A 3D X-ray micro computer tomography perspective of sea ice, frost flowers and snow as sources of reactive halogens

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Fig. 1: Example of a frost flower field in Antarctica. Photo: A. Rankin, 2008

Introduction

1. Springtime ozone depletion events (ODEs) in the polar troposphere have become a recognized phenomenon. Ozone depleted air masses are associated with passage over newly-formed sea ice on which frost flowers are often produced. Due to their high salinity from wicking up brine solution and their large specific surface area, they are thought to be a potentially significant source of reactive halogens to the boundary layer.
2. Frost flowers might also constitute a significant source of sea salt-aerosol, with direct implications for the interpretation of corresponding ice core records. Similarly, the same also applies to fresh snow falling on new sea ice, which can also wick up brine resulting in a high salinity and a large surface area.
3. In all cases, potential source strengths will depend on the concentration and spatial distribution of the sea salt components in the sea ice, frost flowers, and snow.
4. The goal of the study was thus to investigate the evolution of the brine inclusions (specifically Cl^- and Br^-) in sea ice and frost flowers or snow including crystal growth, capillary flow of brine and ageing (sublimation) of the ice structures.

Experimental setup:

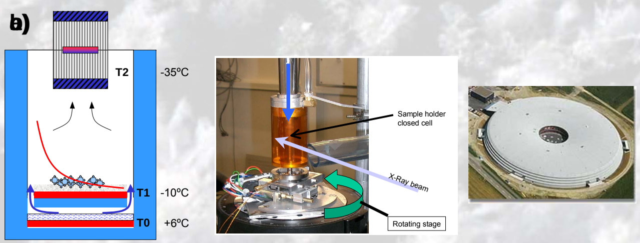

Fig. 2: a) Frost flower 'bluehouse' used to reproducibly grow individual frost flowers on 2-15 µL droplets of artificial and natural sea water solutions. b) Sample holder used for the 3D X-ray micro computer tomography at the Swiss Light Source. It is cooled with a cryojet to keep the sample frozen during the tomography. c) The Swiss Light Source (SLS) synchrotron facility at the Paul Scherrer Institute (PSI). The samples were tomographed at the MSTOMO and TOMCAT beamlines. The typical field of view was 1.4x1.4mm^2 and (2000x2000) pixels resulting in a nominal resolution of 0.7 µm (often binned to 1.4 µm to reduce noise). Between 500 to 1500 projections were acquired for one 3D tomogram. The X-ray energy was set between 13.2keV - 13.8keV, i.e. below and above the absorption edge of bromide.

Results:

Fig. 3: Examples of artificial frost flowers grown on salt solution droplets surrogate for sea ice. Far right: Aged droplet with frost flower where much of the water has sublimated.

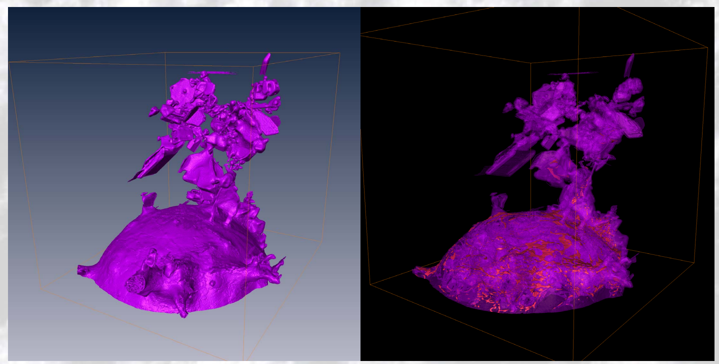

Fig. 4: Tomograms of artificial frost flowers grown on Antarctic sea water enriched in Br^-. Left: Surface. Right: transparent surface with brighter brine inclusions inside. Red: most strongly absorbing voxels potentially corresponding to Br^-.

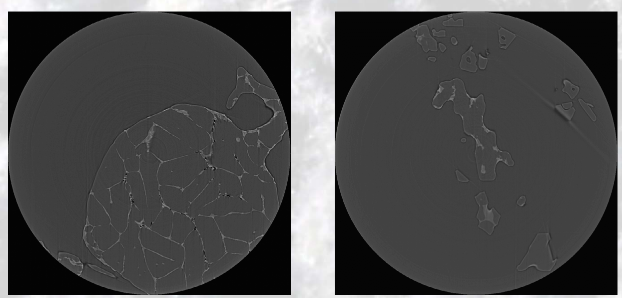

Fig. 5: Examples of reconstructed horizontal slices through a droplet (surrogate for sea ice, left) and a frost flower (right) revealing the internal distribution of brine (bright). Dark spots are drained brine channels.

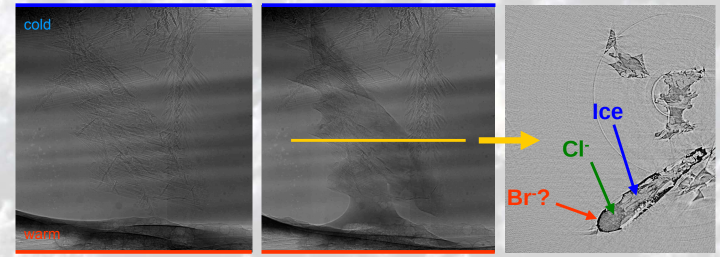

Fig. 6: Left: Growth of frost from the cold top towards the warmer ice covered with brine (a surrogate of snow falling on sea ice). Middle: Brine wicked up by the frost upon contact. Right: Horizontal cross section of frost (brine darker and water brighter).

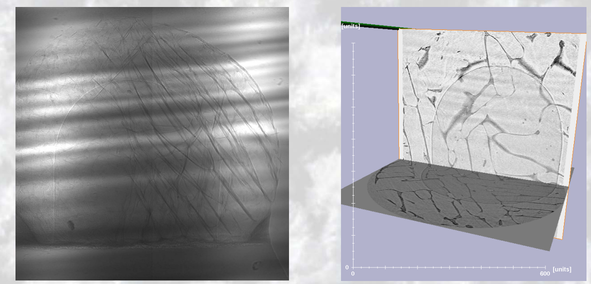

Fig. 7: Aged (sublimated) droplet of a NaCl-NaBr solution. Left: X-ray image of droplet. Right: reconstructed vertical and horizontal cut. Dark is the mesh of solid brine. The grey half-circle stems from the remaining water ice that has not yet sublimated.

Conclusions and outlook:

3D X-ray micro tomograms of artificial frost flowers and sea ice revealed their internal distribution of brine. Preliminary results suggest that Br^- might separate from Cl^- while preferentially 'coating' surfaces at low temperatures (below ~-25C), presumably due to their respective eutectic temperatures. This could significantly enhance the availability of Br^- for heterogeneous reactions that lead to the release of reactive bromine. However, there is the possibility that the observed separation is an artifact of the tomography, which is currently investigated in the ongoing quantitative analyses of the tomograms. During ageing (sublimation), the surface of brine exposed to the air increases and the formation of sea salt aerosols is facilitated as its surrounding matrix vanishes. The above is the case for sea ice surface, frost flowers and snow on sea ice, which will also wick up brine (Fig. 6). Quantification of these processes and of potential differences between natural and artificial sea water are also subjects of the ongoing data analyses.

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