Investigating Brine on Frost Flowers with Absorption Tomography

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Motivation

Frost flowers grow on new sea ice via vapor deposition. Their growth is also affected by the wicking of brine from the sea ice surface. As a result of these processes frost flowers have a high bulk salinity which suggests they may play a role in facilitating halogen activation. While the bulk composition of these frost flowers is well known, there is a lack of knowledge about the microstructure. Knowledge of the bulk composition does not answer questions about the availability of brine for reaction with the atmosphere. For example, the brine can exist in enclosed brine pockets within the crystal or as a surface skim layer on the frost flower. Additionally, while measurements of frost flower surface area can be made, it is unknown how much of this surface is covered by brine and thus how much brine is exposed to the atmosphere. This work explores the use of X-ray absorption tomography as a way to answer these questions. This technique yields information about the overall distribution of brine in frost flowers as well as observations of brine motion in real time.

Sample Preparation

The frost flower samples examined were grown using .5 molar CsCl solution to approximate the ionic content of sea water. The CsCl has a similar phase diagram to NaCl, the primary component of sea salt, but attenuates X-rays much more than ice allowing for better differentiation between brine and ice in the data.

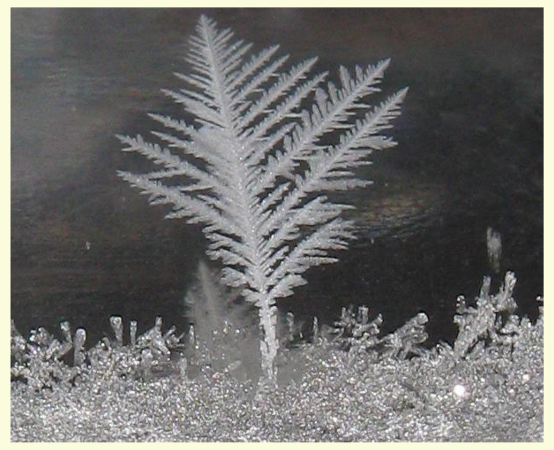

Figure 1: Samples grown for analysis in this study

The solution was poured into a container insulated on the sides and bottom to ensure the solution would freeze from the top down and left in a chest freezer overnight to allow for frost flower growth. The grown frost flowers exhibit similar morphology to natural frost flowers examined in previous studies[2].

Cold Stage Design

Key Components:

- 4 Peltier coolers
- 2 Heat Sinks hooked up to a circulating chiller
- Copper lined sample chamber directly attached to the top peltier coolers
- Kapton windows allow for sample imaging while limiting heat loss

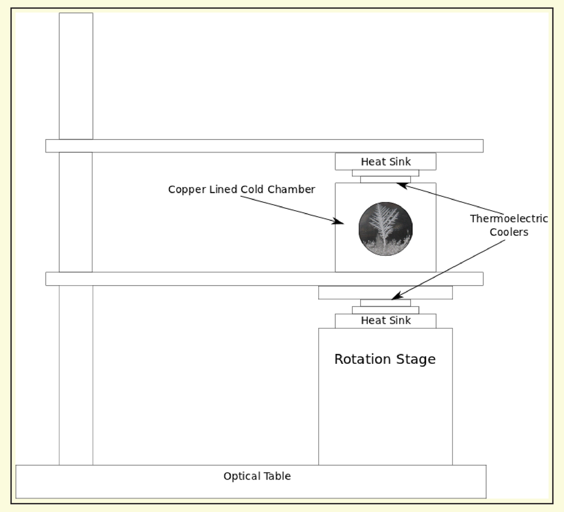

Figure 2: Schematic of the cold stage used to control sample temperature. The cold chamber and Peltier coolers are encased in foam(omitted in schematic for clarity).

The cold stage consists of two pieces, a rotating base and a stationary cap allowing for sample temperatures as low as $-24\,^{\circ}\mathrm{C}$. The sample temperature is measured using a thermocouple in the cold chamber adjacent to the sample.

X-Ray Absorption Tomography Overview

X-ray absorption microtomography yields a three dimensional data set through reconstruction of two dimensional images. These images are generated by placing the sample in the path of a monochromatic X-ray beam and measuring the transmitted X-ray intensity by capturing an image of the transmitted X-ray beam using a single crystal YAG scintillator and CCD camera. The sample is rotated 180 degrees in .25 degree steps to generate the 720 images necessary for a 3-D reconstruction of the sample. Attenuation of the X-ray beam passing through the sample is governed by: $I = I_0 e^{(\frac{\mu}{\rho})\rho l}$ where $\frac{\mu}{\rho}$ is the mass attenuation coefficient. This coefficient varies depending on the material the X-ray beam is passing through. This difference allows one to easily tell brine from ice in the resulting images[4].

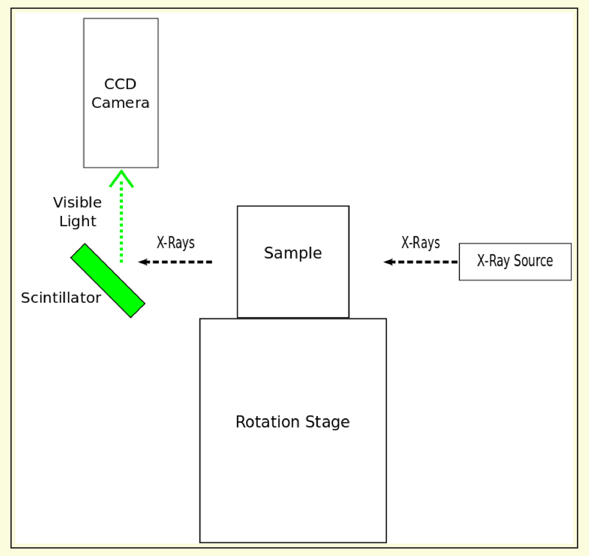

Figure 3: Illustration of tomography optics

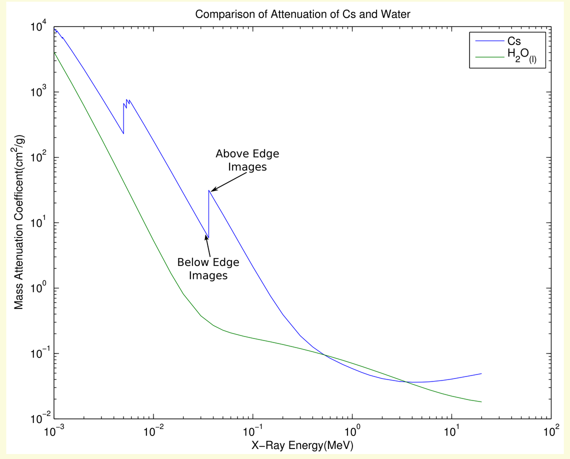

Figure 4: The above plot shows the energies at which the data is collected. At 36 KeV the attenuation of Cs is much higher than that of ice. (Data from NIST[3])

Slices Reconstructed Yield 3-D Rendering

The sample exhibits the 120 degree angles one would expect for hexagonal ice crystals and the overall structure is similar to that seen in photomicrographs of wet frost flowers[2]. There are regions of discontinuous ice that may be due to the high energy of the X-Rays used for imaging or the segmentation procedure used by ImageJ. The sample width and height are on the order of mm, while the sample thickness is less than 100 microns.

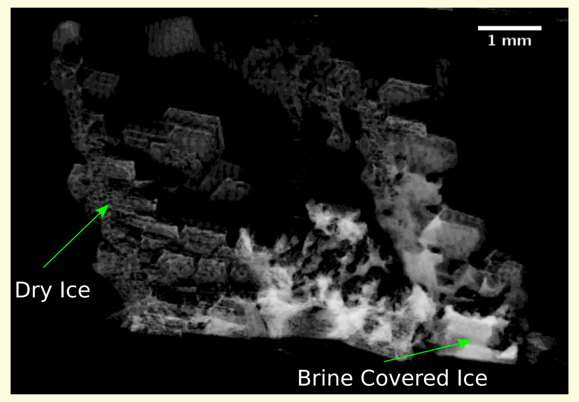

Figure 5: Three dimensional rendering of frost flower tomographic data taken below the Cs absorption edge. The brighter regions represent CsCl wicking up the frost flower. This rendering was done using ImageJ[1]

This aspect ratio is what one would expect from frost flowers, reinforcing the idea that the lab grown samples do not exhibit noticeably different morphology than natural frost flowers.
From this rendering it is clear the brine is not evenly distributed over the sample surface and has instead only wicked up certain regions of the flower covering about a third of the sample. This uneven coverage is also seen in the 2-D slices(Shown in Figure 6).

Thresholding gives Info about Brine Distribution

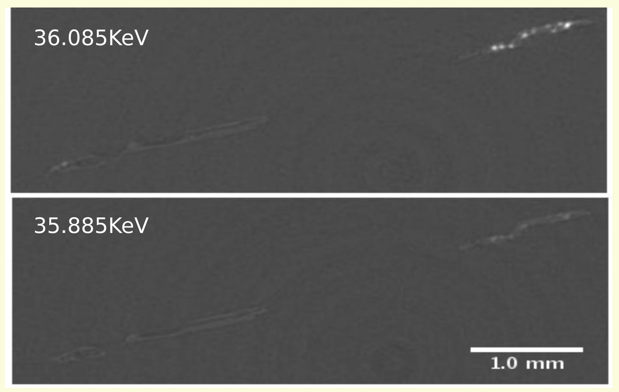

Figure 6: One slice imaged at differing X-ray energies shows the increased absorption of Cs as the increased X-Ray energy causes excitation of K shell electrons.

Figure 7: A thresholded version of Figure 6. Each pixel is designated with a grayscale intensity as background, ice, or brine leading to the image above.

Figure 6 shows the 2-D slices that make up the data set. The edge contrast in the two sets of images clearly indicates the location of the brine pockets in relation to the overall ice structure. The data was analyzed to obtain quantitative information about the relative amounts of brine on the surface. The data was thresholded to determine the overall content of each voxel based on the attenuation measured in each voxel. Each voxel can be placed in one of three categories, background, ice, and brine. This was done starting from an image histogram of the entire volume and refined using a graphical approach to attempt to match the thresholded and original slice images as closely as possible as shown in Figure 7. A 3-D median filter is used to eliminate image noise in the thresholded images.

Calculated Distribution of Brine

Once each voxel is labeled, the thresholded data set can then be analyzed to determine brine location in relation to the ice structure. Having designated each brine voxel, the nearest neighbors are identified to determine if the voxel is on the surface. The nearest neighbors form a 3x3x3 voxel cube, and a brine voxel is defined as being on the surface if a volume equivalent to one face of the cube consists of background voxels. If the brine voxel is not a surface voxel, the cube is extended to 4 voxels and the process is repeated until a sufficient number of background voxels are found.

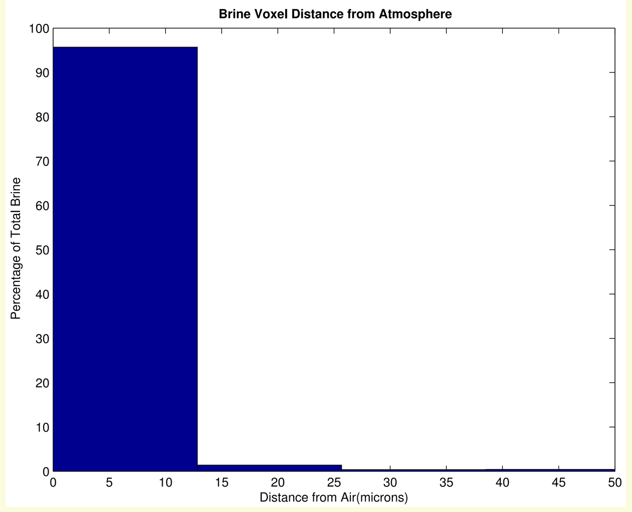

Figure 8: The above plot shows the percentage of brine within certain distances of the surface. The bar width is set using the voxel size of the data set, in this case 12.84 microns. The brine to air distance is calculated by analyzing a sub-volume of increasing size centered on each brine voxel.

The resulting data is then plotted as a histogram(bin size is based on image resolution) and shown in Figure 8. This analysis shows over 95% of the brine is concentrated within 12.84 microns of the surface of the ice which is consistent with the idea of brine wicking up vapor deposited ice.

Tomographic Movies of Brine Motion Show Pulsed Wicking

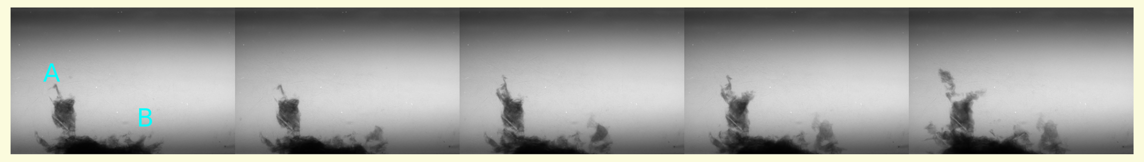

Figure 9: 5 still frames taken from a tomographic movie of a warming sample. Regions A and B evolve significantly over the duration of the movie.

Tomographic movies are an excellent technique to observe the response of brine to temperature change in real time. The experiment is set up by placing pure ice crystals onto frozen CsCl and then watching the warming. The movie is taken by fixing the orientation of the sample relative to the X-Ray beam and taking an image every 5s as the sample is warmed from $-22\,^{\circ}\mathrm{C}$ to $-15\,^{\circ}\mathrm{C}$. The wicking is pulsed rather than a continuous process with long periods of time between brine motion. In real time the movies show that brine wicks up certain regions preferentially as the temperature increases rather than uniformly coating the sample surface. This distribution of brine is also seen in the 3-D rendering of a frost flower sample in Figure 5.

Conclusions

- Absorption tomography provides valuable information about distribution of ionic impurities on ice
- While most ionic impurities exist on the surface, surface coverage is not uniform and thus not all of the surface will be chemically active.
- Knowing bulk concentration alone is not sufficient to determine the effects of this ice brine system on the chemistry of the atmosphere
- **Heterogeneous nature of surface coverage due to movement of brine onto vapor deposited ice via wicking must be taken into account in atmospheric chemical models to provide an accurate assessment of the effect of ice interface chemistry on the atmosphere.**

Acknowledgements

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