Advancing methodology for sub-zero temperature application of DGT technique on sea ice samples for two-dimensional imaging of biogenic metals

BRATKIČ A.[1]*, ZHOU C.[2], TISON J.-L.[3], FRIPIAT F.[4], GAO Y.[2] AND DELILLE B.[1]

[1] *University of Liège, Allée du 6 Août 17, 4000* Liège, *Belgium*

[2] *Vrije Universiteit Brussel,* Boulevard de la Plaine 2, 1050 Ixelles, *Brussels, Belgium*

[3] *Université Libre de Bruxelles, Brussels, Belgium*

[4] *Max Planck Institute for Chemistry, Mainz, Germany*

* *Presenting Author:* arne.bratkic@vub.be

Sympagic (ice-associated) communities colonize the brine-filled spaces and are exposed to major biogeochemical and physical changes during its incorporation into the ice: temperature fluctuations, salinity, dissolved oxygen, light, pH, the surrounding organic matrix, and nutrients. A key adaptive response is the formation of biofilms, which play a major role in macro- and micro-nutrient storage, transformation and mobilization. Considerable enrichment of Fe and other trace metals has been recorded in sea ice, supposedly being adsorbed onto organic matter.

Current methods for collecting pristine ice samples mostly involve melting an ice core, erasing any spatial information and discrimination between solid, liquid and gaseous phases. As a result, sea ice analytical methods have an insufficient spatial resolution to detect or describe microbial processes at submillimetre scale (in biofilms or micro-environments within the brine network), yet there is currently no alternative option for these experiments.

Based on Diffusive Gradients in Thin-films technique (DGT) for imaging 2-dimensional distribution of total labile metal concentrations in soil/sediment by laser ablation ICP-MS, we have advanced a DGT procedure for sea ice application. During the optimization process, we considered atypical conditions for DGT application at sub-zero temperatures; hydrogel freezing, slow diffusion, high brine salinity. We defined diffusive coefficients at water freezing temperatures and assured contact with hydrogel and thus diffusion. Using Peltier element to precisely control the temperature of immediate sea ice environment, slow equilibration to *in situ* temperature of -1.8°C successfully maintained the brine liquid, the ice did not melt, and the hydrogel did not freeze. This was critical for the diffusion to occur, and importantly, allowed degassing from the sea ice. Without gradual equilibration, gases from sea ice were trapped between hydrogel and ice, separating the two and preventing diffusion.

Our result are the first two-dimensional images of biogenic metal micronutrients in the sea ice, revealing a clear spatially diverse signal. Fe, Zn and Mn were associated with organic matter-rich micro-locations where the sympagic communities were clearly visible. The new procedure had immense potential to advance our understanding of the sea ice biogeochemistry. It could provide missing empirical evidence to connect hypothesized reductive conditions in biofilm, bioligand interaction with trace element and OM growth/remineralization on a fine spatial scale, thus increasing our understanding of processes occurring in polar oceans and its feedback on the ongoing global change.