedures. The ice samples containing either CsCl or 4,5,6,7-tetrachloro-2',4',5',7'-tetraiodofluorescein (or Rose Bengal) were analyzed using μ -computed tomography, where the presence of air bubbles and the concentrations of the impurities were related to the absorption of the applied x-ray radiation. The ice samples were generated by placing liquid solutions in a freezer leading to a freezing from the exterior to the interior or by freezing from the bottom to the top or by immersion freezing with liquid nitrogen. The presented results indicate important differences concerning the distribution of the impurities in different compartments of the ice samples. The authors distinguish for the condensed phase two compartments: the solid ice matrix with low

impurity concentrations and liquid like regions (LLR) with aqueous solutions containing impurities at the solubility limit of 2.7 M in the case of CsCl. The μ -CT images allow further identifying if the LLRs are located inside the solid matrix or if they are located at an interface with air bubbles. The distribution of CsCl in the ice samples are not surprising: immersion freezing leads to larger fractions of the impurities incorporated in the solid ice matrix, while the slower freezing enables a more significant formation of LLRs. These experiments constitute the first experimental evidence of the impact of the freezing method on the impurity distribution in ice samples created in the laboratory. This technique has the potential to constitute a new standard for the characterization of ice samples containing impurities that are used for laboratory experiments concerning chemical reactions in ice and snow. Such reactions are important in polar regions, where they contribute to the formation of reactive nitrogen oxides and halogens inside the snow and the subsequent release to the atmosphere. However, the exact mechanisms of the reactions and how they are modified in the different compartments of the snow or ice grains are currently not well understood and can only be studied in laboratory experiments if the impurity distribution in the samples is known. Therefore, the manuscript reports important new findings and techniques that deserve publication in The Cryosphere. Nevertheless, before the publication of the manuscript I suggest addressing the comments described below.

Comments:

Page 8: The authors propose that observed radio densities are composites of the densities of pure water ice and region with a solute ion concentration of 5.4 M, which is related to freezing point depression. This number directly affects all calculations using equation 1. How do uncertainties in the concentration translate into errors of the results? What about the error of the slope of the calibration curve shown in Fig. 1 and the errors of the radio densities for air and ice? I believe a more detailed discussion of the experimental and statistical errors and how they impact the results is needed.

The authors claim that the maximum concentration of 5.4 M in the LLR is well below

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the CsCl solubility. However, its solubility at $-10\text{ }^{\circ}\text{C}$ is not known. Are there any measurements of the temperature dependence of the CsCl solubility indicating that even at $-10\text{ }^{\circ}\text{C}$ it may not be below the assumed maximum concentration? If not, could the authors determine the solubility with the $\mu\text{-CT}$ using saturated solutions at different temperatures?

Page 8: The authors distinguish regions with LLR volumes either smaller or larger than 10 % of the total volume. In my opinion, this is only a gradual difference. What is the reason to identify these two categories?

Page 9f: According to the authors the degassing of the samples with helium leads to a reduction of the volume of the gas bubbles by 50 % compared to the air-saturated samples. I assume that degassing the aqueous samples with helium would only lead to replacing the dissolved nitrogen and oxygen by helium without modifying the gas volume. The degassing is a standard procedure for laboratory experiments. Is there any evidence in the literature that the volume of dissolved gas is actually reduced by a factor of 2 by degassing with helium? This may depend on the solubility of the gases nitrogen, oxygen, and helium. Did they author verify if the solubility of these different gases can explain such a difference in the dissolved gas volume?

Page 13: The authors claim that the obtained results were robust and reproducible. However, Table 1 appears to show only results from one sample for each freezing method. I recommend including data of all experiments (for example in an additional table in the Supplement) and in Table 1 average numbers including some statistical information to provide information on the uncertainty of the experimental results.

Table 1: It remains unclear to me how the numbers for example of the CsCl Mass Fraction are calculated. According to my understanding the observed radio densities for each voxel can be translated into a CsCl concentration for each voxel using the calibration curve in Fig. 1. With the known voxel volume the total mass of CsCl for each volume can be calculated. The sum of the CsCl mass for the three material types

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(water ice, LLR 2-10%, LLR > 10 %) would give the total mass of CsCl present in each material type. In this way an absolute CsCl mass would be obtained that can then be used to calculate fractions if compared to the total CsCl mass in all three material types. Is that the procedure that was applied? If yes I recommend presenting absolute CsCl mass for each material type instead of mass fractions.

Page 8, Fig. 2 and 3: The authors state that the radio density of air is 3996. Using this value and $RD_{ice} = 4848$ leads to a $VLLR/VVoxel$ ratio of -0.034. How is it possible that a significant number of voxels can have $VLLR/VVoxel$ ratios below this value? In fact, shouldn't be the segmentation: Radio density up to 3996: voxel with only air; radio density between 3996 and 4848: ice with air bubbles; radio density above 4848: ice with CsCl? What happens with voxels that include at the same time air bubbles and LLR and both smaller than the resolution of the voxel? Do they give an average radio density signal that let them appear as solid ice without impurities?

Page 14f: The authors describe some results of their experiments using plastic vials presenting only some videos and pictures in the supplementary material. If the authors do not present a quantitative analysis like for the experiments with the glass vials, this remains more or less anecdotal and can be deleted.

The authors present the concentrations using molarities (mol/L). Wouldn't it be better to use molalities (mol/kg) to avoid the impact of density changes on the concentrations?

I think it should be mentioned in the abstract that μ -CT was used.

There is a series of publication by Heger et al. (e.g. J. Photoch. Photobio. A, 187, 275–284, 2007 or J. Phys. Chem. A, 109, 6702–6709, 2005) addressing also the location of impurities in ice samples, but using completely different techniques. I recommend discussing briefly these studies in the introduction.

Page 3, lines 13ff: “As the snowpack consolidates, chemical compounds can remain at the surface of the crystals, or become trapped internally at grain boundaries or triple

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junctions”: I think this sentence is somewhat misleading because the mobility of the impurity is rather linked to processes at the snow grain scale and not at the snowpack scale. Thus, it rather depends on the metamorphism than on the compaction of the snowpack.

Page 3, lines 24ff: “photon fluxes can vary . . . possibly within crystals themselves.” Any evidence for this statement?

Page 4, line 6f: “. . . with solutes in QLLs somewhat surprisingly having less mobility compared to solutes in LLRs.” Is that really surprising assuming that the QLL may be only a few layers of water molecules?

I recommend include at least once the correct technical terminology for the compound “Rose Bengal” in the manuscript.

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